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TEXT BOOK
THERMODYNAMICS

BY

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NEW YORK

JOHN WILEY & SONS, INC.

LONDON: CHAPMAN & HALL, LIMITED

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R. ID. No. 00051930

PRINTED IN U. S. A.

PRESS OF
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BUILDERS OF BOOKS
BRIDGEPORT, CONN.

TEXTBOOK OF THERMODYNAMICS

CHAPTER I

THE THERMAL PROPERTIES OF MATTER

1. The concept of temperature. Heat and cold belong to the most fundamental of our sensations. From time immemorial the phenomena connected with them received a great deal of practical attention because of their vast importance in everyday life, but they were not made amenable to scientific treatment until a comparatively recent date. The possibility of doing this is due to the following empirical facts: (1) When a hot and a cold body are brought in contact, the former gets cooler, the latter warmer. After the lapse of a sufficiently long time a stationary state is reached in which no further changes occur. We say, then, that the two bodies are in *thermal equilibrium.* This equilibrium persists if the bodies are separated and then brought together a second time (provided they were not exposed, in the meantime, to the influence of other hotter or colder bodies). (2) Two bodies which are separately in thermal equilibrium with the same third are in equilibrium with each other. We say, then, that they have the same *temperature.*

The second fact permits us to use one suitable body as a standard or "thermometer" with which to compare the temperatures of others. In order to determine the degree of heat of the thermometer, one, usually, has recourse to the property of matter of changing its size or volume when heated. In this way a *scale of temperatures* is established. The current types of thermometers are well known and need not be described here.

When brought into equilibrium with any body, the thermometer associates the degree of heat of this body with a definite reading of its scale. It replaces the vague notion of hot or cold by a precise numerical datum. Its invention was, therefore, the necessary antecedent of a scientific analysis of the phenomena of heat. (Compare also section 39).

2. Subject of thermodynamics. Definitions. Thermodynamics deals with systems which, in addition to mechanical and electromagnetic parameters, are described by a specifically thermal one, namely, the temperature or some equivalent of it. We have seen that for the very definition of temperature one must invoke the concept of thermal equilibrium. Thermodynamics is, therefore, of necessity, essentially a science about the conditions of equilibrium of systems and about the processes which can go on in states little different from the state of equilibrium. We introduce the following terms which, for the most part, are those in general usage:

A *homogeneous system* is uniform in every part, with respect both to its chemical composition and to its physical condition. The fact mentioned in the preceding section that two bodies set themselves into thermal equilibrium applies, of course, also to two adjacent parts of the same body. The statement that the temperature of a homogeneous system is uniform throughout is, therefore, equivalent to saying that it is in equilibrium.

A *simple* homogeneous system or, for short, a *simple system* is one completely defined by the three parameters V (volume), p (pressure), and T (temperature). Such are gases and liquids in a static condition and solids in a state of isotropic stress removed from the action of gravitational and electromagnetic forces. The case of one or several simple systems is, by far, the most important. Simple systems offer the most interesting applications, and their treatment is sufficiently typical to bring out all the methods of thermodynamics so that a generalization is easily made when necessary. We shall, therefore, restrict ourselves in many of our discussions to simple systems, and shall take up the more general case only when this is required for special applications.

A *heterogeneous system* is composed of a number of homogeneous ones separated either by surfaces of discontinuity or by wall partitions. Those homogeneous parts are called the *phases* of the system.

We shall admit the existence and the use of partitions of different types of which the most important are the *heat-conducting* one which permits two bodies separated by it to set themselves into thermal equilibrium, and the *insulating* or *adiabatic* partition which prevents any exchange of heat.

3. The thermal equation of state. We have mentioned in section 1 that the temperature of a thermometer is usually inferred from its extension. The deeper reason why it is possible to do so lies in a very fundamental and general property of every simple system: there exists a functional relation between the temperature, the volume, and

the pressure which is called the *equation of state*, or more accurately, the thermal equation of state. This relation between T, p, and V can be written in the form

$$p = f(V,T). \tag{1.01}$$

Each of the three variables can, therefore, be regarded as a function of the other two. Subjecting the variables to small changes, we can form the following three partial derivatives:

(1) We keep the pressure constant ($\Delta p = 0$) and give to V and T the small increments ΔV and ΔT. The limit of the ratio, for $\Delta T = 0$, is the partial derivative $\lim(\Delta V/\Delta T) = (\partial V/\partial T)_p$. (It is customary to indicate the parameter which is kept constant as a subscript.) Divided by the volume V, this partial defines the *coefficient of thermal* expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \tag{1.02}$$

which represents the relative (i.e. referred to unit volume) increase of volume per unit increase of temperature, at constant pressure.

(2) Keeping the temperature constant ($\Delta T = 0$), we obtain in a similar way the partial $(\partial V/\partial p)_T$ connected with the *coefficient of compressibility*

$$\beta_1 = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \tag{1.03}$$

which gives the relative decrease of volume per unit increase of pressure, at constant temperature.

(3) When the volume remains constant ($\Delta V = 0$), the partial $(\partial p/\partial T)_V$ is obtained, related to the *coefficient of tension*

$$\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V. \tag{1.04}$$

The inverse partials are, simply, the reciprocals, $(\partial V/\partial T)_p = 1/(\partial T/\partial V)_p$, etc., and do not give us anything new, and even the three partial derivatives which we have formed are not independent as there exists a relation between them. This becomes apparent when we write down the general expression for the total infinitesimal change Δp which results when both the volume and the temperature are changed by infinitesimal amounts. It is, according to the rules of differentiation,

$$\Delta p = \left(\frac{\partial p}{\partial V}\right)_T \Delta V + \left(\frac{\partial p}{\partial T}\right)_V \Delta T.$$

In the special case, $\Delta p = 0$, the ratio $\Delta V/\Delta T$ is, precisely, the partial $(\partial V/\partial T)_p$. Since the left side of the equation vanishes in this case, we can solve it with respect to this ratio and find

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V \Big/ \left(\frac{\partial p}{\partial V}\right)_T. \tag{1.05}$$

This relation can be regarded as a differential form of the equation of state (1.01).

In the general case of a homogeneous system described by other parameters (in addition to temperature and volume) there exist several equations of state as will become clear in section 7.

Exercise 1. In nitrogen at $t = 20°$ C and $p = 0.134$ atm, $\alpha = 0.00368$ and $\beta = 0.00368$. Calculate the compressibility β_1.

Exercise 2. Suppose that one of the equations of state of a homogeneous system depending on many variables has the form

$$y = y(X_1, X_2, \ldots X_n, T).$$

The increment of y, analogous to the expression for Δp, is

$$\Delta y = \frac{\partial y}{\partial X_1}\Delta X_1 + \ldots + \frac{\partial y}{\partial X_n}\Delta X_n + \frac{\partial y}{\partial T}\Delta T.$$

Show that by keeping all the variables $y, X_1, \ldots X_n, T$ constant, except two, one can obtain $n(n+1)/2$ new relations of the type (1.05) between triples of partials. (Remark: The set of relations so obtained includes all that are independent. From them there can be derived a great number of other (dependent) relations of a similar form.)

4. The perfect gas. Absolute temperature. The so-called permanent gases of nature follow, more or less closely, a number of well-known laws. The first of these is the Boyle–Mariotte law according to which, for a constant temperature, the product of pressure and volume remains constant

$$pV = \text{const.} \tag{1.06}$$

When we inquire about the behavior of a gas at varying temperatures, it is convenient to use a gas thermometer filled with this same gas as the thermometric fluid. The pressure of the thermometer is kept constant (p_0), and the zero of the temperature scale ($t = 0$) is chosen arbitrarily, say, as that corresponding to a volume V_0.

The temperature t is, then, defined as proportional to the relative increase of the volume over V_0,

$$t = \frac{1}{\alpha}\frac{V - V_0}{V_0}, \tag{1.07}$$

or

$$V = V_0(1 + \alpha t), \tag{1.08}$$

α being a constant.

According to the law of Charles–Gay-Lussac, the formula (1.07) is universal for all permanent gases: Used as thermometric fluids in the same thermometer, they give, within a good approximation, the same readings, or, in other words, they have all pretty closely the same coefficient of expansion α. The uniformity can be best judged in the following way. Suppose we use a centigrade scale: that is, we choose the temperature of melting ice as $t = 0$ and that of boiling water as $t = 100$. Equation (1.08) gives, then, for the volume at $t = 100°$, $V_{100} = V_0(1 + 100\alpha)$, whence $\alpha = (V_{100} - V_0)/100V_0$. The quantity defined in this way is called the *mean coefficient of expansion*, between 0° and 100°, and is denoted by $\alpha_{0,100}$. In general this quantity depends on the pressure p_0 kept constant during the expansion. The mean coefficients of expansion $\alpha_{0,\,100}$ were investigated by Henning and Heuse who measured them with considerable accuracy in helium, hydrogen and oxygen. These measurements are well represented by the expressions of Table 1,[1] where p_0 is expressed in atmospheres. Degrees of the centigrade scale will be indicated by the symbol ° C.

TABLE 1

Gas	$\alpha_{0,\,100} \times 10^7$
He	$36\,604 - 25p_0$
H_2	$36\,604 - 16p_0$
N_2	$36\,604 + 167p_0$

We arrive at a more rational choice of the zero point of our scale if we displace it by $-1/\alpha$, defining the new temperature as

$$T = t + 1/\alpha. \tag{1.09}$$

The position of the old zero point $t = 0$ on the new scale is then $T_0 = 1/\alpha$, and eq. (1.08) takes the form $V_{T,p_0} = V_0 T/T_0$. The temperature T is proportional to the total volume of the gas. We substitute this into eq. (1.06) which we refer to the temperature T,

[1] E. Henning and W. Heuse, Zs. Physik 5, p. 285, 1921.

writing $pV = p_0 V_{T,p_0}$, and obtain a formula representing the combination of the Boyle–Mariotte and Charles–Gay-Lussac laws:

$$pV = CT, \tag{1.10}$$

where C is an abbreviation for the constant $C = p_0 V_0 / T_0$.

A simple system in equilibrium is completely homogeneous and uniform in all its parts (compare section 2). The properties of our gas, in every small region of it, are, therefore, completely defined by the temperature T and pressure p and cannot depend on its total extension or mass. If we compare two specimens of the same gas of different masses, but at the same temperature and pressure, their respective volumes V must be, obviously, proportional to their masses. It follows then from eq. (1.10) that the constant C must be also proportional to the mass of the gaseous system under consideration.

We shall use as the unit of mass of a chemically homogeneous or *pure* substance the *mol*, also called the *gram-molecule*. If μ denotes the molecular weight of this substance, its mol contains just μ grams. To simplify our terminology we shall apply the term "molecular weight" also to monatomic substances where it has the same meaning as "atomic weight." Let us consider a homogeneous system which consists of N mols of a pure substance. The volume occupied by one mol of it is called the *specific molal volume* or, simply, the *molal volume* and is denoted by v.

We can apply this to our gas system if it is chemically homogeneous. The total volume V and the constant C can be represented as

$$V = Nv, \quad C = NR, \tag{1.11}$$

where R is an abbreviation for $R = p_0 v_0 / T_0$ or the constant C referred to one mol of the gas. The equation of state (1.10) takes then the form

$$pV = NRT, \tag{1.12}$$

or

$$pv = RT. \tag{1.13}$$

The third empirical law which we have to invoke is that of Avogadro. It tells us that the molal volume v is, within a close approximation, the same for all permanent gases, namely, under normal conditions (p = 1 normal atm = 1.013249×10^6 dyne cm^{-2}, $t = 0°$ C) it is $v_0 = 22414$ cm^3. Consequently, the *gas constant* R is also universal. It is an immediate consequence of the definition of the mol, that 1 mol of any substance contains the same number n_A of molecules, which is called the *Avogadro number*. It has been determined with

fair accuracy and has been found to be $n_A = (6.064 \pm 0.006) \times 10^{23}$ mol^{-1}. A much-used quantity is the ratio

$$k = R/n_A, \tag{1.14}$$

which represents the gas constant per molecule and is called the *Boltzmann constant.* With its help eq. (1.13) can be written in an alternative form. If we denote by Z the total number of molecules in N mols of a gas having the volume V, and by $z = Z/V$ the number per unit volume, we can write $Z = Nn_A$, $NR = Nn_Ak = Zk = Vzk$, and from (1.12)

$$p = zkT. \tag{1.15}$$

If, instead of a single gas, we consider a mixture, we must again have recourse to experience. Observations on mixtures of permanent gases show that, with a good approximation, each of the constituent gases behaves as if the others were not present. In the case of σ gases contained in a vessel of the volume V in the respective quantities of $N_1, \ldots N_\sigma$ mols, each of them exerts a partial pressure upon the walls of the vessel which can be computed in the same way as if the gas were single, i.e. by the formula

$$p_hV = N_hRT. \tag{1.16}$$

The total pressure of the mixture is the sum of these partial pressures

$$p = p_1 + p_2 + \ldots + p_\sigma, \tag{1.17}$$

and its equation of state is obtained by summing the formulas (1.16) for $h = 1, 2, \ldots \sigma$

$$pV = (N_1 + \ldots + N_\sigma)RT. \tag{1.18}$$

None of the above laws is followed by any of the permanent gases quite rigorously, and the formula (1.18) which embodies all four of them is, therefore, only an approximate expression of the facts. If we compare two gas thermometers filled with different gases and having the same fixed points, the readings between the fixed points will not be strictly identical because the rate of expansion is, in reality, not constant but slightly dependent upon the temperature, in a different way for the different gases. The same thing is true for non-gaseous thermometric fluids like mercury and alcohol. The scale of temperatures established by any particular thermometer construction is, therefore, special and arbitrary. In order to have a scale which does not depend on the individual properties of any special substance, we imagine the so-called *perfect gas*: an ideal fluid which strictly

follows the equation of state given by formula (1.12). Let us, further, imagine a thermometer filled with a perfect gas and let us specify its scale in such a manner that between the points of freezing and of boiling water (both at 1 norm atm = 760 mm Hg) are 100 equal divisions. The temperature which we would measure with such a thermometer is called the *absolute temperature.* We shall, consistently, denote it by T (capital), reserving t (small) for the temperature measured in an arbitrary scale.

It might be thought, at first sight, that such a definition of the absolute temperature must be futile since the perfect gas, and the perfect thermometer filled with it, are ideals which do not exist in nature. We shall show, however, in section 29 that there is a simple procedure to determine the absolute temperature, in every case, by indirect measurements. Every thermometer can, therefore, be calibrated in the absolute scale within the accuracy with which it can be read, and such calibrated thermometers are, in fact, readily available.

Making use of the results of this calibration, we can state that the point of freezing water corresponds to $T_0 = 273.1°$ of the absolute scale. Combined with the value of the molal volume mentioned above ($v_0 = 22414$ cm^3), this leads to the following numerical values for the gas constant: $R = (82.049 \pm 0.009)$ atm cm^3 deg^{-1} mol^{-1} (if the pressure is measured in normal atmospheres) or $R = (8.3136 \pm 0.001) \times 10^7$ erg deg^{-1} mol^{-1}) (if it is measured in dynes per cm^2). For Boltzmann's constant defined by (1.14) there follows the numerical value $k = 1.371 \times 10^{-16}$ erg deg^{-1}. The question how closely the permanent gases approximate the behavior of a perfect gas will be more fully discussed in section 6. Here we shall only state that, according to their degree of perfection, they can be arranged in the following order: carbon dioxide, oxygen, air, nitrogen, argon, hydrogen, helium. Carbon dioxide is the least and helium the most nearly perfect gas of this series. The deviations of helium from eq. (1.13) of perfect gases are, in fact, quite small under most conditions. Except at extremely low temperatures, helium can be used as the perfect thermometric fluid unless a very high accuracy is required. (Compare also section 29.)

Exercise 3. Show that the coefficients of thermal expansion and of compressibility are for a perfect gas

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T}, \tag{1.19}$$

$$\beta_1 = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{p}, \tag{1.20}$$

and check the validity of the relation (1.05). Calculate the coefficients numerically (per 1 deg, and 1 mm Hg as units) at normal conditions: $T = 273°.1$, $p = 760$ mm Hg.

5. The equation of Van der Waals. The next step in the approximation to the properties of real matter is represented by an equation given by Van der Waals. In spite of its simplicity, it comprehends both the gaseous and the liquid state and brings out, in a most remarkable way, all the phenomena pertaining to the continuity of these two states. This equation has the form

$$p = \frac{RT}{v - b} - \frac{a}{v^2}, \tag{1.21}$$

where a and b are two numerically small constants and v is the molal volume. It was derived by statistical considerations of so simple a nature that, even in a book devoted to thermodynamics, we can say a few words about the interpretation of the constants. It is shown in the kinetic theory that eq. (1.13) corresponds to a gas whose molecules are material points which do not collide or otherwise interact with one another. If we consider a gas with molecules of *finite* size, mutually exclusive as to their extension but not interacting in any other way, the difference is that the centers of the molecules cannot spread out in the whole volume of the gas but only in that part of it which is not occupied by other molecules and not immediately adjacent to them. In the first approximation, for the molal volume v there must be substituted the *covolume*, $v - b$, where the constant b is proportional to the sum of the volumes of all molecules in one mol of the gas. The equation of state becomes, therefore, $p = RT/(v - b)$. On the other hand, if the molecules of the gas *do interact* at a distance, say, attract one another, there must be added to the external pressure p the *internal pressure* due to this attraction. Whatever its law is, it is safe to assume that two volume elements of the gas $\Delta\tau_1$ and $\Delta\tau_2$ act upon each other with a force F_{12} proportional to the product of the masses in them, i.e. $F_{12} \propto \Delta m_1 \Delta m_2$. If we choose the mol as the unit of mass, we have $\Delta m_1 = \Delta\tau_1/v$, $\Delta m_2 = \Delta\tau_2/v$, so that $F_{12} \propto \Delta\tau_1 \Delta\tau_2/v^2$. This means that, when the density of the gas in a given vessel is changed by adding more gas or subtracting it, all the internal forces change in the ratio $1/v^2$. Since the pressure is defined as the force per unit area, this applies also to the internal pressure and we obtain for it the expression a/v^2 which is added to p in Van der Waals' equation.[1]

[1] It must be assumed, also, that the force F_{12} decreases rapidly with the distance between the volume elements $\Delta\tau_1$ and $\Delta\tau_2$. Otherwise the coefficient a would not

Let us plot the pressure p against the molal volume v keeping the temperature T in eq. (1.21) constant. Such a curve is called an "isothermal." As long as the molal volume v is very large, b is negligible compared with v, and a/v^2 compared with p. In the region of large volumes the curve is, therefore, identical with that given by the equation of perfect gases, namely, a hyperbola asymptotically approaching the horizontal axis $p = 0$ for $v = \infty$. When the volume is very small and close to its lower limit b, the second term on the right side is again negligible compared with the first and the curve becomes again hyperbolic. However, its asymptote is not the vertical $v = 0$ (as in the case of the perfect gas) but the vertical $v = b$. The shape of the isothermals in the intermediate range is given in Fig. 1. They are curves with one minimum and one maximum which are real for low temperatures and complex for high so that, above a certain temperature T_c (critical temperature), the pressure is, in them, a monotonically decreasing function of the volume ($dp/dv < 0$). Below T_c the curves are not continually decreasing but have a middle part (between the minimum and the maximum) in which p increases with v, ($dp/dv > 0$). It is obvious that this middle part, dotted in our curves, can have no physical reality. In fact, let us imagine the fluid in a state corresponding to this part of the curve contained in a heat-conducting vertical cylindrical vessel whose top is formed by a piston. The piston can slide up and down in the cylinder, and we put on it a load exactly balancing the pressure of the gas. If we take a little weight off the piston, there will no longer be equilibrium and it will begin to move upward. However, as it moves the volume of the gas increases and with it its pressure. The resultant force upon the piston gets larger, retaining its upward direction. The piston will, therefore, continue to move and the gas to expand until it reaches the state represented by the maximum of the isothermal. Vice versa, if we add ever so little to the load of the balanced piston, the gas will collapse to the state corresponding to the minimum of the

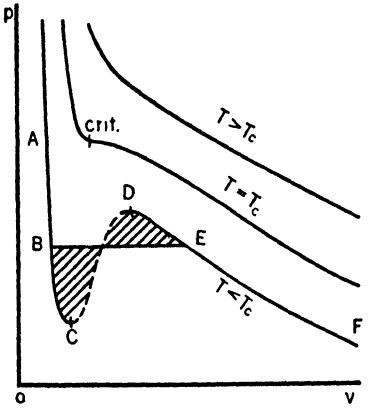


FIG. 1.—Isothermals according to Van der Waals' theory

be an internal constant of the gas but would depend on the shape and size of the container. It does not follow from the above argument and is a separate assumption that a is independent of T and p.

isothermal. The relation $dp/dv \leqq 0$ is, therefore, the condition of dynamical stability, and in regions where it is not satisfied the fluid is in an absolutely unstable state.

Leaving out the physically unreal dotted portion, the low temperature curves break up into two disconnected branches. The one of small molal volume corresponds to the liquid state of matter while that of high volume represents its gaseous state. The important fact that the same equation applies to both states of aggregation was called by Van der Waals *the continuity of the liquid and gaseous states.* Experiments show that the following things actually happen when we gradually increase the volume (in a heat bath of constant temperature), starting from a point A of the liquid state (Fig. 1). The expansion goes along the liquid branch of the isothermal up to a certain point B. In this state the liquid begins to evaporate so that the system is no longer homogeneous, but heterogeneous, consisting of a liquid and a gaseous phase. As the volume is further increased, more and more liquid is evaporated while the specific properties of the two phases remain unchanged. In this part of the isothermal expansion the pressure (called the *boiling pressure* at the temperature T) is constant, so that it is represented by a horizontal line, and remains so until all the liquid is evaporated (point E). From then on the system is again homogeneous and expands along the gas branch EF of the isothermal. Why the system behaves in such a way, and where the point B lies, are typical problems of thermodynamics which will be answered at length in section 43. The part BC of the liquid branch (like DE of the gas branch) represents only relatively unstable states: the vaporization of a liquid is greatly facilitated by the presence in it (or on its surface at the walls) of little bubbles of foreign gases. If these gases are driven out by a preliminary thorough boiling of the liquid and a suitable heat treatment of the vessel, it is possible to make the system expand along the liquid branch beyond the point B, bringing it into the so-called *superheated state.* In this state the pressure may become negative, in other words, the liquid is able to support a certain amount of tension; but at the slightest provocation it will jump over into the thermodynamically stable state on the straight line BE.

Above the critical temperature there is no discontinuity in the isothermal, and it is arbitrary whether to call the fluid a liquid or a gas. Usually, it is considered a gas and, then, the statement applies: *It is impossible to liquefy a substance at temperatures higher than the critical.* If the substance follows eq. (1.21) of Van der Waals, its critical temperature can be determined in the following way. Below it, the iso-

thermals have a maximum and a minimum which are analytically determined by the condition

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0. \tag{1.22}$$

As the temperature rises, the maximum and the minimum draw closer and closer together, and, in the critical isothermal, they coincide, forming a point of inflection. This point corresponds to the so-called *critical state* of the substance characterized by the values p_c, v_c, T_c of pressure, molal volume, and temperature which are known as the *critical constants*. The analytical condition for a point of inflection is

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0. \tag{1.23}$$

In the critical point all three equations (1.21), (1.22), (1.23) must be satisfied. It is, therefore, easy to express the critical constants in terms of the Van der Waals constants a, b, R by solving these three equations with respect to the three variables p, v, T. The result is

$$p_c = \frac{1}{27}\frac{a}{b^2}, \qquad v_c = 3b, \qquad T_c = \frac{8}{27}\frac{a}{Rb}. \tag{1.24}$$

One can use the critical constants as the units in which to express, respectively, the pressure, specific volume, and temperature. The state of the substance is then described by the so-called *reduced* variables

$$\pi = \frac{p}{p_c}, \qquad \varphi = \frac{v}{v_c}, \qquad \tau = \frac{T}{T_c}. \tag{1.25}$$

If we substitute these quantities for p, v, T and, at the same time, replace the Van der Waals constants by the critical, the equation of state (1.21) takes the form

$$\pi = \frac{8\tau}{3\varphi - 1} - \frac{3}{\varphi^2}. \tag{1.26}$$

Referred to the reduced variables, the equation does not contain any specific constants and is, therefore, the same for all Van der Waals substances. States of two substances in which they have the same respective values of π, φ, and τ are called *corresponding states*, and eq. (1.26) expresses the *law of corresponding states*: *If two of the reduced variables, π, φ, τ, are the same, respectively, for different substances the third is also the same and their states are corresponding.* The mathematical reason for the validity of the law of corresponding

states in connection with Van der Waals' equation is that it contains just as many constants as variables, namely three. However, the law of corresponding states is not restricted to Van der Waals substances. It is often satisfied with a fair degree of precision in groups of substances which show marked deviations from eq. (1.21), as will be shown more fully in the next section.

It is well to add here a few words about gas mixtures. The additivity of partial pressures which exists in perfect gases, according to eq. (1.17) does not hold in mixtures of Van der Waals gases. The physical reason for that additivity is that each perfect gas behaves as if the others were not present, and this means that there is no interaction between their molecules. On the contrary, the aim of Van der Waals' theory is, precisely, to take into account the interaction. For a binary mixture (i.e. consisting of two gases) the kinetic theory has been carried through by Lorentz.[1] The equation of state obtained by him for such a mixture is formally identical with the ordinary Van der Waals eq. (1.21), but the symbols v, a, b have a different meaning. If the mixture contains N_1 mols of the first gas and N_2 of the second, $v = V/(N_1 + N_2)$, while the quantities a and b depend on the mol fractions $x_1 = N_1/(N_1 + N_2)$ and $x_2 = N_2/(N_1 + N_2)$ and have the form

$$\left.\begin{aligned} a &= a_{11}\ x_1^2 + 2a_{12}\ x_1x_2 + a_{22}\ x_2^2, \\ b &= b_{11}\ x_1^2 + 2b_{12}\ x_1x_2 + b_{22}\ x_2^2. \end{aligned}\right\} \tag{1.27}$$

The coefficients a_{11}, a_{22} are those of the pure gases, while a_{12} characterizes the mutual action; the same applies to the coefficients b.

Exercise 4. Calculate by means of eqs. (1.24) the Van der Waals constants a, b and the ratio RT_c/p_cv_c for the following substances from the critical data ($R = 82.07$):

	T_c	p_c	v_c
Methyl acetate.....	506.9	46.33	227.6
Methyl formate.....	487.2	59.25	172.0

Exercise 5. Derive the coefficients of thermal expansion (1.02) and of compressibility (1.03) for the equation of Van der Waals. (Remark: as this equation is readily resolved with respect to p, it is convenient first to express α and β_1 in terms of partials of p, by means of (1.05) or in any other way.)

6. Behavior of real substances. As far as gases are concerned, it was pointed out in the preceding section that eq. (1.13) of a perfect

[1] H. A. Lorentz, Ann. Physik 12, p. 127, 1881. For a discussion of this equation, in relation to experimental data, see: J. D. Van der Waals, Continuity of the Gaseous and Liquid States. Vol. II. German edition of 1900.

gas is already a good approximation as long as the molal volume v is large. Although the equation of Van der Waals has its limitations (see below), the numerical values of its constants a and b are apt to give an idea how much a given substance deviates from the law of perfect gases and indicate the order of accuracy here involved. We give in Table 2 these constants and the critical data of a number of gases.

TABLE 2

Gas	Chemical Symbol	t_c° C	p_c (atm)	$b = \frac{1}{3}v_c$ (cm³)	$a \times 10^{-6}$ (atm cm⁶)
Helium	He	−267.9	2.25	23.71	0.03415
Neon	Ne	−228.35	26.85	17.10	0.2120
Hydrogen	H_2	−239.9	12.8	26.61	0.2446
Argon	A	−122.4	48.0	30.22	1.301
Nitrogen	N_2	−147.13	33.5	38.52	1.346
Oxygen	O_2	−118.82	49.7	32.58	1.361
Carbon monoxide	CO	−138.7	34.6	39.87	1.486
Carbon dioxide	CO_2	31.0	72.9	42.69	3.959
Nitrous oxide	N_2O	36.5	77.66	44.18	3.788
Water vapor	H_2O	374	217.5	30.52	5.468
Chlorine	Cl_2	144	76.1	56.26	6.501
Sulfur dioxide	SO_2	157.15	77.65	56.39	6.707

The constant b, depending on the molecular volume, is not greatly different for the different gases. The relative correction in the magnitude of the pressure, due to the presence of this constant in eq. (1.21), is roughly b/v. In the neighborhood of the normal conditions ($t = 0°$ C, $p = 1$ atm), the molal volume is about 22 400 cm³/mol and the correction has the numerical value of 0.001 to 0.002. On the other hand, there is a considerable variation, from gas to gas, in the constant a, and the correction $-a/v^2$ depending on it varies widely. For helium under normal conditions it is only −0.00007, for nitrogen and oxygen −0.0027. For the latter two gases, it is of the same order of magnitude as the first correction (0.0017 and 0.0015), and, since its sign is opposite, the total correction is reduced. For water steam at the boiling point ($t = 100°$ C, $p = 1$ atm), it becomes −0.006.

It was known already to Van der Waals himself that his equation does not give an accurate representation of the properties of a fluid in all ranges of temperatures. In fact, it is possible to determine the coefficients a and b from the data about pressures and volumes relating to a single isothermal. When the coefficients, obtained in this way for widely different isothermals, are compared, they turn out not to

be the same, especially, a is found to increase as the temperature is lowered. Another indication that eq. (1.21) is not accurate in the vicinity of the critical state is as follows. Theoretically there exists the following relation between the critical data p_c, v_c, T_c if the expressions (1.24) are valid:

$$K = \frac{RT_c}{p_c v_c} = \frac{8}{3} = 2.67. \tag{1.28}$$

In reality, the ratio of the empirically measured critical data $RT_c/p_c v_c$ is nearly the same within large groups of substances but it has not the value 2.67 required by the theory. The constancy of the ratio R is an indication that the law of corresponding states still approximately holds when the Van der Waals equation fails. In Table 3 we give the critical data of a few organic substances.

TABLE 3

Substance	Formula	T_c	p_c	v_c	$RT_c/p_c v_c$
Ethyl ether	$C_4H_{10}O$	467.0	35.6	281.9	3.814
Benzene	C_6H_6	561.7	47.89	256.2	3.755
Bromobenzene	C_6H_5Br	670.2	44.64	323.4	3.813
Chlorobenzene	C_6H_5Cl	632.4	44.62	307.9	3.776
Ethyl formate	$C_3H_6O_2$	508.5	46.76	229.0	3.895
Ethyl acetate	$C_3H_8O_2$	523.3	38.00	286.0	3.885
n-Pentane	C_5H_{12}	470.4	33.04	310.9	3.762
i-Pentane	C_5H_{12}	461.0	32.92	307.3	3.734
Octane	C_8H_{18}	569.4	24.65	490.9	3.864
Heptane	C_7H_{16}	539.4	26.88	537.8	3.945
Hexane	C_6H_{14}	507.4	29.62	366.9	3.830
Carbon tetrachloride	CCl_4	556.3	44.98	275.9	3.677
Tin tetrachloride	$SnCl_4$	591.9	36.95	351.2	3.755

In spite of the shortcomings just mentioned, the Van der Waals equation is extremely useful. It gives an excellent quantitative account of the behavior of gases whose density is not too high. Beyond this it offers a qualitative picture of the phenomena of condensation, critical state, etc. However, it must be always remembered that it cannot be used for quantitative predictions of phenomena involving high densities. Many other equations of state were proposed but, in part, they apply only to a narrow range of the variables, in part, they offer a gain in accuracy insufficient to compensate for the much more complicated form. Therefore, we shall mention here only two of them.

(A) *The mean empirical, reduced equation of Kamerlingh Onnes*[1] is expressed in terms of the reduced variables (1.25),

$$\pi\varphi = K\tau\left[1 + B\frac{K}{\varphi} + C\left(\frac{K}{\varphi}\right)^2 + D\left(\frac{K}{\varphi}\right)^4 + E\left(\frac{K}{\varphi}\right)^6 + F\left(\frac{K}{\varphi}\right)^8\right]. \quad 1.29$$

K is the ratio (1.28) of the critical data, while the coefficients depend on τ

$$B = b_1 + \frac{b_2}{\tau} + \frac{b_3}{\tau^2} + \frac{b_4}{\tau^4} + \frac{b_5}{\tau^6},$$

b_1, b_2, . . . being constants. The other coefficients have the same structure.

This equation grew out of the studies of its author on the validity of the law of corresponding states. He found that there exist large groups of substances which obey the law of correspondence to the following extent. The substances of a group can be arranged in a series so that each of them has a close correspondence with the preceding substance while the series, as a whole, shows progressive and considerable changes in the constants. The above equation applies to a fictitious substance representing the mean type of the series. The results of Kamerlingh Onnes show us two things: (1) how extremely complicated the conditions become when a high accuracy is aimed at; (2) that the law of corresponding states has an approximate validity beyond that of any of the simpler equations of state.

(B) *The equation of state of Beattie and Bridgeman*[2]

$$p = \frac{RT(1-\varepsilon)}{v^2}(v + B) - \frac{A}{v^2}, \quad \begin{cases} A = A_0(1 - a/v), \\ B = B_0(1 - b/v), \\ \varepsilon = c/vT^3, \end{cases} \quad (1.30)$$

A_0, B_0, a, b, c being constants. This equation is one of the most recent that have been proposed so that its authors had the benefit of the experience of their predecessors and of more accurate experimental data.[3] It gives good results over a wide range of the variables.

[1] H. Kamerlingh Onnes and W. H. Keesom, Die Zeistandsgleichung. Encyklopaedie math. Wiss. Vol. V1, Article 10.

[2] J. A. Beattie and O. C. Bridgeman, Proc. Am. Acad. 63, p. 229, 1928.

[3] Another of the more recent equations is that due to A. Wohl (Zs. physik. Chemie 87, 1, 1914; 99, p. 207, 1921). It is often quoted, but the writer has difficulty in understanding it, as he is not convinced that it satisfies the requirements of an equation of state.

The above equations of state apply, primarily, to gases, secondarily, to liquids at temperatures not far from the critical. It is not necessary to say much about matter in the condensed state. The thermal expansion and compressibility of condensed substances are so small (compared with those of gases) that they are not important in most thermodynamical applications. In the first approximation, they are altogether neglected; in the second, they are taken as constant over finite ranges. The process of *transition from the liquid to the gaseous state* is in real substances the same as that described in connection with the Van der Waals equation and illustrated by Fig. 1. As an example we give in Fig. 2 the actually observed isothermals in carbon dioxide. (The molal volume is given here in fractions of the normal volume at 0° C and 1 atm, $v_n = 22\,256$ cm^3; the critical point is marked by the symbol ×).

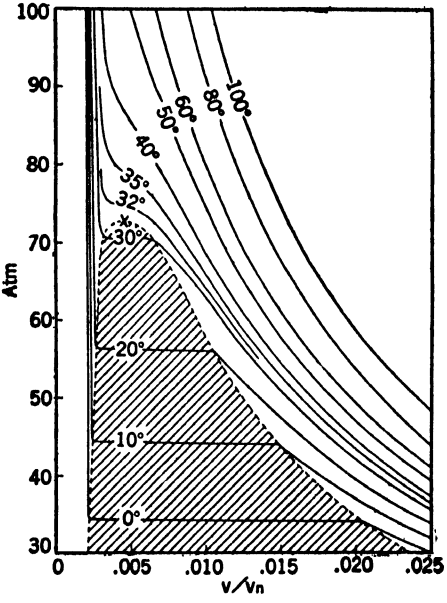


FIG. 2.—Empirical isothermals in carbon dioxide.

Exercise 6. Calculate the critical data in terms of the constants of the equation of state

$$\left(p + \frac{a}{Tv^2}\right)(v - b) = RT \qquad \text{(Berthelot)}$$

by way of the formulas (1.22), (1.23), (1.24).

Exercise 7. Do the same for the equation

$$p(v - b) = RT \exp\left(-c/RTv\right). \qquad \text{(Dieterici)}$$

(Remark: when the first and second partials of p vanish, those of $\log p$ also vanish.)

CHAPTER II

THE FIRST LAW OF THERMODYNAMICS

7. The element of work. The concept of work is defined in mechanics as follows. When a material point moves under the action of a force F, through the infinitesimal distance dl in the direction of F, the elementary work done by this force is Fdl. When the directions of the path dl and of the force do not coincide but include an angle α only the projection of F on the direction of motion $F_l = F \cos \alpha$ contributes to the work, and the element of work has the expression

$$DW = F_l\, dl = Fdl \cos \alpha = F_x\, dx + F_y\, dy + F_z\, dz, \qquad (2.01)$$

if we denote, respectively, by F_x, F_y, F_z and dx, dy, dz the projections of F and of dl upon cartesian axes of coordinates. In the case of the general dynamical system of n degrees of freedom, the element of work is expressed in a similar way

$$DW = y_1\, dX_1 + y_2\, dX_2 + \ldots + y_n\, dX_n \qquad (2.02)$$

where $X_1, \ldots X_n$ are the geometrical coordinates and $y_1, \ldots y_n$ the generalized forces. If the work is due in part to non-mechanical forces (electric, magnetic, capillary, etc.), the form of this expression is not changed: there only appear additional terms of the same type.

Of particular importance to us is the form which the element of work takes in simple systems (section 2). The only force with which such a system can act upon the outer world is the pressure upon its boundaries. The pressure is the force per unit surface of the wall and has the direction of the normal to it. Consequently, the force acting upon an element $d\Sigma$ (Fig. 3) of the surface is $F = pd\Sigma$ in the direction n. Let us suppose that, because of the pressure in the system, its surface gets slightly displaced from the position AB into $A'B'$ so that the element $d\Sigma$ moves into the new position $d\Sigma'$ through the very small distance Δl. The work of the force upon this element is then, according to the expression (2.01), equal to $pd\Sigma\Delta l \cos(n,\Delta l)$, and the work of the forces of pressure upon all the surface to $DW = p \int d\Sigma\Delta l \cos(n,\Delta l)$. In the limit, when Δl is infinitesimal, every element, in being displaced from $d\Sigma$ to $d\Sigma'$, sweeps

over an oblique cylinder whose volume is, precisely, $d\Sigma\Delta l \cos(n,\Delta l)$. The integral $\int d\Sigma\Delta l \cos(n,\Delta l)$ is, therefore, the total increase of the volume of the system dV:

$$DW = pdV. \tag{2.03}$$

We shall, in general, denote *by capital letters quantities referred to the whole system* (N mols) and *by small letters quantities referred to 1 mol* of it. w represents, therefore, the *molal work* ($W = Nw$, N being the mol number), or

$$Dw = pdv. \tag{2.04}$$

It is work *done by the system*: We define the sign in such a way that work of this kind is counted as positive, while work done by outer

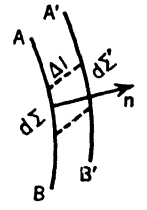


FIG. 3.—Element of work in simple system.

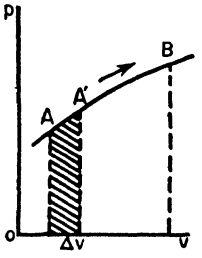


FIG. 4.—Graphical representation of work.

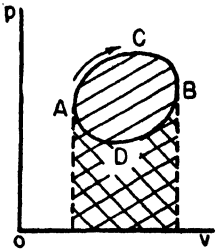


FIG. 5.—Work in cyclic process.

forces against the system is considered as negative. The expression (2.04) receives a simple graphical representation in the (p, v)- diagram (Fig. 4). Let the points A, A' correspond respectively to the initial state of the system and to its state after an infinitesimal expansion dv. The product $pdv = Dw$ is, then, represented by the infinitesimal area under the element AA', the shaded strip of our diagram. If a finite process of expansion is such that it can be represented by a curve of the (p, v)-diagram, for instance, by the segment AB, the total work (per mol) done in it by the system is equal to the integral of the expression (2.04)

$$w = \int_A^B pdv. \tag{2.05}$$

Its graphical representation is, obviously, the total area under the segment AB. Since the work w is, in this case, positive, Fig. 4 permits us to formulate the following rule. An area represents positive work when it lies *to the right* of the curve giving the process (for the observer looking in the direction of the process, i.e. from A to B). This rule is

borne out also in the case of a *cyclic* process where the system returns to its initial state (Fig. 5). While expanding (ACB), the system does positive work; while contracting (BDA), negative. The negative area (double shaded) is to the left of the curve BDA and must be subtracted from the positive area under ACB. The difference is the net (positive) work done by the system; it is represented by the area enclosed by the circuit $ACBD$ and lying to the right of it.

Exercise 8. (If the force is measured in dyne/cm^2 and the volume in cm^3, the work is expressed in erg). Calculate the work of vaporization of water. When 1 mol of water (18 grams) is vaporized at 100° C, the increase of volume is $v_B - v_A = 30\,186$ cm^3 mol^{-1}. The pressure in the process is constant and equal to 1 atm: $p = 1.013 \times 10^6$ dyne/cm^2.

Exercise 9. Calculate the work necessary to compress 1 mol of a gas from the normal state ($v_A = v_0 = 22\,414$ cm^3, $p_A = 1$ atm) to half the normal volume ($v_B = \frac{1}{2}v_0$), assuming that the process follows the law of Boyle–Mariotte: $pv = p_A v_A$.

8. Linear differential expressions and exact differentials. It will be well to recall to the reader a few mathematical facts which, although simple, are very fundamental in thermodynamics since the whole of this science may be said to be built up on them. Mathematically speaking, formulas (2.01) to (2.04) are examples of linear differential expressions, whose general form is

$$L(x_1, \ldots x_n) = \sum_{k=1}^{n} M_k(x_1, \ldots x_n)dx_k. \tag{2.06}$$

For instance, in the particular case of only two variables x,y it reduces to

$$L(x,y) = M(x,y)dx + N(x,y)dy. \tag{2.07}$$

The most interesting question which arises with respect to these expressions is whether they are " exact differentials", meaning whether they can be obtained by differentiating some function $f(x_1, \ldots x_n)$ of the same variables. According to the rules of differentiation the total differential of f is

$$df = \sum_{k=1}^{n} \frac{\partial f}{\partial x_k} dx_k. \tag{2.08}$$

We see, therefore, that the linear differential expression (2.06) is an exact differential when

$$M_k = \frac{\partial f}{\partial x_k}, \quad (k = 1, 2 \ldots n); \tag{2.09}$$

in words, when the coefficients M_k are the partial derivatives of a function $f(x_1, \ldots x_n)$. If we single out the two independent variables x_k, x_l the second partial does not depend on the order of differentiation

$$\frac{\partial}{\partial x_l}\left(\frac{\partial f}{\partial x_k}\right) = \frac{\partial}{\partial x_k}\left(\frac{\partial f}{\partial x_l}\right).$$

From the formulas (2.09) there follows, therefore,

$$\frac{\partial M_k}{\partial x_l} = \frac{\partial M_l}{\partial x_k}, \quad (k,l = 1, 2 \ldots n), \tag{2.10}$$

the so-called *reciprocity relations*. It is clear that the validity of the reciprocity relations is a necessary condition for the expression (2.06) being an exact differential. Moreover, it is shown in calculus that this condition is also sufficient: Whenever the relations (2.10) are satisfied, a function can be found such that the coefficients M_k are its partial derivatives. This function is called the *potential* of the expression.

We conclude from this that a linear differential expression of the type (2.06) is not, in general, an exact differential. If the functions $M_k(x_1, \ldots x_n)$ are selected at random, they will, in general, not satisfy the reciprocity relations. The exact differential is, therefore, a rare exception.

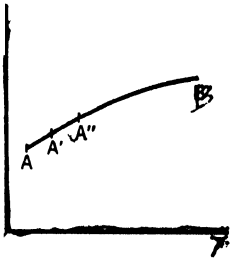


FIG. 6.—Notion of line integral.

Of great importance is the concept of the *line integral of a linear differential expression.* To fix our ideas, we shall explain this notion for the case of expression (2.07) with only two variables x, y, which we shall interpret as the cartesian coordinates of a plane (Fig. 6). The line integral along the curve from A to B

$$\int_A^B [M(x,y)dx + N(x,y)dy]$$

is constructed in the following way. The first element is obtained by substituting, for the arguments of the functions M and N, the values of x and y in the point A and, for dx and dy, the increments which lead from A to an infinitely close point A' on the curve. For the second element one takes the values of M and N at the point A' and the increments leading to the point A'', and so one moves from point to point along the curve, until its end B is reached. The integral is the sum of all the elements so constructed. In the case of n variables they

must be interpreted as the coordinates of an n-dimensional hyperspace, and the generalization is obvious.

When the linear differential expression is an exact differential (2.08), its line integral can be given explicitly. For instance,

$$\int_A^B \sum_k M_k dx_k = \int_A^B df = f(x_1^{(B)}, \ldots x_n^{(B)}) - f(x_1^{(A)}, \ldots x_n^{(A)}).$$

The line integral depends, then, only on the coordinates of the initial point $x_1^{(A)}, \ldots x_n^{(A)}$ and of the final $x_1^{(B)}, \ldots x_n^{(B)}$ and not on the path between them. It has the same value for all the curves going from the same initial to the same final point. In particular, when the curve is closed, the initial and the final points coincide and the expression (2.11) is equal to zero:

$$\oint \sum_{k=1}^{n} M_k dx_k = 0. \tag{2.11}$$

If $\sum_{k=1}^{n} M_k dx_k$ *is an exact differential, its line integral over any closed circuit vanishes.* It is shown in mathematics that the inverse theorem is also true: *If the line integral of a linear differential expression vanishes for every arbitrarily chosen closed circuit, it is an exact differential.*

To summarize, we can say that the following three possible properties of the linear differential expression (2.06) are completely equivalent: (1) It is an exact differential; (2) its coefficients satisfy the reciprocity relations (2.10); (3) its line integral vanishes for any closed curve. If the expression has one of these three properties, it has also the other two.

Supposing that the linear differential expression (2.06) is *not* an exact differential, the further question arises whether it can be transformed into one by multiplying it by a suitable function $\lambda(x_1, \ldots x_n)$. If this is the case, we say that it *admits an integrating multiplier* or, simply, that it is *integrable.* After multiplication by λ the coefficients of the expression become λM_k, and, if it is integrable, there must be satisfied, instead of (2.10), the reciprocity relations

$$\frac{\partial(\lambda M_k)}{\partial x_l} = \frac{\partial(\lambda M_l)}{\partial x_k}, \quad (k, l = 1, 2, \ldots n). \tag{2.12}$$

In the case of the differential expression (2.07) with two variables, there is only one reciprocity relation, $\partial(\lambda M)/\partial y = \partial(\lambda N)/\partial x$, which can be regarded as a partial differential equation with λ as the dependent variable. Since such an equation has always a solution, *a linear*

differential expression with two variables is always integrable. This is no longer the case if n is larger than 2. For instance, when $n = 3$, there exist the three relations

$$\frac{\partial(\lambda M_2)}{\partial x_3} = \frac{\partial(\lambda M_3)}{\partial x_2}, \quad \frac{\partial(\lambda M_3)}{\partial x_1} = \frac{\partial(\lambda M_1)}{\partial x_3}, \quad \frac{\partial(\lambda M_1)}{\partial x_2} = \frac{\partial(\lambda M_2)}{\partial x_1},$$

of which two are independent. In general, it is impossible to satisfy two equations by one function. This is brought out by the fact that λ can be eliminated from the three relations which leave as the result of this elimination

$$M_1\left(\frac{\partial M_2}{\partial x_3} - \frac{\partial M_3}{\partial x_2}\right) + M_2\left(\frac{\partial M_3}{\partial x_1} - \frac{\partial M_1}{\partial x_3}\right) + M_3\left(\frac{\partial M_1}{\partial x_2} - \frac{\partial M_2}{\partial x_1}\right) = 0. \quad (2.13)$$

(The simplest way of checking this is to substitute the form of the coefficients $M_k = (\partial f/\partial x_k)/\lambda$ following from (2.12). This equation is known as the *condition of integrability.* Unless it is satisfied the differential expression does not admit an integrating multiplier. In the general case of n variables, there must be satisfied a condition of the type (2.13) for each triple of variables.

It should be noted that the integrating multiplier, when it exists, is not unique. In fact, suppose that the linear differential expression (2.06) is transformed by multiplication by λ into the exact differential $df(x_1, \ldots x_n)$. The further multiplication by any function of f, say $\varphi(f)$, changes it into $\varphi(f)df$, which is also an exact differential. Therefore, $\lambda\varphi(f)$ is another integrating multiplier.

Exercise 10. Check by means of eq. (2.12) that $L(p, v) = pdv - vdp$ admits an integrating multiplier, namely $\lambda = 1/v^2$.

Exercise 11. Decide by means of the criteria (2.10) and (2.13) whether the following linear differential expressions are exact differentials, integrable, or non-integrable:

(*a*) $(2xydx + x^2dy + x^2ydz)e^{x}_{y}$,

(*b*) $zdx + xdy + ydz$,

(*c*) $yzdx + zxdy + xydz$,

(*d*) $(y + z)dx + (z + x)dy + dz$

9. Application to the element of work. In order to apply these mathematical theorems to the physical concepts of section 7, we have to find out whether in a simple system the element of work, $Dw = pdv$, is an exact differential. As pointed out in section 3, the state of a simple system is completely determined by two of the three variables

p, v, T. Let us use for its description T and v: The fact that dT does not appear in the linear differential expression Dw means, then, that the coefficient of dT is zero. The expression should be written $Dw = pdv + 0.dT$, and it is easy to see that it does not satisfy the reciprocity relation (2.10) or $\partial p/\partial T = \partial 0/\partial v$, since the left side is equal to the coefficient β_1 (1.04) and is, generally, finite and the right is 0. We conclude, therefore, that *the element of work is not an exact differential.* This is confirmed by considering the line integral of Dw over a closed circuit: we found in section 7 that it is represented by the enclosed area while, in the case of an exact differential, it would be equal to nothing. The same applies to the general case of a system with n degrees of freedom. The difference between the element of work (2.02) in mechanics and in thermodynamics is that, in mechanics, the generalized forces y_k are supposed to depend only on the coordinates of position $X_1, \ldots X_n$, whereas, in thermodynamics, they are, in addition, functions of the temperature T.

$$y_k = y_k(X_1, X_2, \ldots X_n, T), \qquad k = 1, 2, \ldots n. \tag{2.14}$$

The term with the differential dT has the coefficient zero, and, therefore, it is impossible to satisfy some of the reciprocity relations, just as in the case of the simple system. This is the reason why we use for the element of work the symbol Dw: we wish to reserve the symbol d for exact differentials.

A system can be considered as defined only then when the forces it exerts on its environment are known. In other words, eqs. (2.14) must be considered as given. As they are completely analogous to the equation of state, $p = p(v,T)$, of the simple system, we conclude that *a homogeneous system has one less equation of state than it has independent variables.* (Compare also section 27).

10. Heat and heat capacity. As the invention of the thermometer led to the concept of temperature (section 1), so another physical instrument, the calorimeter, helped to develop the important concept of heat. We have already seen that, when two systems of different temperatures are brought in contact, the warmer cools down and the colder heats up until equilibrium is reached. A calorimeter is a standard system with which different bodies are brought in contact in order to study their respective losses of temperature in relation to its gain. To fix our ideas, let us suppose that the calorimeter consists of one kilogram of water (initial temperature T_1) into which the bodies experimented upon (initial temperature $T_2 > T_1$) can be dropped, after which the combined system assumes a final temperature T inter-

mediate between the two ($T_2 > T > T_1$). The notion of heat was evolved from such measurements in the eighteenth century when the calorimeter technique was not yet very precise. Within this limited accuracy the following result was obtained: In experiments with the same body, the final temperature T adjusts itself for all variations of the initial temperatures T_1 and T_2 in such a way that the ratio

$$C = \frac{T_2 - T}{T - T_1} = \text{constant.} \tag{2.15}$$

C is, therefore, a characteristic constant of the particular body or system and is called its *heat capacity*. Comparing different bodies of the same material, it was, further, found that their heat capacities are proportional to their masses. For a body of the mass M, one can write $C = Mc'$, where c' is the heat capacity per unit mass or the *specific heat* of the material. Pouring into the calorimeter an additional kilogram of water, we can determine the heat capacity C_w of this water like that of any other system. In the units implied in formula (2.15) it turns out to be 1, and this is also the heat capacity of the calorimeter itself, which was taken to consist of the same amount of water ($C_w = 1$). Equation (2.15) can, therefore, be rewritten as follows

$$C\,(T - T_2) + C_w\,(T - T_1) = 0. \tag{2.16}$$

This relation has the form of an equation of conservation: It suggests that there is something that does not change in the process of calorimetric conduction. We call this invariable function or quantity *heat*. In fact, both terms of the left side have the form

$$Q = C(T - T'), \tag{2.17}$$

where T' is the initial and T the final temperature. The first term relates to the body experimented upon and is negative; it represents the heat lost by that body. The second, oppositely equal to the first, is the heat imparted to the calorimeter.

The modern improved measurements have completely borne out the fact that there is conservation of heat in all processes of conduction. However, its definition in terms of the temperature had to be refined somewhat, since it was found that the heat capacity is not strictly constant but depends on the temperature interval. If Q is the heat imparted to a system when its temperature is raised from T' to T, we define

$$\bar{C} = Q/(T - T') \tag{2.18}$$

as the *mean heat capacity* for this interval. When the interval is small, $T' = T - \Delta T$, this can be written $\bar{C} = \Delta Q/\Delta T$, and in the limiting case of $\Delta T = 0$ it becomes

$$C = \frac{DQ}{dT}, \tag{2.19}$$

the *heat capacity at the temperature* T. (We prefer the symbol D because DQ is not an exact differential, as we shall see in section 13). Multiplying this by dT and integrating, we find the more accurate expression for the heat imparted to the system

$$Q = \int_{T'}^{T} C dT, \tag{2.20}$$

which takes the place of the approximation (2.17) and must be, also, substituted into the equation of conservation (2.16):

$$\int_{T_2}^{T} C\,dT + \int_{T_1}^{T} C_w\,dT = 0. \tag{2.21}$$

The accepted unit of heat is the *(gram-)calorie*, the heat which must be imparted to 1 g of water in order to raise its temperature by 1° C. There are several different definitions of it in use, the most important being: (*a*) The 15° calorie, the heat necessary to warm 1 g of water from 14°.5 to 15°.5 C. (*b*) The *mean calorie*, one one-hundredth of the heat which raises the temperature of the same mass of water from 0° to 100° C. The latter is larger than the former in the ratio 1.00024. One thousand gram-calories form one kilogram-calorie.

As to *specific heats*, we shall refer them, in the case of chemically pure substances, to 1 mol of matter and denote by c the *molal heat*, i.e. the heat which raises the temperature of 1 mol of the material by 1° C. This definition is incomplete because the specific heat depends also on the pressure conditions during the measurement; we shall have to say more about this in section 14. Some authors use two terms: atomic heat (heat capacity of 1 mol of a monatomic substance) and molecular heat (1 mol of a chemical compound), but we shall apply the single term, molal heat, to both cases.

Joseph Black, who established the " doctrine of specific heats," discovered also another phenomenon, the *latent heat of transformations*. He observed (1761) that during the process of melting of ice (while the temperature of the water-ice mixture remains constant) a definite amount of heat must be imparted to it, to transform it from the solid

state into the liquid, which he called the *latent heat of fusion.* Later he also proved the existence of a *latent heat of vaporization* and approximately measured it. We shall denote the total latent heat by L and the *molal* latent heat by l.

Chemical reactions are also accompanied by a positive or negative heat development called the *heat of reaction.* If heat must be imparted to the system in order to make the reaction proceed, it is called endothermic; in the opposite case, *exothermic.* We shall adhere to the convention that *Q is positive when it is imparted to the system.* Therefore, the heat of an exothermic reaction will be counted as negative, of an endothermic as positive.

In modern usage, the phenomena of change of volume and pressure with temperature (treated in Chapter I) are spoken of as the *thermal properties of matter,* while heat capacities, latent heats, etc., belong to the *caloric properties of matter.*

Exercise 12. Into a calorimeter consisting of 200 g of water (initial temperature $t_1 = 20°$ C) are thrown pieces of metal weighing 300 g and having the initial temperature $t_2 = 100°$ C. The temperature of equilibrium t is for (*a*) aluminum ($\mu = 27.0$) 39°.5 C, (*b*) iron ($\mu = 55.8$) 31°.9 C, (*c*) zinc ($\mu = 65.4$) 29°.8 C, (*d*) silver ($\mu = 107.9$) 26.°2 C. Find the specific heats per 1 g and the molal heats of these four metals. (μ denotes the atomic weight.)

Exercise 13. The molal latent heat of fusion of water ($\mu = 18$) is $l = 1440$ cal mol^{-1}. We drop into a mixture of 1000 g ice and 1000 g water 300 g of copper ($\mu = 63.6$, molal heat $c = 5.73$ cal mol^{-1}). How much ice will melt before the system comes to equilibrium at 0° C?

11. History of the first law. The notion of energy and of its conservation was, first, established as a theorem restricted to the science of mechanics. Leibnitz showed in 1693 that, in an isolated mechanical system, there remains constant the sum of the kinetic and the potential energies, called by him the live and the dead forces (vis viva and vis mortua). If the system is not isolated, these energies are convertible into work done against outer forces. About seventy years later was formulated the law of the invariability of heat in all processes of conduction, as stated in the preceding section. The first law of thermodynamics asserts that mechanical energy and heat, the two quantities subject to laws of conservation, are not generically different, but equivalent to each other and interconvertible.

A vague suspicion that mechanical action can have heating effects seems to have existed since early times, but the first precise statement that mechanical work can be converted into heat and the first attempts to put this theory upon an experimental foundation were due to Benjamin Thompson, a native of Connecticut, better known under

his Bavarian title of Count Rumford (1798). Supervising the boring of cannons in the arsenal of Munich, Rumford was struck by the high temperature which the brass shavings attained and by the general large development of heat in the process. He could think only of two causes, other than the conversion of work into heat, which, conceivably, could have produced this effect: On the one hand, there may exist, he thought, a latent heat of breaking up solid brass into chips; on the other, the borer may induce some chemical action of the air upon brass attended by heat development. The first possibility was disproved by special measurements of two different kinds. One should expect that the surmised latent heat is due, largely, to a difference in the heat capacities of the solid metal and of the shavings. However, no such difference could be detected by calorimetric determinations especially undertaken for the purpose. Still more conclusive was a second line of reasoning: When a blunt borer rotating with much friction was substituted for the sharp one, the production of chips decreased many times while the yield of heat remained about the same. As to the possible action of air, Rumford tried to meet this objection by immersing the whole apparatus in water so that the air had no access to any of the heated parts. This change of conditions had no appreciable effect on the rate of the heat development. Rumford gives very explicit data how much heat the power of a live horse produces per hour. Translated into modern units, they are estimated to mean that 1 (gram)-calorie is equivalent to 5.45×10^7 erg, a result which is 31% above the value at present accepted. A sequel to Rumford's work was a paper by his associate in the Royal Institution of London, Sir Humphry Davy (1799). In order to refute the objection that the heat, in the above experiments, could have come from the water (which might have exercised upon brass a chemical influence similar to that of air), Davy studied the conversion of work into heat in vacuo. By means of a clockwork he rubbed two pieces of ice against each other under the jar of an air pump. The effect was unmistakable, inasmuch as the ice melted faster with rubbing than without, but no quantitative determinations were attempted.

The brilliant lead of Rumford and Davy was not followed up by other investigators. Forty years passed as a period of quiescence during which these problems were, practically, never mentioned as far as the literature of physics and chemistry is concerned. Not until the decade from 1840 to 1850 was the principle of conservation of energy established and accepted, owing to the independent work of several men belonging to different nations. The French engineer Séguin

(1839) formulated the theory of the equivalence of work and heat with great clarity and carried out much experimental work trying to prove it. The idea of these experiments was excellent and amounted to a reinterpretation of the formula of adiabatic expansion from the point of view of conservation of energy (compare section 18). Their execution and analysis, however, were imperfect, and Séguin himself admitted that his results succeeded only in making his contention probable and did not constitute a convincing proof. Quite independently and with equal lucidity the principle was stated by the German physician Robert Julius Mayer (1842), who also computed the ratio between the units of heat and work (mechanical equivalent of heat) from data on the specific heat of gases then available (compare section 15). This method, although not quite free from objection, disclosed an unusual insight into the nature of the phenomena involved in it. The result at which he arrived is 1 calorie $= 3.57 \times 10^7$ ergs, or 15% below the correct value. However, Mayer seems to have overlooked that even the most ingenious hypothesis needs an experimental demonstration in order to become a scientific law: no experiments were either planned or suggested by him. The credit of having set the principle of conservation of energy upon a firm experimental foundation is, entirely, due to James Prescott Joule of Manchester (England). Owing to delicate health, Joule did not receive a regular course of instruction but was tutored at home; among his teachers was the chemist, John Dalton. Joule conceived the idea of the equivalence of heat and work at an early date and began his experiments upon it in 1840 at the age of 20. They were carried through in his private laboratory built for him by his father, a retired brewer. He was led to the problems of conservation of energy from a study of electric currents, having ascertained (in 1840) that there is a constant relation between the work necessary to maintain a current and the heat generated by it (Joule's heat). In his first determination of the mechanical equivalent of heat (1843) he utilized just this fact: The current was supplied by an electromagnetic generator and passed through a resistance immersed in a calorimeter. While this circuit operated at a stationary rate, he determined, on one hand, the work put into the generator, on the other, the heat developed in the calorimeter (result: 1 cal $= 4.6 \times 10^7$ erg). Best known is his direct determination of 1849 in which he produced heat by churning water and other liquids with paddle-wheels, and which gave 1 cal $= 4.154 \times 10^7$ erg (for a long time, the accepted standard value, unsurpassed for several decades), but his work included the study of a great variety of processes relating to the interconvertibility of mechanical, thermal, electrical,

and chemical energies. As one of the founders of the principle of conservation of energy must be also regarded Hermann Helmholtz, at that time a young surgeon in the Prussian army. He at once recognized its importance and scope and was instrumental in bringing it to the attention and acceptance of scientists by publishing a brilliant paper (1848) in which he followed its workings through numerous applications to the sciences of physics, chemistry, and physiology.[1]

It is very remarkable that none of these four men was by training a physicist. Séguin was brought up as an engineer, Mayer and Helmholtz as physicians, while Joule having received an irregular education cannot be classified with any professional group. The significant fact that the contemporary physicists had no part in the development of a most important phase of their science cannot be denied, even if Helmholtz and Joule later became ornaments of their profession. The reason for this has been pointed out by Ostwald and others: It was the time of reaction after the collapse of Schelling's "Naturphilosophie". All the physicists had been, for a longer or shorter period, under the influence of that movement. Now they were tired of fruitless generalities and anxious to make amends for the wasted time by conscientious factual research. They became suspicious of anything that was reminiscent of a speculative anticipation of nature. This frame of mind accounts for the hostility with which the mechanical theory of heat was received in physical circles. On the other hand, the active interest developed by engineers on its behalf hardly needs any explanation: The production of power from fuel is the engineer's everyday pursuit which compels him to think continuously about the connection between heat and work.

These facts help us to understand the aloofness of the physicists and the active participation of an engineer in investigating the equivalence of mechanical and caloric energy. It remains, however, unexplained how this principle could enlist the interest of two distinguished medical men. The writer began to feel that there might lie a historical problem in this and that it would be worth his while to inquire into the interests and the scientific background of physicians and physiologists of the period between 1820 and 1840. These suspicions were confirmed

[1] Posthumous notes of S. Carnot disclose that this author, who wrote his "Réflexions sur la puissance motrice du feu" strictly from the point of view of the indestructible caloric fluid, in later years (before his death in 1832) became more friendly to the idea of the equivalence of heat and work. However, it is hardly possible to assign him a share in the discovery of the first law, on the strength of this, because he did not possess either a rigorous formulation of it or any new empirical evidence to support it. Besides, his notes were published for the first time in 1878, a quarter of a century after the law had ceased to be controversial.

by the following passage in one of Joule's papers: " On conversing a few days ago with my friend Mr. John Davies, he told me that he had himself, a few years ago, attempted to account for that part of animal heat which Crawford's theory had left unexplained, by the friction of the blood in the veins and arteries, but that finding a similar hypothesis in Haller's 'Physiology', he had not pursued the subject farther " (Postscript to the paper in Phil. Mag. **23**, 1843). These lines tell us about a third physician who was familiar with the idea of the equivalence of heat and work. Moreover, they give us a hint that the source of his interest in the subject lay in the theory of animal heat, with a reference to Haller's physiology as a clue.

At present, the name of Albert Haller may not be generally known, but in the eighteenth century he was considered a scientific colossus and enjoyed an international prestige, as an authority in medicine and botany, which is equaled only by that of Newton, in his sphere and at his time. A native of Berne (Switzerland), he became the main scientific figure at the university of Göttingen. In German-speaking countries his reputation was further enhanced by important poetical writings. His " Outline of Physiology " appeared in 1747 and was immediately translated into French and English. It is not too much to say that it marked a new epoch in that branch of science and became the main influence in the education of several generations of physicians. The last German edition was published in 1822, and we have seen that Dr. Davies consulted this treatise even about the year 1840. The passage which Dr. Davies must have had in mind is contained in section 303 of the first volume.[1] On the preceding pages Haller analyzes the uses of the lungs and comes to the conclusion that the animal heat is produced in this organ and imparted to the blood passing through it. Of considerable interest to us is his hypothesis as to how the heat originates: In his own words, it arises " from the alternate extension and contraction, relaxation, and compression of the pulmonary vessels, by which the solid parts of the blood are perpetually rubbed together and closely compressed in the attrition that is made during expiration, as it is more rapidly moved and ground together during expiration". Very important is, also, the following sentence: " Nor is it any objection to this that water cannot be made hot by any friction. Nor in reality is this assertion true; for water by violent winds and motion, as well as milk, acquires some degree of warmth". These quotations contain Haller's theory of respiration which, for a long time, dominated the science of medicine. It is quite a surprise to find that this theory was essentially based on the idea

[1] Not section 304 of Vol. II, as Joule gives the reference.

that heat can be generated by mechanical work, although it was enunciated 50 years prior to the work of Rumford.[1]

We have found a convincing proof of the fact that, at a certain epoch, the physiologists were much concerned with the problem of the relation between work and heat, and we shall see below that they were keenly aware of the work of Rumford and Davies, seeing in it a confirmation of Haller's hypothesis. It is surprising, at first sight, that this interest could have persisted until the middle of the nineteenth century, since the modern combustion theory of respiration, suggested already by Priestley, received strong support from the measurements of Lavoisier and Laplace (about 1781) and was rediscovered independently by the English physician Crawford (referred to by Joule as Crawford's theory). A closer investigation shows, however, that there were excellent reasons which prevented the acceptance of the combustion theory as a complete explanation of animal heat. Lavoisier and Laplace had found that the oxidation of carbon contained in the carbohydrates of the blood is insufficient to account for the developed heat, and they expressed the conjecture that the balance is produced by the oxidation of hydrogen. An experimental test of this hypothesis required measurements extremely delicate and difficult for the primitive technique of those times. A long time passed, therefore, before they were even attempted. At length (in 1821), the Académie des Sciences announced a prize for the investigation of this problem, and this induced Dulong and Despretz to start work on it. Despretz's essay was submitted to the academy in due time and received the prize on June 1, 1823 (published in the Ann. Chem. Phys. (2) **26**, p. 337, 1824). He concluded from measurements on 200 animals that the complete heat of oxidation of both carbon and hydrogen accounts for the larger part of the animal heat but not for the whole of it. There remained a defect of about 20% for the explanation of which Despretz fell back upon Haller's theory, saying that it could be produced " by the motion of the blood and the friction of its different parts". The results obtained by Dulong were quite in agreement with those of Despretz's. He read his paper before the academy in 1822, but he did not contend with it for the prize and he resisted the urging of his friends to have it published (appeared after his death: Ann. Chim. Phys. (3) **1**, p. 440, 1841). The reasons for this strange reluctance became clear when his posthumous papers were examined: Dulong had no faith in the thermochemical data on which his own and Despretz's conclusions were based. He intended to redetermine

[1] Even Haller cannot claim priority in this matter, since similar views were held in the seventeenth century by the Iatro-Physical School.

the heats of formation of carbon dioxide and of water in order to revise his essay. This redetermination, finally carried out, was the last scientific work done by Dulong: he obtained new and more accurate data but died before bringing his results into shape for publication (posthumously edited by Cobart, Ann. Chim. Phys. (3) **8**, p. 183, 1843). While his work confirmed the previously accepted heat of formation of carbon dioxide as fairly accurate, it established an entirely new value for the heat of formation of water, showing that the old data were much too low. This correction was more than sufficient to remove the discrepancy between the animal heat and the chemical heat development of respiration and constituted a conclusive proof of the oxidation theory. However, it must be remembered that this knowledge came rather late: between 1823 and 1843 the last word of physiological science was the existence of a defect of animal heat which, apparently, was left unaccounted for by the combustion theory.

There remains the question how widely this knowledge was diffused among physiologists and physicians. The writer happened to come across a very comprehensive German " Handbuch " of physiology of that time written in six volumes by leading authorities under the editorship of Karl Friedrich Burdach. The account of the theory of respiration, due to Ernst Burdach, is contained in the sixth volume, which appeared in the year 1840. Many pages are devoted to the history of the two theories, and both sides of the question are discussed at considerable length. After a lucid presentation of Haller's views (p. 544), Burdach turns to " the doctrine of the resemblance of respiration and combustion". It appears from his account that in the period between 1820 and 1840 the physicians interested in the theory of respiration were preoccupied, like Joule's friend Dr. Davies, by " that part of animal heat which Crawford's theory left unexplained". Most of them pointed to Haller's theory as to the most likely explanation and maintained that the origin of the unaccounted heat lay in the mechanical action of friction in the arteries. These mechanical effects were, in their turn, supposed to be produced by the " vital principle " (puissance vitale) invented by Barthez. Burdach gives many references to authors who advocated this view. Among them were some of the leading men of science, like Despretz and Treviranus, but also some of the rank and file. For instance, the writer had the opportunity of reading in the originals a German pamphlet by F. Lau (Bonn 1830) and an English paper by J. M. Winn (Phil. Mag. **14**, p. 174, 1839). They are of great interest as an indication into how wide a circle the problem had spread. Lau and Winn were, apparently,

ordinary practitioners without much knowledge of the literature of the question or understanding of its deeper implications. Yet, their theories were only modifications of Haller's views. It is interesting to note that Burdach himself, who was not in sympathy with these explanations, did not question the fact that heat can be produced by friction, but regarded it as a matter of common knowledge, citing, in this respect, Rumford and Davy. He only doubted whether this cause would be sufficient to account for the desired effect quantitatively.

The above facts throw a new light on the role of the medical profession in the history of the principle of conservation of energy. There was, actually, no break of tradition between the work of the eighteenth and the nineteenth centuries. However, this tradition was handed down through the unexpected channel of the science of physiology, whose representatives acted, for half a century, as the custodians of the idea of equivalence of heat and mechanical work. If this statement implies that the historical role of Mayer and Helmholtz consisted in turning back this principle to physics, the branch of science where it naturally belongs, this is in no way a detraction from the merits of these two great men: They were not merely passive transmitters of a concept, because there is an enormous gap between the vague knowledge current among physicians, that heat is generated by mechanical action, and the scientific formulation of the principle of equivalence, which could be bridged only by men of unusual ability. Helmholtz, eventually, developed into one of the greatest scientists of all times, and Mayer showed in his later physiological writings (1845) a clearer understanding of the nature of animal metabolism than any of his contemporaries. Nevertheless Mayer was entirely unsuccessful in his endeavors to persuade the physicists and chemists of the validity of his conception. The reason for this was, without doubt, that he could not offer them much in the way of an experimental proof at a period when they were particularly reluctant to accept anything on insufficient empirical evidence. A few years latter Helmholtz had far better success because, in the meantime, Joule's work had put the principle of conservation of energy on a secure experimental foundation.

CHAPTER III

THE FIRST LAW OF THERMODYNAMICS AND THE CALORIC PROPERTIES OF MATTER

12. Reversible and irreversible processes. It was pointed out in section 2 that the thermodynamical description of a system, by such variables as its temperature and pressure, implies that it is in equilibrium. In general, this equilibrium is disturbed if the system is subjected to any physical process. For instance, if we exert a mechanical action upon it or bring it under the influence of a source of heat, the result is a complicated transient state, of longer or shorter duration, during which all the physical characteristics of the system are different in every point of it. The quantitative description of such an occurrence is, therefore, entirely outside the scope of thermodynamics. It is possible to follow through by thermodynamical methods only processes which take place so slowly that they can be regarded as a succession of states of equilibrium. Strictly speaking, the change of the system in a finite time must be even infinitesimal and the rate of change infinitely slow.

Such infinitely slow processes have an important theoretical advantage in that they are *reversible*, that is, they can be gone through in both directions. In fact, let us take the example of a simple system: If we change two of the three variables, say v and T, so slowly that the system can be regarded as in equilibrium at any moment, the equation of state applies all the time and the third variable p is also completely determined. When we go through the same values of v and T in the opposite direction, the succession of states of the system is, simply, reversed. For every infinitesimal step, the work done by the system is expressed by $Dw = pdv$. When the process is reversed, dv changes its sign while p has the same values so that the work retains the same absolute value as in the direct process, but has the opposite sign, i.e. is done by outer forces against those of the system. We shall see in the next section that the heat received by the system in every infinitesimal part of the process is also a linear differential expression so that the same conclusions hold with respect to it: If a certain amount of heat is imparted to a system in an infinitely slow process,

the same amount is withdrawn from it when the process is reversed. We have restricted ourselves to simple systems, only, to fix our ideas: All our results apply also to the most general thermodynamical system because, for every phase of it, there exist equations of state of the type (2.14) and the elements of work and heat have always the form of linear differential expressions.

When we turn to processes of a finite speed, we can no longer assert that they are reversible. As an example, we consider a gas in a vertical cylindrical vessel with a piston as its top. The reversible way of compressing such a gas would be to increase the load on the piston infinitely slowly by adding infinitesimal weights. When a finite weight is added at a time, the compression goes at a finite rate, but owing to the lag in the propagation of stresses, the compression and the pressure immediately under the piston will be higher than in the remainder of the gas and higher than in the reversible process. To produce the same reduction of volume, the outer forces have, therefore, to do more work than in the infinitely slow case: A part of the work is consumed by elastic waves, currents, and other wasteful processes in the gas, the so-called phenomena of *internal friction*. On the other hand, if we expand the gas back to the original volume, proceeding at a finite speed, the same lag will cause the pressure at the piston to be lower than in an infinitely slow expansion. The gas will do, therefore, less work than in the latter process. It follows from this that the compression and expansion, at a rate which is not infinitely slow, are irreversible processes since the work which must be applied in the compression is larger than that received from the system in the expansion.

The extreme case of rapid expansion is that when there is no outer force at all, for instance, when the piston is suddenly removed. Such an *expansion into the void* takes place without the system doing any work. It is quite obviously irreversible, since it is necessary to apply work of outer forces to compress the system back to the initial volume. Another example of an irreversible process is the phenomenon of thermal conduction of which we have made use in defining the concepts of temperature (section 2) and of heat (section 10): If we bring in contact two bodies having a finite difference of temperatures, heat flows, spontaneously, from the warmer to the cooler, but never in the opposite direction. All processes of nature proceed at a finite speed, and experience tells us that they are all accompanied by effects of the nature of friction or conduction which make them irreversible. The engineer would call these effects " wasteful ", since they do not produce any work, and the irreversible process " less efficient " than the

reversible. Strictly speaking, the reversible processes are an ideal which exists only in our imagination. However, this is enough to make its discussion very useful; besides, many real processes are conducted at so slow a rate that they can be regarded as reversible within the limits of experimental error. Only such processes can be mathematically described in thermodynamics, or represented by means of curves in diagrams. If the system is not in equilibrium no unique values of temperature and pressure can be assigned to it.

13. Analytical formulation of the first law. Internal energy. The purport of the first law has been made sufficiently clear in Chapter II. Its gist is that heat is convertible into mechanical work and other forms of energy, and vice versa, in the ratio of the mechanical equivalent of heat: 1 15°-gram-calorie $= 4.185 \times 10^7$ erg. By means of this conversion factor we shall always express heat and work in the same units. What is, then, the fate of an infinitesimal amount of heat DQ, imparted to a system by bringing it in contact with a suitable heat reservoir? Since thermodynamics deals only with states which are infinitely close to equilibrium we need not consider its conversion into kinetic energy: The heat DQ will, in part, cause the system to do the work DW against outer forces; in part, it will be used to raise the temperature and, perhaps, to overcome the resistance of inner forces attending a change in volume and in other inner properties. We denote the portion utilized for the latter purpose by DU and obtain the equation:

$$DQ = DU + DW. \tag{3.01}$$

We know that the element of work DW is not an exact differential, but we do not yet know what the elements DQ and DU are, in a mathematical sense, and it will be our next objective to find this out. This is the reason why we use the symbol D: According to the convention made in section 8, the symbol d is reserved for expressions which, we are sure, are exact differentials.

Let us now consider a reversible process in which the heat Q is imparted to our system by bringing it, successively, in contact with an infinity of heat reservoirs differing in temperature by infinitesimal amounts. For every step of this process eq. (3.01) holds, and we have, simply, to integrate it from the initial state of the system (1) to its final state (2): $Q = \int_1^2 DQ$, and, according to section 7, $W = \int_1^2 DW$. We find, therefore,

$$\int_1^2 DU = Q - W. \tag{3.02}$$

Of particular interest is the case when the process is *cyclic* so that at the end of it the system is, precisely, in the same state as in the beginning. The system itself does not, then, contribute anything to the energy balance. If we compare the conditions before and after the cycle is carried through, the only changes are outside the system. Namely, the heat Q is withdrawn from the reservoirs and the work W done against outer forces. The law of conservation of energy leads, therefore, to $Q - W = 0$, instead of (3.02), whence

$$\oint DU = 0, \tag{3.03}$$

for any reversible cyclic process. As we have seen in section 8, eq. (2.11), it follows from the property (3.03) of the integral that the expression DU is an exact differential. This means that there exists a certain function U of the variables defining our system whose total differential dU is identical with the differential expression DU. This function U is known as the *internal energy*. Every function which is completely determined by the variables of the system we shall call a *characteristic function* of it. The internal energy is, therefore, one of the " characteristic functions " of thermodynamical systems.

Instead of eq. (3.01) we have to write, therefore,

$$DQ = dU + \text{Đ}W. \tag{3.04}$$

The element DQ being the sum of an exact and a non-exact differential is itself not an exact differential according to the criteria of section 8. The integral (3.02) over a reversible process takes now the form

$$Q = U_2 - U_1 + W. \tag{3.05}$$

In words: the heat imparted to the system is used, partly, to increase its internal energy from the initial value U_1 to the final U_2, and partly to do outer work. Though derived for a reversible process, this equation has a wider range of application. In fact, suppose that in an initial state of equilibrium the system has the internal energy U_1. We subject it, then, to an irreversible process and, after it is over, wait until the system and its environment are again in equilibrium. Suppose it is now found that the internal energy has become U_2, that outer sources have lost the heat Q, and that the work W has been done against outer forces. The law of conservation of energy leads again to the relation (3.05). In this sense it can be applied also to an

irreversible process. In the particular case when the process is cyclic, the initial and the final state are identical, $U_2 - U_1 = 0$, and

$$Q = W. \tag{3.06}$$

The gist of the first law of thermodynamics is that work can be produced only at the expense of heat or some other form of energy. Therefore, it can be formulated as the *impossibility of a perpetual motion machine* (perpetuum mobile), as those delusive devices are called which claim to do useful work, continually, without drawing on any energy source. In its application to purely mechanical engines, this principle had already been recognized by Stevinus, Newton, and Leibnitz. The discoveries of the middle of the nineteenth century (section 11) extended it to engines of any kind.

Exercise 14. 300 g of mercury are dropped from a height of 600 cm into a calorimeter consisting of 500 g of water at 10° C. In this process the potential energy of the mercury is, first, converted into kinetic energy and then into heat. What will be the final temperature of the water and mercury? (The specific heat of mercury is 0.0334 cal g^{-1} deg^{-1}, the acceleration of gravity $g = 980.7$ cm sec^{-2}).

Exercise 15. The latent heat of vaporization of water is $l = 9730$ cal mol^{-1} (per 18 g). What part of it is spent on the work of expanding the steam, as calculated in exercise 8?

14. Molal heat at constant volume and at constant pressure. We are going to apply the first law, as formulated in eq. (3.05), to the special case of a simple, chemically pure system. We shall refer Q, U, W to one mol of the material of the system, denoting the molal quantities by the small letters q, u, w. Moreover, according to (2.04), the element of work is, for a simple system, $Dw = pdv$, whence

$$Dq = du + pdv. \tag{3.07}$$

The molal heat is, according to the definition (2.19) of specific heats, given by

$$c = Dq/dT \tag{3.08}$$

and depends upon the conditions under which the element of heat Dq is imparted to 1 mol of the system. Two cases are of special practical interest: (1) the volume of the system is kept constant ($dv = 0$) while heat is added to it; (2) its pressure is kept constant ($dp = 0$).

The internal energy u depends on the variables which define the system: in the case of a simple system, we can regard it as a function of any two of the three parameters p, v, T. To treat the case of

constant volume it will be useful to describe it in terms of temperature and molal volume:

$$u = u(T, v), \tag{3.09}$$

a relation which is often called the *caloric equation of state.* Its total differential has, then, the expression

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv, \tag{3.10}$$

which, substituted into (3.07), gives

$$Dq = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right] dv. \tag{3.11}$$

If we put $dv = 0$, we obtain, comparing this with (3.08), the *molal heat at constant volume*

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v. \tag{3.12}$$

On the other hand, to treat the case of constant pressure, we must find an expression of Dq in terms of the differentials dT and dp. The simplest way of doing this is to recall that, because of the equation of state, v itself can be regarded as a function of T and p so that

$$dv = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dp.$$

Substituting this into (3.11)

$$Dq = \left\{\left(\frac{\partial u}{\partial T}\right)_v + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right]\left(\frac{\partial v}{\partial T}\right)_p\right\} dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right]\left(\frac{\partial v}{\partial p}\right)_T dp. \tag{3.13}$$

Putting $dp = 0$, we find by comparison with (3.08) the *molal heat at constant pressure*

$$c_p = \left(\frac{\partial u}{\partial T}\right)_v + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right]\left(\frac{\partial v}{\partial T}\right)_p. \tag{3.14}$$

The subtraction of (3.12) from (3.14) leads to the important relation

$$c_p - c_v = \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right]\left(\frac{\partial v}{\partial T}\right)_p. \tag{3.15}$$

The reason why c_p is larger than c_v is obvious: If the system is permitted to expand while the element of heat Dq (per mol) is imparted to it, this heat is used, not only to raise the temperature of the system,

but also to do work, namely, work against outer forces to the extent $p(\partial v/\partial T)_p\, dT$ and against inner forces of the system itself in the amount $(\partial u/\partial v)_T \cdot (\partial v/\partial T)_p\, dT$.

In the case of condensed systems (liquids and solids) the coefficient of expansion $(\partial v/\partial T)_p$ is so small that it can be neglected for most purposes. Within this approximation it is unnecessary to distinguish between molal heats at constant volume and at constant pressure ($c_p = c_v = c$). We postpone a detailed discussion of the molal heats, as to their experimental values as functions of temperature, until Chapter XVIII, but it will be necessary to say something about the approximate laws for permanent gases and for solids in the next two sections.

Exercise 16. The approximate value of $(\partial u/\partial v)_T$ for N_2, at 0° C and 1 atm, is 0.0047. Estimate $(\partial v/\partial T)_p$ from the data of Table 1, and say by what percentage $c_p - c_v$ deviates from R.

15. The internal energy of perfect gases. The question in what measure the internal energy of gases depends on their volume can be decided in an experimental way. A very suitable experiment for this purpose is the *expansion of a gas into the void* mentioned in section 12. Provided that the system is adiabatically isolated, neither heat is imparted to it in this process nor does it do any external work, so that the terms Q and W in eq. (3.05) of conservation of energy vanish, and it is reduced to $U_2 - U_1 = 0$ or, referring it to 1 mol of the gas, $\Delta u = u_2 - u_1 = 0$. If the expansion is small, we can write with the help of (3.10) and (3.12)

$$\Delta u = c_v \Delta T + (\partial u/\partial v)_T \Delta v = 0$$

or

$$\left(\frac{\partial u}{\partial v}\right)_T = c_v \frac{\Delta T}{\Delta v}.$$

If the internal energy is independent of the volume, $(\partial u/\partial v)_T = 0$, there follows $\Delta T = 0$: the expansion into the void is not attended by any change of temperature. It is possible to test this point by conducting the process while the system is in contact with a calorimeter, instead of being adiabatically isolated. Joule carried out the experiment (1845) in the following form: two large, closed copper vessels were connected by a short copper pipe containing a stop cock. While the stop cock was shut, one of them was filled with gas at high pressure, the other evacuated and both were immersed into the same water calorimeter. When the stop cock was opened, the gas rushed into the empty vessel without doing work, but no change of temper-

ature of the calorimeter could be discovered for any of the gases used. (A somewhat similar experiment, tried by Gay-Lussac as early as 1807, had a quite different purpose). It may be concluded from this that the dependence of the internal energy of permanent gases upon their volume is small, but the large heat capacity of the calorimeter reduced the accuracy of the experiment too much to say more. To increase the accuracy, it is desirable to remove the calorimeter altogether and to measure directly the temperature of the expanded gas. However, this is impossible in the original form of the experiment: after the stop cock is opened, the gas is in a turbulent state with no uniformity of pressure or temperature. It comes to rest only after a period of time long enough to vitiate the results by heat losses through convection. A modification which avoids these difficulties was suggested by William Thomson (later Lord Kelvin) and carried through, jointly, by Joule and Thomson in a series of investigations extending from 1852 to 1862. They maintained a stationary stream of gas through a tube A_1A_2 (Fig. 7), obstructed in the middle by a cotton plug C. Owing to the friction in the plug, there was no turbulence in the flow and the gas was in a homogeneous state on either side of the obstruction. Before passing it, its pressure, molal volume, temperature, and internal energy were p_1, v_1, T_1, u_1, afterwards p_2, v_2, T_2, u_2. The difference of temperatures $T_2 - T_1$ was measured by a thermoelectric couple. Heat exchange with the environment was prevented by protecting the tube with heat-insulating material. As to the kinetic energy of the gas, and the friction losses in the plug, they are proportional to the square of the velocity of the flow, which was chosen so low that they were entirely negligible, compared with the other energy items. Let us set up the energy balance for a portion of the gas which is contained (at a certain moment) between the cross-sections M_1 and M_2, for the time during which 1 mol of the gas flows through the tube. At the end of this time it will occupy the new position between N_1 and N_2 and we can apply to this process the eq. (3.05) of conservation of energy which reduces here to $U_2 - U_1 + W = 0$, since no heat is imparted to the gas ($Q = 0$). As a result of the displacement, 1 mol of the gas (with the internal energy u_2) appears on the right side of the plug and 1 mol (of the energy u_1) disappears on the left: $U_2 - U_1 = u_2 - u_1$. On the right side, work is done by this part of the gas in pushing forward the adjacent portions through the volume v_2 at the constant pressure p_2; on the left, work is done

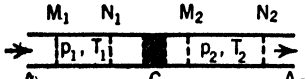


FIG. 7.—Joule-Thomson process.

against it while it is displaced through the volume v_1 (pressure p_1): $W = p_2v_2 - p_1v_1$. Our equation assumes, therefore, the form

$$u_2 + p_2v_2 = u_1 + p_1v_1. \tag{3.16}$$

We shall postpone the analysis of this equation and of the results of Joule and Thomson until section 28. Suffice it to say here that, generally, the partial $(\partial u/\partial v)_T$ turned out to be small, but not equal to zero. Comparing the different permanent gases at room temperature, it decreases in the order in which the gases become more perfect (section 6) and is almost negligible for helium. It is, therefore, logical to define the perfect gas as characterized by an internal energy entirely independent of its volume: $(\partial u/\partial v)_T = 0$, so that, from (3.12) and (3.10),

$$du = c_v\, dT. \tag{3.17}$$

This implies, of course, that c_v is independent of v, because of the condition (2.10). As to its dependence upon the temperature, the experiments with real gases show, again, that it is the smaller, the nearer the gas approaches in its equation of state the behavior of perfect gases. In the definition of the perfect gas c_v is, therefore, taken to be constant. Integrating eq. (3.17), there follows the expression of the internal energy of perfect gases

$$u = c_vT + u_o, \tag{3.18}$$

where u_o (the so-called " zero point energy ") is an integration constant. This formula gives a good approximation to the internal energy of real monatomic gases, although it is not safe to extrapolate it to extremely low temperatures (section 105). In the case of diatomic and polyatomic gases, the approximation is fair only for a limited range of temperatures (on both sides of the room temperature): At very low temperatures the molal heat decreases because the rotational motions of the molecules require less energy; at very high temperatures it increases because the molecular vibrations begin to come into play. In view of this situation it is well to give the expression also for the case when the gas is *thermally perfect* (i.e. obeys the equation $pv = RT$) but *calorically imperfect*, to the extent that its specific heat, being independent of v, is a function of T

$$u = \int_0^T c_v\, dT + u_o. \tag{3.19}$$

In the special case c_v = const, this becomes identical with (3.18).

In either case, eqs. $(\partial v/\partial T)_p = R/p$ and $(\partial u/\partial v)_T = 0$ hold, whence from (3.15):

$$c_p - c_v = R. \tag{3.20}$$

This is the equation which J. R. Mayer used for the determination of the mechanical equivalent of heat, taking, for c_p and c_v, data expressed in calories (per degree and mol) and, for R, in mechanical units (compare section 12). Theoretically, his method was not free from objection, since, at the time, there was no foundation for the hypothesis that in the expansion of gases no energy is needed to overcome internal forces. In practice, however, the later work of Joule and Thomson showed that the formula is satisfied fairly well: Mayer would have obtained a pretty accurate value of the equivalent if good data of c_v and c_p had been available. The modern value of the gas constant in caloric units is $R = 1.9864$ cal deg mol^{-1}.

In the case of monatomic gases the molal heats are very close to $c_v = 3R/2$, $c_p = 5R/2$, so that the ratio is $\gamma = c_p/c_v = 5/3$. The data for the more important gases at 15° C are given in Table 4.

TABLE 4

MOLAL HEATS OF GASES

Gas	$\gamma = c_p/c_v$	c_p/R	$(c_p - c_v)/R$	Gas	$\gamma = c_p/c_v$	c_p/R	$(c_p - c_v)/R$
A	1.668	2.52	1.00	CO_2	1.304	4.41	1.03
Ne	1.66			N_2O	1.303	4.44	1.03
Xe	1.66			NH_3	1.31	4.49	1.06
Hg	1.67			CH_2	1.31	4.27	1.01
H_2	1.410	3.44	1.00	H_2S	1.32	4.35	1.05
N_2	1.404	3.50	1.00	SO_2	1.29	4.89	1.10
O_2	1.401	3.52	1.00	CN	1.26	5.36	1.09
CO	1.404	3.50	1.00	C_2H_2	1.26	5.02	1.03
NO	1.400	3.52	1.00	C_2H_4	1.255	5.08	1.03
HCl	1.41	3.56	1.00	C_2H_6	1.22	5.84	1.05
Cl_2	1.355	4.10	1.08				

A more detailed account of specific heats of gases will be found in Chapter XVIII.

Exercise 17. For water vapor in the range between $t = 0°$ C and $t = 650°$ C Nernst gives the empirical formula

$$c_p = 8.62 + 0.002\, t + 7.2 \times 10^{-9}\, t^2 \text{ cal mol}^{-1} \text{ deg}^{-1}.$$

Assuming that eq. (3.20) is satisfied, find c_v and determine the increase of internal energy $u_{650} - u_0$.

Exercise 18. For CO_2 between $-75°$ C and $+20°$ C the empirical formula is

$$c_p = 8.71 + 66 \times 10^{-4}\, t - 22 \times 10^{-7}\, t^2 \text{ cal mol}^{-1} \text{ deg}^{-1}.$$

Find $u_{20} - u_{-75}$.

16. Molal heats of solids. We shall postpone the detailed theory and discussion of specific heats till Chapter XVIII and shall give here only two laws pertaining to solids. Though not rigorous, they are satisfied with a fair approximation at ordinary temperatures and are very useful because of their simplicity.

(A) *The law of Dulong and Petit* (1819). The molal heats of all elementary solids have approximately the same value, close to 6 cal deg^{-1} mol^{-1}. (Compare Table 5).

TABLE 5

MOLAL HEATS OF ELEMENTARY SOLID SUBSTANCES

Element	$t°$ C	c	Element	$t°$ C	c	Element	$t°$ C	c
Ag	0°	6.00	Fe	0°	5.85	Zn	0°	5.99
Au	0°	6.07	Mg	0°	5.83	C (graph)	0°	1.82
Bi	25°	6.07	Ni	0°	6.05	C (diam)	0°	1.25
Cd	0°	6.15	Pb	0°	6.25	B	0°	1.9
Co	0°	5.83	Pt	0°	6.13			
Cr	0°	5.35	Sb	0°	6.00			
Cu	0°	5.81	Sn	0°	6.33			

(B) *Neumann's law* (1831). The components of solid chemical compounds have, approximately, the same heat capacity in the compound as in the free solid state. In other words, the molal heat, divided by the number of atoms n in the molecule, is roughly equal to six (Table 6).

TABLE 6

MOLAL HEATS OF SOLID COMPOUNDS

Substance	$t°$ C	c	n	c/n	Substance	$t°$ C	c	n	c/n
AgCl	28	12.53	2	6.27	PbS		12.12	2	6.06
CuO	22	10.39	2	5.20	SnS		12.63	2	6.32
CuS	25	11.89	2	5.95	ZnO	16–99	10.15	2	5.08
KCl	23	12.4	2	6.2	ZnS		11.17	2	5.58
LiCl		11.96	2	5.98	CaF_2	15–99	16.82	3	5.61
MnS		12.11	2	6.06	Cu_2S	19–52	19.1	3	6.37
NaBr	0–20	12.12	2	6.06	PbF_2	0–34	17.69	3	5.90
NaCl	24	12.14	2	6.07	$PbCl_2$	0–20	18.25	3	6.08
PbO	23	11.57	2	5.79	PbO_2	24	15.50	3	5.17

17. The heat function and the isobaric process. On both sides of eq. (3.14) of Joule-Thomson appears the expression

$$\chi = u + pv. \tag{3.21}$$

The quantity χ is known as the (molal) *heat function*, also called *heat content* and *enthalpy*. Like the internal energy u, the heat function is completely determined by the variables of the system: It is another example of a "characteristic function" (section 13). Differentiating eq. (3.21), we find $du = d\chi - vdp - pdv$ and, substituting this into the expression (3.07) of the element of heat imparted to a simple system,

$$Dq = d\chi - vdp. \tag{3.22}$$

In a similar way, referring all quantities not to 1 mol of a substance but to the whole simple system, we define as the total heat function $\mathbf{X} = U + pV$ and find $DQ = d\mathbf{X} - Vdp$. The heat function acquires a particular importance in the so-called *isobaric process*, i.e. a process which takes place without change of pressure (p = const, $dp = 0$). For an infinitesimal isobaric change the last equation gives $DQ = d\mathbf{X}$. In the case of a finite reversible change of the system, at constant p, from the state (1) to the state (2), we obtain by integration

$$Q = \mathbf{X}_2 - \mathbf{X}_1. \tag{3.23}$$

The heat imparted to the system in a reversible isobaric process is equal to the difference of its heat functions in the final and initial states. Under usual laboratory conditions, processes of change of the physical state (melting, vaporization) are conducted at constant pressure, as well as most chemical reactions. The formula (3.23) has, therefore, a wide range of applications. For instance, the latent heat per mol is, obviously, equal to the difference of the molal heat functions of the material in the two states of aggregation

$$l = \chi_2 - \chi_1. \tag{3.24}$$

If we choose T and p as the variables describing simple systems, we can write eq. (3.22) in the form

$$Dq = \left(\frac{\partial \chi}{\partial T}\right)_p dT + \left[\left(\frac{\partial \chi}{\partial p}\right)_T - v\right] dp, \tag{3.25}$$

and comparing with (3.13), (3.14),

$$c_p = \left(\frac{\partial \chi}{\partial T}\right)_p. \tag{3.26}$$

In the case of a perfect gas, the heat function can be given explicitly: According to (1.13), $\chi = u + RT$, whence from (3.19) and (3.20)

$$\chi = \int_0^T c_p\, dT + u_0, \tag{3.27}$$

and if c_p = const,

$$\chi = c_p T + u_0. \tag{3.28}$$

Exercise 19. One mol of water is vaporized at 100° C and the vapor heated to 650° C. Calculate the increase of χ in this process, using the data given in exercises 15 and 17.

18. The isothermal and adiabatic processes. It will be useful to discuss here the simplest thermodynamical processes, especially, with respect to the amounts of heat received and work done. Since the perfect gas is, so far, the only system whose behavior we know completely, both as to its equation of state and its internal energy, we can give explicit analytical formulas only for perfect gases. The internal energy being a "characteristic function" (compare section 13), its change is determined by the initial (1) and final (2) state of the system and is independent of the particular process. In the case of perfect gases it is, according to eq. (3.18),

$$u_2 - u_1 = c_v(T_2 - T_1), \tag{3.29}$$

or if the gas is only thermally perfect, and calorically imperfect, according to (3.19),

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v\, dT. \tag{3.30}$$

On the other hand, the work w depends on the special process and, consequently, also the heat q which can be determined from the first law of thermodynamics (referred to 1 mol of a chemically pure system),

$$q = u_2 - u_1 + w. \tag{3.31}$$

We have already discussed the *isobaric* process (p = const) in the preceding section. The process consisting in heating a simple system without change of volume (V = const) is so trivial that little need be said about it. It is called "isochoric" and, obviously, takes place without external work: $w = 0$ and $q = u_2 - u_1$.

Of great importance is the *isothermal process* (T = const). We have already used the concept of isothermal curves (section 5), regarding them as the loci geometrici of all possible states of a system corresponding to the same temperature. However, we can interpret

them as the graphical representation of the following reversible process: The system is contained in a vessel with heat-conducting walls immersed in a large heat bath of the temperature T. The geometrical variables of the system (e.g. the volume V, if it is simple) are then infinitely slowly changed by external forces through their whole range of variability. If the compression or expansion takes place with finite velocity the temperature of the system will not remain strictly uniform, so that a process cannot be isothermal unless it is conducted in a reversible way. In the case of a thermally perfect gas, eqs. (3.29) and (3.30) give both $u_2 - u_1 = 0$, so that $q = w$. Moreover, $p = RT/v$, $Dw = pdv = RTdv/v$, and since T is constant,

$$q = w = RT\int_1^2 \frac{dv}{v} = RT \log \frac{v_2}{v_1} = RT \log \frac{p_1}{p_2}. \qquad (3.32)$$

Equally interesting is the *adiabatic process*: This is the name for anything that can happen in a system surrounded by a heat-insulating or "adiabatic" (compare section 2) envelope which cuts off any interchange of heat with the environment. This cover does not, in general, prevent the system from doing work against outer forces, as is illustrated by the example of a gas in a cylindrical vessel closed by a sliding piston, both of adiabatic material. The gas could do work expanding and lifting by its pressure a load on the piston. Unlike the isothermal, the adiabatic process can be conducted either reversibly or irreversibly. Since no heat is imparted in it to the system ($Q = 0$), the first law of thermodynamics (3.05) takes the form

$$W = U_1 - U_2. \qquad (3.33)$$

The system can do work only at the expense of its internal energy. In particular, the work of adiabatic expansion of a perfect gas from the state (1) to the state (2) is (per 1 mol), according to (3.29),

$$w = c_v(T_1 - T_2). \qquad (3.34)$$

This is the formula which Séguin was trying to verify in his attempt to establish the first law experimentally (section 11). It implies the same tacit assumption which was made by Mayer: he took it for granted that the expansion of real gases proceeds without internal work.

When the adiabatic process is conducted reversibly, to every infinitesimal step of it applies the differential equation

$$DQ = dU + DW = 0, \qquad (3.35)$$

and in the particular case of the compression or expansion of a perfect gas, $c_v\,dT + Dw = 0$. We substitute for Dw as above, and obtain $c_v\,dT + (RT/v)dv = 0$. Dividing by c_vT and using the notation of section 15, $\gamma - 1 = R/c_v$,

$$\frac{dT}{T} + (\gamma - 1)\frac{dv}{v} = 0. \tag{3.36}$$

In the derivation of this formula only the thermal equation of state was used. It is valid also for the case where c_v and γ depend on temperature. However, when the specific heats are constant (calorically perfect gas) its integral is particularlv simple. The equation is, then, easily integrable and gives

$$Tv^{\gamma-1} = \text{const.} \tag{3.37}$$

We can substitute $T = pv/R$ from the equation of state:

$$pv^{\gamma} = \text{const.} \tag{3.38}$$

These two formulas are equivalent forms of the equation of the adiabatic for perfect gases, first derived by Poisson (1823) on the basis of the old ideas of a caloric fluid. Like the isothermals, the adiabatics can be represented as a family of curves in the (p,v)-diagram. These curves have the same asymptotes as the isothermals $pv = \text{const}$, namely the axes $p = 0$, $v = 0$; but the slope of the adiabatic ($dp/dv = -\gamma p/v$) is always steeper than the slope of the isothermal ($dp/dv = -p/v$) passing through the same point.

One of the most accurate ways of determining the ratio $\gamma = c_p/c_v$ experimentally is the measurement of the velocity of sound in the gas in question. The theory of elasticity gives for the velocity of sound a the formula (already derived by Newton)

$$a^2 = -\frac{v^2}{\mu}\frac{dp}{dv}, \tag{3.39}$$

where μ is the molecular weight of the gas. The rate of compression and expansion in a sound wave is so fast that there is no time for any appreciable heat interchange by conduction and the process must be considered as adiabatic.[1] If the medium is a perfect gas, we find, therefore

$$a^2 = \gamma pv/\mu. \tag{3.40}$$

[1] Compare section 122 with respect to the limitations of the method of sound velocities.

Exercise 20. Calculate numerically the work done by a perfect gas in its isothermal expansion from $v_1 = v_0$ to $v_2 = \frac{1}{2}v_0$ at 0° C. Express it in ergs and in calories.

Exercise 21. Give the expression for the work of adiabatic expansion in the case of a Van der Waals gas. Taking the coefficients a and b from Table 2 on p. 14, calculate it numerically for H_2 and N_2 and $v_1 = v_0$, $v_2 = \frac{1}{2}v_0$ and obtain the difference between the work done by these two real gases and the perfect gas.

Exercise 22. Give the general form of the integral of the eq. (3.36) of adiabatic expansion, when c_v (and c_p) is a function of T. Apply it to the empirical formula for water vapor given in exercise 17.

Exercise 23. Calculating the work of adiabatic expansion from the formula (3.38), check the result (3.34).

19. The cyclic process of Carnot. The French engineer S. Carnot devised (in 1824) a process which represents a schematic approximation of the essential features in the operation of a heat engine. Suppose that we have two heat reservoirs of so large a capacity that their respective temperatures T_1 and T_2 ($< T_1$) are not appreciably changed if we withdraw or add to them a finite amount of heat. They correspond in Carnot's scheme to the boiler and the cooler of a steam engine. We shall explain Carnot's process, giving to the operating part of his ideal engine, at first, a special construction: Let it consist of a cylindrical vessel, with a sliding piston as its top, filled with N mols of a perfect gas. The cylindrical side walls and the piston are made of adiabatically insulating material while the flat bottom is heat conducting but can be overspread with a suitable adiabatic cover. In the beginning the gas is in a state represented by the point $A(p_1, v_1, T_1)$ of the (p,v)-diagram (Fig. 8), and the process consists of four divisions: (1) The bottom is heat conducting and in contact with the first heat reservoir; by an infinitely slow reduction of the outer pressure on the piston the gas is expanded in a reversible *isothermal* way at the temperature T_1 to the point $A'(p'_1, v'_1, T_1)$. (2) The bottom is made adiabatic by applying the cover and the expansion continued, reversibly and *adiabatically*, to the point $B'(p'_2, v'_2, T_2)$. (3) The bottom is again made conducting and brought in contact with the second reservoir; the gas is reversibly compressed along the isothermal $T = T_2$ to the state $B(p_2, v_2, T_2)$. (4) Finally, the bottom is adiabatically covered a second time and the compression conducted, reversibly, along the adiabatic BA. The point B is chosen in such a way that this adiabatic brings the gas back to its initial state A, thus completing the cycle.

The general Carnot process has in common with that just described that it operates between the same two heat reservoirs and consists of four analogous divisions: Two of them are an expansion and com-

pression of the working part of the engine, respectively, in contact with the two heat reservoirs (boiler and cooler); the other two are an adiabatic expansion and compression. However, it is less specialized in two respects. In the first place, the working substance need not be a perfect gas but can be any real or ideal thermodynamical system. In the second place, the four divisions of the cycle may be conducted not reversibly but with a finite velocity (irreversibly).

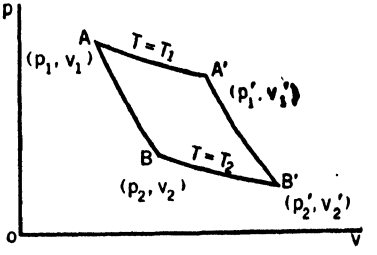


FIG. 8.—Carnot's cyclic process.

Since no heat is imparted to the working system in the adiabatic expansion and compression, its total heat intake Q during the cycle consists, in all cases, of the heat Q_1 (positive) received from the reservoir of higher temperature (T_1) and the heat Q_2 (negative) received from that of lower (T_2), so that $Q = Q_1 + Q_2$. As the final state of the working system is identical with the initial, we can apply the equation of the first law in the form (3.06):

$$W = Q = Q_1 + Q_2.$$

From the standpoint of the engineer, Q_1 is the heat conveyed to the engine to make it operate and supplied by the consumption of fuel. Not all of it is transformed into work, because Q_2 is negative. The heat given to the cooler ($-Q_2$) is, to his mind, a wasteful loss of energy which is, however, necessary in order to bring the working part of the engine back to its initial state and to ensure a continuous operation by, periodically, repeating the cycle. The ratio η of the useful work W to the consumed heat Q_1 is called the *efficiency* or the *conversion factor* of the engine

$$\eta = \frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1}. \tag{3.41}$$

We shall compute the efficiency for the special case when the cyclic process is conducted reversibly with N mols of a perfect gas as operating substance (Fig. 8). From the expression (3.32) of the heat imparted to the gas in an isothermal process

$$Q_1 = NRT_1 \log (v'_1/v_1), \quad Q_2 = -NRT_2 \log (v'_2/v_2).$$

On the other hand eq. (3.37) applied to one of the adiabatic divisions gives $T_1 v_1^{\gamma-1} = T_2 v_2^{\gamma-1}$ or $(v_1/v_2)^{\gamma-1} = T_2/T_1$, and to the

other: $(v'_1/v'_2)^{\gamma-1} = T_2/T_1$. There follows $v_1/v_2 = v'_1/v'_2$ or $v'_1/v_1 = v'_2/v_2$. Consequently

$$Q_1 + Q_2 = NR(T_1 - T_2) \log(v'_1/v_1),$$

and

$$\eta = \frac{Q_1 + Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}, \tag{3.42}$$

a relation which can, also, be written in the form

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{3.43}$$

and will prove very important in the next chapter.

Exercise 24. Use the formula of adiabatic expansion derived in exercise 22 to show that the relation $v'_1/v_1 = v'_2/v_2$ holds also in that case. The efficiency of Carnot's process is the same when c_v is a function of T.

Exercise 25. What is the thermodynamical efficiency of engines having coolers at 0° C and boilers at 100° C, 150° C, 400° C?

CHAPTER IV

THE SECOND LAW OF THERMODYNAMICS

20. Several formulations of the second law. The second law of thermodynamics is older than the first. It was discovered by S. Carnot, who enunciated it in the same pamphlet (1824) in which he gave the theory of his cyclic process. The reinterpretation and extension of the second law on the basis of the energy concept is due to Lord Kelvin (1851) and Clausius (1850–1863). There exist several equivalent formulations of this principle of which we give here the following:

1st enunciation (Kelvin): *It is impossible to transfer heat from a colder system to a warmer without other simultaneous changes occurring in the two systems or in their environment.*

The reader will recognize that this is a more precise and amplified statement of one of the facts which we mentioned in the very beginning of this course (section 1), where we introduced the notions of equilibrium and temperature, and again in section 10, where we defined the concept of heat. We said there that heat flows spontaneously always from the higher temperature to the lower and never in the opposite direction. The second law goes beyond this and asserts that one cannot completely undo the results of the process of heat conduction even in any indirect way. We shall show in the following sections that the above formulation is completely equivalent to the

2nd enunciation: *It is impossible to take heat from a system and to convert it into work without other simultaneous changes occurring in the system or in its environment.*

This law does not prohibit a process like the adiabatic expansion of a system (in which work is done at the expense of heat in the form of its internal energy) because this process is attended by "another simultaneous change", namely, the change of volume of the system. Neither does it forbid the operation of Carnot's engine (preceding section): In his cycle heat is taken from one reservoir, but its conversion into work is not complete. The simultaneous change, which makes this process permissible, is the transfer of part of the heat to another reservoir of lower temperature. The transferred heat is less available for conversion into work in a similar way because this would require a

third heat reservoir of still lower temperature. It is, therefore, often said that this heat is "dissipated" or "degraded". In general, a difference of pressures or of temperatures is necessary to obtain work; therefore, the phenomena of internal friction and of heat conduction which tend to reduce or destroy these differences must be regarded as attended by dissipation of energy. The establishment of the first law of thermodynamics made an end to all hopes of building a perpetual-motion machine (of the first kind) which could continually do work without some other form of energy being supplied to it. However, for all practical purposes a machine which could convert into work the enormous stores of internal energy contained in the oceans, the atmosphere, and the body of our earth would serve just as well. Ostwald called such a machine, which could work without temperature differences, a *perpetual-motion machine of the second kind.* It is obvious that its operation would be in violation of the second law, so that we arrive at the

3[d] enunciation (Ostwald): *It is impossible to construct a perpetual-motion machine of the second kind.*

This formulation makes the second law analogous to the first, which asserts the impossibility of a perpetual-motion machine of the first kind.

21. Efficiency of heat engines. Equivalence of the formulations. We have calculated, in section 19, the efficiency $\eta = (Q_1 + Q_2)/Q_1$ of the Carnot engine when operated reversibly with a perfect gas as the working substance. We shall call this particular type of construction and operation the *perfect Carnot engine.* The second law of thermodynamics permits us to say something about the conversion factor of the *general Carnot cycle*, which is the schematic prototype of any heat engine. In the real case, when the working part is any thermodynamical system and the cycle conducted either reversibly or irreversibly, we shall denote the efficiency by $\eta' = (Q'_1 + Q'_2)/Q'_1$. Let us suppose, for a moment, that $\eta' > \eta$. We shall prove that this supposition is impossible, by carrying through the cyclic process alternately with a real and a perfect Carnot engine which share the same two heat reservoirs. The length of the isothermal divisions AA' and $B'B$ (Fig. 8) of the perfect engine is at our disposal and can be adjusted in such a way as to make the work done by the two cycles equal:

$$W' = W \quad \text{or} \quad Q'_1 + Q'_2 = Q_1 + Q_2. \tag{4.01}$$

Moreover, the perfect engine being reversible, it can be run backward, in which case the quantities Q_1, Q_2, W simply reverse their signs, so that work is consumed and heat produced in the process. What

will now be the result of a double cyclic process in which the real engine goes through one cycle forward and the perfect backward? No work will appear in the net balance, because the first engine does as much work as the second consumes. The only effect will be that the heat $Q'_1 - Q_1$ will be taken from the first reservoir and $Q'_2 - Q_2$ from the second. These quantities are oppositely equal, according to eq. (4.01): $Q'_1 - Q_1 = -(Q'_2 - Q_2)$. Let us now recall our supposition $\eta' > \eta$ or $(Q'_1 + Q'_2)/Q'_1 > (Q_1 + Q_2)/Q_1$. Since the numerators are equal, this leads to $1/Q'_1 > 1/Q_1$ or $Q'_1 < Q_1$ and, consequently, $Q'_2 > Q_2$. A positive amount of heat $Q'_2 - Q_2$ is taken from the reservoir of lower temperature T_2 and transferred to that of higher T_1 without any other changes occurring, either in the reservoirs or in the working parts of the engines. The supposition $\eta' > \eta$ leads, therefore, to a contradiction with the second law of thermodynamics, and we must conclude that it is impossible and that only the possibilities

$$\eta' \leqq \eta \tag{4.02}$$

are permissible.

In the particular case, when the process in the real engine is also conducted in a reversible way, we can run the perfect engine forward and the real backward. Repeating the same argument with transposed (primed and unprimed) symbols, we can, then, prove that $\eta' < \eta$ is impossible and that $\eta' \geqq 0$ must hold. This result is compatible with (4.02) only when we have the sign of equality: $\eta' = \eta$. *All reversible Carnot engines have the same efficiency*, no matter what the construction of their working part is. The sign $<$ in eq. (4.02) refers, on the contrary, to irreversible cycles. Summarizing these conclusions and making use of the expression (3.42), we can give the general law for the efficiency η of any engine carrying out the cyclic process of Carnot:

$$\eta \leqq \frac{T_1 - T_2}{T_1}, \tag{4.03}$$

where the sign of inequality ($<$) refers to irreversible, that of equality ($=$) to reversible, operation. In the reversible case, there holds also the relation

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0, \tag{4.04}$$

which it is only another way of writing eq. (3.42).

An irreversible Carnot process is always less efficient and more wasteful than a reversible inasmuch as a smaller fraction of the heat Q

taken from the first reservoir (boiler) is converted into useful work. However, eq. (4.03) with the sign $<$ will also apply when only one of the four divisions of the cycle is conducted irreversibly and the three others reversibly. We can conclude from this that in the expansion of a system in contact with a heat reservoir less heat is received by the system and less work is done when the expansion is conducted in an irreversible than in a reversible way between the same initial and final states. In fact, let these two kinds of expansion be the first divisions of two Carnot cycles, while the remaining three divisions are identical and reversible in both. We denote the heat items in the first (partially irreversible) cycle Q'_1, Q_2 and in the second Q_1, Q_2. The condition $\eta' < \eta$ or $(Q'_1 + Q_2)/Q'_1 < (Q_1 + Q_2)/Q_1$ leads to $Q'_1 < Q_1$, since Q_2 is negative. The change of internal energy is in both cases the same, because it depends only on the initial and final state, so that the smaller heat intake is attended also by the smaller production of work.

We have used above the first enunciation of the second law given in section 20. However, the second leads to, precisely, the same results. Their equivalence is shown, in a general way; by the following simple reasoning. Consider a process which contradicts the second enunciation, that is, one which produces the work W taking heat from a reservoir at the temperature T_2, without any other simultaneous changes. We can feed this work into a reversible Carnot engine which runs in the backward direction, adjusting it so that in a cycle just the work W is consumed, and using the reservoir T_2 as the cooler. The net result will be that a certain amount of heat will be transferred from this reservoir to one of higher temperature T_1 (the heater of the Carnot engine), "without any other simultaneous changes". In other words, a process which violates the second law in the sense of enunciation 2, violates it also in the sense of enunciation 1. As to the third enunciation, it is in substance identical with the second being, merely, a restatement of it in different words.

Exercise 26. Give an alternative proof of the relation (4.02), for the second enunciation, analogous to that given in the text, for the first. Instead of adjusting the two engines so as to satisfy (4.01), adjust them so that the total heat received by the cooler in the double cycle vanish.

22. The concept of entropy. All that follows from the second law of thermodynamics for a reversible Carnot cycle is embodied in the formula (4.04). We now extend our considerations by asking: What follows from it in the case of any other ***reversible*** cyclic process (different from that of Carnot's) carried out with a thermodynamical system. Our arguments and formulas will refer to systems of the most general

kind, but we shall illustrate them by a drawing (Fig. 9) relating to a simple system, the only one which can be represented in a two-dimensional diagram. We repeat what was said in section 13 about carrying out such a process. We must have an infinity of heat reservoirs differing in temperature by infinitesimal amounts. The system is brought in contact with them, successively, and at the same time subjected to infinitely slow compressions or expansions. The cycle is, then, visualized by the solid closed curve of the figure. In its infinitesimal part corresponding to the segment AA' the system receives an element of heat DQ. Let us now draw through the point A the isothermal AC and through the point A' the adiabatic $A'C$, and denote by DQ_1 the heat which the system would receive if it were subjected to the infinitesimal isothermal process AC.

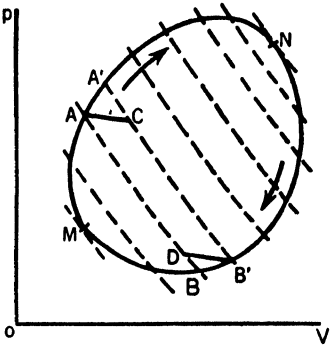


FIG. 9.—General cyclic process.

The relation between DQ and DQ_1 is obtained by considering the little cyclic process $AA'CA$ and setting up the equation (3.06) of the first law for it: the isothermal part AC is carried out in the reverse direction and we have $DQ - DQ_1 = DW$. The expressions DQ and DQ_1 are infinitesimal of the first order, but the work DW done in the little cycle is represented by the area of the triangle $AA'C$ and is, therefore, infinitesimal of the second order, infinitely small compared with the other two terms. It must be omitted from the equation, leaving $DQ = DQ_1$: we can, therefore, change our notations, denoting the work done in the segment AA' also by DQ_1. This conclusion holds for any system and not only for a simple one: Although the work done in an infinitesimal cyclic process cannot, in general, be represented in a two-dimensional diagram, it is, nevertheless, always infinitely small of the second order.

Let us now continue the adiabatic through the point A' and draw one through A until they intersect the closed curve a second time in B', B. According to the result just obtained, the heat DQ_2 received by the system in the part of the process $B'B$ is the same which corresponds to the isothermal segment $B'D$ passing through B'. We see, therefore, that the two heat items DQ_1 and DQ_2 are precisely the same which the system would receive from the boiler and cooler if it formed the operating part of a Carnot engine carrying out the reversible Carnot cycle $ACB'DA$. Denoting by T_1 and T_2 the temperatures which the

system has in the points A and B', we can apply to DQ_1 and DQ_2 the relation (4.04) for a reversible cycle of Carnot

$$\frac{DQ_1}{T_1} + \frac{DQ_2}{T_2} = 0. \tag{4.05}$$

If we cut up into strips the whole area of the closed curve representing the cycle, by a system of adiabatics drawn at infinitesimal distances from one another (the dotted lines of Fig. 9), eq. (4.05) will hold for the pair of segments of the cycle in every strip. Integrating over all strips

$$\int \frac{DQ_1}{T_1} + \int \frac{DQ_2}{T_2} = 0.$$

The first integral represents the summation over all elements of the cycle between the points M and N, the second term the summation over the other half of the curve from N to M. We can, therefore, replace the two terms by the single integral

$$\oint \frac{DQ}{T} = 0, \tag{4.06}$$

extended over the whole cycle. This result applies to any cyclic process, so that the integral of the linear differential expression DQ/T taken over any closed path vanishes. We know from section 8 that, in this case, the expression DQ/T is the exact differential of some function S of the variables of the system:

$$\frac{DQ}{T} = \frac{dU + DW}{T} = dS. \tag{4.07}$$

In the language of that section we say that DQ, while not an exact differential, is integrable. The integrating multiplier is $1/T$, the reciprocal of the absolute temperature as measured by a perfect gas thermometer.

Clausius who first introduced the function S called it the *entropy* of the system (derived from the Greek word ἐντρέπομαι = turn inside, an allusion to its one-sided character). If we integrate eq. (4.07) over a reversible process leading from state (1) to state (2), we find

$$S_2 - S_1 = \int_1^2 \frac{DQ}{T}. \tag{4.08}$$

The integral depends only on the initial and final value and is independent of the path, provided that this path is reversible (compare

section 8), and the entropy is a "characteristic function", i.e. completely defined when the state of the system is defined. We can take as state (2) in formula (4.08) any state of the system and as (1) some state (n) which we arbitrarily choose as normal

$$S = \int_{(n)} \frac{DQ}{T} + S_n. \tag{4.09}$$

Owing to the fact that the entropy is defined by the differential equation (4.07), it contains a constant of integration. As such appears in the expression (4.09) the entropy S_n of the normal state. As far as the first and second laws of thermodynamics are concerned, it cannot be determined by any theoretical reasoning.

In the case of a homogeneous system, the heat DQ received in every element of a reversible process is distributed uniformly, so that the entropy S also acquires a uniform distribution over the system. We can speak, therefore, of the specific entropy and, when the system is chemically pure, of the entropy per mol or *molal entropy* which we shall denote by s (small). We may further ask: What is the joint entropy S of two systems which, individually, possess the entropies S_1 and S_2? According to the defining equation (4.09), S is obtained by carrying out a reversible process with the combined system. The reversibility requires, however, the equilibrium of all parts at every stage of the process, so that our two constituent systems must have at every moment the same temperature T. If we denote the elements of heat imparted in an infinitesimal step of the process, respectively, by DQ, DQ_1, DQ_2, there follows $DQ = DQ_1 + DQ_2$, $DQ/T = DQ_1/T + DQ_2/T$ and, from eq. (4.07),

$$dS = dS_1 + dS_2, \quad \text{or} \quad S = S_1 + S_2. \tag{4.10}$$

The entropy is additive. We repeat, however, that the additive property rests on the fact that two systems in thermodynamical equilibrium have the same temperature. If two systems are, initially, not at the same temperature but can be brought into thermal contact, it has a good sense to ask about their joint entropy, and we shall define it as additive. In other cases this question is without meaning. It is, of course, possible to imagine a case in which the two parts are adiabatically insulated from one another but can interact by means of movable pistons and similar devices. They could be in partial equilibrium without equality of temperature, but this is a dynamical problem rather than a thermodynamical. The notion of an entropy

of such a combination is artificial and without interest in thermodynamics.[1]

The entropy difference (4.08) takes a very simple form when the initial and the final states are of the *same temperature*. We can, then, take an isothermal process as the path of integration (T = const).

$$S_2 - S_1 = \frac{1}{T}\int_1^2 DQ = \frac{Q}{T}. \tag{4.11}$$

23. The entropy principle. Let us discuss how the entropy of a system changes in an adiabatic process. If the process is reversible, eq. (3.35) or $DQ = 0$ applies to every infinitesimal step of it. It follows, then, from (4.07)

$$dS = 0, \quad \text{and} \quad S = \text{const}. \tag{4.12}$$

The reversible adiabatic process leaves the entropy unchanged: it is, therefore, also called "isentropic".

When we turn to the irreversible adiabatic process, we are on new ground. We cannot expect to get an answer to our question from the considerations of the preceding section because they were restricted to reversible processes. Therefore, we have to fall back, once more, upon the second law as enunciated in section 20. In the same way as in introducing the entropy concept we shall use a (p, V)-diagram (Fig. 10) as an illustration, although our argument will be valid for the most general thermodynamical systems. Suppose that the system is subjected to an irreversible adiabatic process which brings it from the state A (with the temperature T_1 and entropy S_1) to the state $B(T_2, S_2)$. The transition itself, being irreversible, is not capable of a graphical representation (compare section 12). What can be said about the entropy change $\Delta S = S_2 - S_1$? We can bring the system

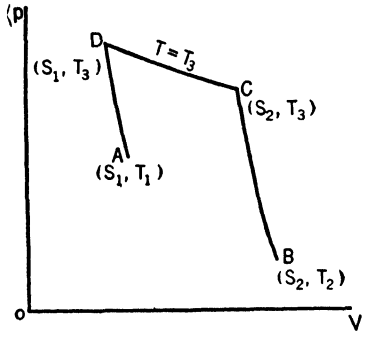


FIG. 10.—Entropy change in irreversible adiabatic process.

[1] The only known significant case in which the entropy is not additive occurs in the theory of radiation. When a pencil of rays is split by partial reflection into two (the reflected and retracted), they have, in general, temperatures different from each other's and from that of the parent pencil. At the same time the sum of their entropies is not equal to the entropy of the parent pencil. Compare: M. Von Laue, Ann. der Phys. 20, p. 365, 1906; P. S. Epstein, Phys. Zs. 15, p. 673, 1914.

back into its initial state A in the following reversible way: First, we let it undergo a reversible adiabatic process BC roughly opposite to the first, until it comes to the temperature T_3, while its entropy remains constant and equal to S_2. From the state C on, we conduct it in a reversible isothermal (CD) until the initial entropy S_1 is again reached; then we complete the cycle, bringing the system adiabatically back to the state A. The temperature T_3 can be chosen arbitrarily higher or lower than either T_1 or T_2, or between these values. It is important to have this freedom of choice because certain processes (as transformations) can be conducted only at special temperatures. The system receives no heat in the three adiabatic branches of the cycle, and the heat Q in the isothermal part. Applying eq. (3.06) of the first law to the cyclic process (from A to A) we write

$$Q = W,$$

where W is the total work done by the system. If Q and W were positive, the result of the process would be that the heat Q is taken from the heat bath, maintaining the constant temperature T_3 in the isothermal branch CD, and converted into work "without any other simultaneous changes." This is a violation of the second law (enunciation 2), and we conclude $Q \not> 0$ or $Q \leqq 0$. The application of eq. (4.11) to the isothermal CD gives $Q = T_3(S_1 - S_2)$, since S_1 is here the final and S_2 the initial state. The inequality implies, therefore, $S_1 - S_2 \leqq 0$ or

$$\Delta S = S_2 - S_1 \geqq 0.$$

The same argument can be easily adapted to the more general case where the system consists, initially, of many parts which are *not in equilibrium*. At the end of the irreversible adiabatic process it may have the same parts in new states or, even, other parts since some of the parts may have become merged, others separated into several units. At any event, the system can be brought back to the initial condition by the following reversible procedure. The final parts are brought, separately, in a reversible adiabatic way to the same suitably chosen temperature T_3. At this temperature they are isothermally rearranged into the original parts, unmixing some of them if necessary (compare section 50). Still at the same temperature T_3 each of the part systems is separately brought to its initial entropy. The cycle is completed by bringing the parts back to their initial states in independent, reversible, adiabatic processes. The conclusions drawn above for the simpler case obviously apply without change in the more complicated one. They apply, of course, also to every part of the irreversible process for which a definite entropy change can be defined. Under no circum-

stances can this change be negative. It follows from this that, in the case $S_2 - S_1 = 0$, the change must be zero for every smallest part: $dS = 0$. That is to say, $\Delta S = 0$ refers to the reversible process and $\Delta S > 0$ to the irreversible: *The irreversible adiabatic process is always attended by an increase of entropy.*

The summary of the results of this and the preceding section is the "entropy principle", due to Clausius, which represents an analytical formulation of the second law of thermodynamics. It consists of two parts:

4th enunciation: (*a*) *There exists a characteristic thermodynamical function called the entropy. The difference of entropies of a system in the states* (1) *and* (2) *is given by the expression*

$$S_2 - S_1 = \int_1^2 \frac{DQ}{T}, \tag{4.13}$$

where the integral is to be taken over any reversible path connecting the two states.

(*b*) *In an adiabatic process the entropy either increases or remains unchanged*:

$$\Delta S \geqq 0 \tag{4.14}$$

where the upper sign (>) *refers to the irreversible, the lower* (=) *to the reversible, case.* The adiabatic processes include also the case when the system is "left to itself", meaning by this that it is completely cut off from any interaction with its surroundings and does not receive any energy from outside, either in the form of heat or of work.

The parts (*a*) and (*b*) of the entropy principle contain all that can be deduced from the enunciations of section 20. Sometimes, a third general law is included in the entropy principle: the fact that *all systems tend towards equilibrium* so that the entropy always does increase when the conditions of the system permit it. We prefer, however, to discuss this law separately in section 30. As enunciated here, the entropy principle is completely equivalent to the formulations given in section 20. In fact, their validity is a sufficient condition because we derived the principle from it. But it is also a necessary condition because the adiabatic processes prohibited in those formulations are attended by a decrease of entropy. (Compare exercise 27).

Since a spontaneous irreversible process is one of increasing entropy, we can use the condition $\Delta S > 0$ as the criterion of irreversibility.

Exercise 27. Show that, in the fictitious case when the efficiency of the Carnot engine is $\eta' > \eta$, the expression on the left side of (3.43) is negative. This means that the sum of the entropies of the heater and cooler decreases.

24. Entropy of the perfect gas. In the case of a simple homogeneous and chemically pure system, the entropy can be referred to 1 mol of its material (section 23), and eq. (4.07) takes the form

$$ds = \frac{Dq}{T} = \frac{du + pdv}{T}. \tag{4.15}$$

The only system for which the expressions of u and p were given in the preceding chapters is the perfect gas: According to (1.13) and (3.17) we have $du = c_v\,dT$ and $p = RT/v$,

$$ds = c_v \frac{dT}{T} + R\frac{dv}{v}. \tag{4.16}$$

This, really, is an exact differential of the function

$$s = c_v \log T + R \log v + s'_0, \tag{4.17}$$

where s'_0 is an arbitrary constant, the so-called *entropy constant of the perfect gas*. Using the equation of state, we can express v by p and T, or T by p and v, and so obtain two other forms of the molal entropy

$$s = c_p \log T - R \log p + s_0, \tag{4.18}$$

$$s = c_v \log p + c_p \log v + s''_0, \tag{4.19}$$

since $c_p = c_v + R$, according to (3.20). The constants are related in the following way: $s'_0 = s_0 - R \log R$, $s''_0 = s_0 - c_p \log R$. It is easy to see that eqs. (3.37) and (3.38) of the adiabatic are equivalent to the condition s = constant.

It is well to mention also the case when the gas is perfect, in thermal respects, but the molal heat c_v is a function of temperature (end of section 15). Equation (4.16) leads then to the expressions

$$\left.\begin{aligned} s &= \int \frac{c_v dT}{T} + R \log v + s'_0, \\ s &= \int \frac{c_p dT}{T} - R \log p + s_0. \end{aligned}\right\} \tag{4.20}$$

Exercise 28. Check the statement that the process of expansion into the void (section 15) from the molal volume v_1 to v_2 is irreversible (i.e. $\Delta s > 0$) for the perfect gas, by computing the entropy difference $s_2 - s_1$ between the final and the initial state.

Exercise 29. Two vessels contain each one mol of the same perfect gas at the respective temperatures T_1 and T_2. They are brought in contact and the two specimens allowed to come into equilibrium through the heat-conducting walls without change of volume. Compute total entropy in initial and final states and

show that it increases. (Remark: The arithmetical mean of two numbers $\frac{1}{2}(a+b)$ is always larger than the geometrical $\sqrt{ab}$.)

25. The reciprocity relation of thermodynamics. The requirement that the expression (4.15) must be an exact differential imposes a restriction on the analytical form of the internal energy u: the caloric equation of state (3.09) is not quite independent of the thermal. In fact, the exact differential must satisfy the reciprocity relations (2.10) of section 8. In the case of a simple system, there are only two independent variables and only one reciprocity relation. Let us substitute for Dq the form (3.11)

$$ds = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v dT + \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + p\right]dv. \tag{4.21}$$

Then the reciprocity relation has the form

$$\frac{\partial}{\partial v}\left[\frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v\right]_T = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial u}{\partial v}\right)_T + \frac{p}{T}\right]_v. \tag{4.22}$$

In carrying out the differentiation, we shall remember, that u is here regarded as a function of v and T only, and drop the subscripts in the second derivative

$$\frac{1}{T}\frac{\partial^2 u}{\partial v \partial T} = \frac{1}{T}\frac{\partial^2 u}{\partial T \partial v} + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_v - \frac{1}{T^2}\left[\left(\frac{\partial u}{\partial v}\right)_T + p\right].$$

The order of differentiation in the second partial can be transposed and the two terms depending on it cancel out. There remains

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p, \tag{4.23}$$

which gives, substituted into (4.21),

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v. \tag{4.24}$$

In the case of perfect gases, $(\partial p/\partial T)_v = p/T$ and $(\partial u/\partial v)_T = 0$. We justified the assumption $c_v = f(T)$, for them, by the measurements of Joule and Thomson on real gases (section 15). We see that this assumption is consistent with the second law, as we have already checked in the preceding section. Vice versa, accepting the second law, we can conclude theoretically that u is independent of v and a function of T only, for substances satisfying the equation $pv = RT$. This fact is well supported by observations on real permanent gases. When

the measurements are very accurate, the deviations from the law of perfect gases begin to tell. The incentive which caused Thomson and Joule to undertake their investigation was the fact that Regnault's data for $(\partial p/\partial T)_v$, when substituted into (4.23), gave a finite value of $(\partial u/\partial v)_T$ for real gases.

In the case of gases strictly obeying the eq. (1.21) of Van der Waals, we find from (4.23)

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2}. \tag{4.25}$$

This partial is independent of T. Since du is also an exact differential, we can apply the reciprocity relation to it and conclude that the other partial $c_v = (\partial u/\partial T)_v$ is independent of v. The internal energy has then the expression

$$u = \int_0^T c_v dT - \frac{a}{v} + u_0, \tag{4.26}$$

and the term $-a/v$ represents the inner potential energy of the forces of interaction between the molecules.

Equation (4.23) can be used to simplify the expression (3.15) of the difference of molal heats $c_p - c_v$, making it dependent upon easily measurable quantities

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p. \tag{4.27}$$

This formula was extensively tested by measurements of the velocity of sound in gases (section 18) up to pressures of 200 atm and found to be in good agreement with observations.[1]

Exercise 30. Show that the entropy of the Van der Waals gas is

$$s = \int \frac{c_v dT}{T} + R \log (v - b) + s'_0. \tag{4.28}$$

Exercise 31. Derive by integrating (4.23)

$$p = T\int \left(\frac{\partial u}{\partial v}\right)_T \frac{dT}{T^2} + Tf(v). \tag{4.29}$$

Exercise 32. Starting from (4.23) prove the relation

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v. \tag{4.30}$$

[1] P. P. Koch, Ann. Phys. **26**, p. 551; **27**, p. 311, 1908.

Exercise 33. A further relation can be derived by partial differentiation. Substitute in $u(T, v)$ the expression of T in terms of p and v so that $u = u[T(p, v), v]$. By differentiating with respect to v derive

$$\left(\frac{\partial u}{\partial v}\right)_p = \left(\frac{\partial u}{\partial v}\right)_T + \left(\frac{\partial u}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p$$

Transform this with the help of (3.12), (4.23), and (4.27) into

$$\left(\frac{\partial u}{\partial v}\right)_p = c_p \left(\frac{\partial T}{\partial v}\right)_p - p. \tag{4.31}$$

26. Measurement of entropy of differences. From the definitions of molal heat (3.08) and of entropy (4.15) there follows the relation $c = Tds/dT$, which is valid for all ways of imparting heat to the system. In the two simplest cases of constant volume and of constant pressure this leads to

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v, \quad c_p = T\left(\frac{\partial s}{\partial T}\right)_p. \tag{4.32}$$

Dividing by T and integrating, we obtain the following two expressions for the entropy

$$s(T, v) = \int \frac{c_v dT}{T} + f_1(v), \tag{4.33}$$

$$s(T, p) = \int \frac{c_p dT}{T} + f_2(p), \tag{4.34}$$

whose equivalence with (4.32) can be checked by differentiating them partially with respect to T, at constant v and p, respectively.

If we wish to find the entropy increase (per mol) experienced by a substance when its temperature is raised, *at constant volume*, from T_1 to T_2, the first equation gives

$$s(T_2, v) - s(T_1, v) = \int_{T_1}^{T_2} \frac{c_v}{T} dT. \tag{4.35}$$

On the other hand, the *increase at constant pressure* is from the second equation

$$s(T_2, p) - s(T_1, p) = \int_{T_1}^{T_2} \frac{c_p}{T} dT. \tag{4.36}$$

The above expressions give the entropy changes, as long as the system does not undergo any transformation of state. When a transformation occurs, it involves a latent heat l (per mol) and an increase of entropy which is, according to (4.11),

$$s_2 - s_1 = \frac{l}{T}, \tag{4.35'}$$

since the transformation takes always place at constant temperature. Here, too, the cases v = const and p = const must be distinguished. At *constant volume* no work is done and the latent heat is, simply, equal to the increase of the internal energy. At *constant pressure* it is equal to the increase of the heat function (compare section 17):

$$l_v = \Delta u, \quad l_p = \Delta \chi. \tag{4.36'}$$

We see from this discussion that the determination of entropy differences involves only measurements of molal and of latent heats. The same data which are necessary to find internal energies and heat contents give also the knowledge of entropies.

We have tacitly assumed that the system we are dealing with is a chemically pure substance. If this is not the case, we can readily adapt eqs. (4.35) and (4.36) to any system in which no chemical reaction takes place, simply writing the total entropies and heat capacities (capital letters) instead of the molal. With respect to chemical reactions, two cases may occur: (1) The reaction is conducted at constant temperature. This case is completely analogous to that of a transformation, the entropy increase being

$$S_2 - S_1 = \frac{Q}{T}, \tag{4.35''}$$

with

$$Q_v = \Delta U, \quad Q_p = \Delta \mathbf{X}. \tag{4.36''}$$

(2) There is a continuous displacement of chemical equilibrium as the temperature is raised. Then the heat of reaction must be included in the heat capacity; we shall consider a case of this sort in section 121.

Exercise 34. Calculate the entropy increase in the following process: 1 mol of liquid water (18 g) at 100° C is vaporized at the pressure of 1 atm. and the vapor is heated (at constant pressure) to 650° C. Take data from exercises 8 and 19.

Exercise 35. (*a*) The molal heats c_p for Ag, Al, and graphite are:

T° K.....	50	100	150	200	250	273.1	298.1
Ag.....	2.69	4.82	5.54	5.84	5.97	6.02	6.04
Al.....	0.90	3.13	4.44	5.13	5.54	5.68	5.82
C (graphite)...	0.13	0.41	0.79	1.22	1.65	1.86	2.ed

Calculate in a rough graphical way the increase of the heat function as ion temperature is raised from 50° to 298°.1 K (p = const). of the

(*b*) Calculate from the same data (in a rough graphical way) the in entropy between 50° and 298°.1 K.

Exercise 36. Calculate the heat and the entropy imparted to a p (4.43) the following two reversible processes: (*a*) starting from the state p_1 is conducted first at $p = p_1$ to p_1, v_2, then at $v = v_2$ to p_2, v_2. (*b*) The introduc-

at $v = v_1$ to p_2, v_1, then at $p = p_2$ to p_2, v_2. Suppose c_v and c_p to be constant. Show that the heat imparted to the system is different in the two processes but the entropy change is the same.

27. The extended law of corresponding states. The relation (4.23) between the caloric and the thermal equations of state can be written in the integrated form

$$u = \int \left[T\left(\frac{\partial p}{\partial T}\right)_v - p \right] dv + f(T). \tag{4.37}$$

We have seen in section 6 that, within certain groups of substances, the thermal equation satisfies the law of corresponding states. It may be asked, therefore, if a similar law does not apply to the caloric equation of state (4.37). As the most precise expression of the law of correspondence we may take that following from the *mean reduced equation* (1.29) of Kamerlingh Onnes. According to that equation, the quantity $K = RT_c/p_c v_c$ is a constant for a given substance and, at the same time, a universal function of the reduced variables π, φ, τ. Consequently, it must be a universal constant, as also

$$\frac{p_c v_c}{T_c} = \kappa, \tag{4.38}$$

since $\kappa = R/K$ is another universal constant. If we substitute into the combination pv/T the expressions of the parameters in terms of the reduced variables ($p = p_c\,\pi$, $v = v_c\,\varphi$, $T = T_c\,\tau$), we find immediately

$$\frac{pv}{T} = \kappa\,\frac{\pi\varphi}{\tau} = f_1(\pi, \varphi, \tau). \tag{4.39}$$

In words, *the quantity pv/T has the same value for different substances in corresponding states.* In a similar way, substituting π, φ, τ into the integral of eq. (4.37), we find that this integral, divided by T, is a universal function of the reduced variables. This fact suggests he hypothesis that the same applies to the second term and to the ·ole expression (apart from the zero energy)

$$\frac{u - u_0}{T} = f_2(\pi, \varphi, \tau). \tag{4.40}$$

·iantity might be also the same for different substances in · states. This hypothesis was, in fact, made by ·nnes and others. We shall call the simultaneous validity

of eqs. (4.39) and (4.40) the *extended law of corresponding states*. Though far from rigorous, this law is satisfied with a fair approximation within certain ranges of temperatures by large groups of substances (compare section 47). It may be pointed out that, in the case of perfect gases, the two functions f_1 and f_2 have the simplest possible form: they are reduced to the constants R and c_v.

An immediate consequence of these equations is that the expression (4.15) of the entropy differential is also a universal function F of π, φ, τ, whence

$$\Delta s = F(\pi_2, \varphi_2, \tau_2) - F(\pi_1, \varphi_1, \tau_1). \tag{4.41}$$

The molal entropy difference between corresponding states is the same for all substances (obeying the extended law).

There were physicists who went even beyond this in their extension of the law and applied it to more general systems, having other variables than p, V, T. Suppose, for instance, that the element of work is, in the sense of section 7, $dW = pdV + ydX$, whence the entropy differential (4.07)

$$dS = \frac{dU + pdV + ydX}{T}. \tag{4.42}$$

The generalized force y can be treated exactly on the same footing as p (exercise 38), and it is possible to argue that the expression yX/T should have similar properties (with respect to corresponding states) as pV/T and U/T. We shall see in section 86 that this idea was fruitfully applied to the theory of surface tensions.

Exercise 37. Substitute for p, v, T the reduced variables into the integral of eq. (4.37), divided by T, and show that the result is a universal function of π, φ, τ.

Exercise 38. Substitute in (4.42)

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V, X} dT + \left(\frac{\partial U}{\partial V}\right)_{X, T} dV + \left(\frac{\partial U}{\partial X}\right)_{T, V} dX,$$

and set up the reciprocity relations in analogy with (4.22), (4.23).

28. Theory of the Joule-Thomson process. We are now in a position to subject the experiments of Joule and Thomson, described in section 15, to a closer analysis. We found there that the relation between the states of the streaming gas (Fig. 7) on both sides of the plug is given by eq. (3.16), which we can write in the form

$$\Delta\chi = \chi_2 - \chi_1 = 0, \tag{4.43}$$

making use of the definition (3.21) of the heat function. The introduc-

tion of this function permits us to express the entropy differential in a new way: From eqs. (3.25) and (4.15)

$$ds = \frac{1}{T}\left(\frac{\partial \chi}{\partial T}\right)_p dT + \frac{1}{T}\left[\left(\frac{\partial \chi}{\partial p}\right)_T - v\right]dp. \tag{4.44}$$

We apply the reciprocity condition (2.10) to this expression and obtain, in complete analogy with the way in which we found the formulas (4.23) and (4.15),

$$\left(\frac{\partial \chi}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p \tag{4.45}$$

and

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p. \tag{4.46}$$

Of course, this is not a new relation but only another form of the reciprocity condition (4.23) into which it can be transformed by applying the formulas (1.05) and (3.21). Owing to this equation and to (3.26), the differential of the heat function becomes

$$d\chi = c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp. \tag{4.47}$$

Suppose that in the Joule-Thomson experiment the difference of pressures $\Delta p = p_2 - p_1$ and of temperatures $\Delta T = T_2 - T_1$ is so small that it is permissible to neglect squares and higher powers and use eq. (4.47) for expressing $\Delta\chi$ in terms of Δp and ΔT. The condition (4.43) gives then

$$\mu = -\frac{\Delta T}{\Delta p} = \frac{v - T(\partial v/\partial T)_p}{c_p}. \tag{4.48}$$

This change of temperature per unit pressure drop, $\mu = -\Delta T/\Delta p$, is, usually, called the *differential Joule-Thomson effect.* With the help of this formula its sign and magnitude can be calculated theoretically if the equation of state and c_p are known. We see that the sign of the effect depends on that of $T(\partial v/\partial T)_p - v$, or, transforming this by means of (1.05), upon the sign of the inequality

$$\mu = \left[T\left(\frac{\partial p}{\partial T}\right)_v + v\left(\frac{\partial p}{\partial v}\right)_T\right] \Big/ c_p\left(\frac{\partial p}{\partial v}\right)_T \gtreqless 0. \tag{4.49}$$

The differential Joule-Thomson effect has the sign opposite to that

of the bracket expression (because $\partial p/\partial v$ is negative). In the case of Van der Waals gases, this condition takes the form

$$\frac{2a}{v^2} - \frac{RTb}{(v-b)^2} \gtreqless 0. \tag{4.50}$$

When the density is low, the constant b in the denominator of the second term gives rise to corrections of the second order only, and can be neglected in the first approximation, leaving the condition

$$T \gtreqless T_i, \qquad T_i = 2a/Rb = 6.75T_c, \tag{4.51}$$

taking into account (1.24). T_i is called the *inversion temperature*: below it, the effect is positive and consists in a cooling of the gas; above, it is negative and the gas gets warmer in passing through the cotton plug. We see from (4.50) that the two Van der Waals constants have an opposite influence, so that the sign depends on which of them dominates. From the physical point of view, we have here an interplay of two phenomena: On the one hand, when a is different from zero, the expanding gas does work against inner forces (compare eq. (4.26) of preceding section) and this decreases its temperature accounting for a part (a/v^2) of the expression (4.50). On the other hand, the outer work $p_2v_2 - p_1v_1$ of the process does not vanish for Van der Waals gases, even when the temperatures remain unchanged. It can be positive or negative and contributes the remainder of (4.50). On the whole; the larger part of a positive effect is due to inner work.

The interplay of the two effects is more complicated when the density is not low. The expression (4.50) with the sign of equality, determining the inversion point, is best written in terms of the reduced variables (1.25)

$$\frac{1}{\varphi^2} - \frac{4}{3}\frac{\tau_i}{(3\varphi - 1)^2} = 0. \tag{4.52}$$

Eliminating φ from this expression and the reduced Van der Waals equation (1.26), we find

$$\tau_i = 3\left[1 \pm \frac{1}{6}\sqrt{9 - \pi}\right]^2. \tag{4.53}$$

This formula shows us that there are *two inversion points*. The coefficient μ is negative above the upper inversion point and below the lower, being positive in between. The position of these points depends on the pressure: the upper of them sinks as the pressure is increased, the lower rises.

In a qualitative way these predictions of the Van der Waals theory are fulfilled by real gases. The lower inversion lies in the liquid state and has been observed in several substances. It is, further, borne out by the experimental data that, the more perfect a gas is, the lower its upper inversion point lies and that it is depressed by pressure, while the lower point is raised by it. However, the Van der Waals equation cannot be used for a quantitative calculation of the Joule-Thomson effect or of the inversion point because its approximation is insufficient in the range of pressures and temperatures here involved. This is apparent from the figures given in Table 7.

TABLE 7

DIFFERENTIAL INVERSION POINTS

Substance	p atm	T_i° K	Authority
		Upper	
He	1	23.6	Roebuck and Osterberg 1934
H_2	113	(192.7)	Olszewski 1901
Air	150	553	Hoxton 1919
"	203	523	
		Lower	
A	250	164	Roebuck and Osterberg 1933
"	50	125	
Air	150	140	Hausen 1926
"	125	133	
CO_2	18 to 100	249	Burnett 1923

Hoxton[1] gives the following empirical formula for air, in the range from 0° to 280° C and from 1 to 220 atm,

$$\mu = -\Delta T/\Delta p = 0.1975 - \frac{138}{T} + \frac{319p}{T^2}, \tag{4.54}$$

where p is measured in atmospheres.

The cooling by means of the Joule-Thomson process has acquired a great importance in the technique of low temperatures and of liquefying gases. Mostly, it is not used as the sole agency of cooling but in combination with adiabatic expansion. Air, oxygen, and nitrogen can be subjected to the process at room temperature since their inversion points lie higher. For hydrogen, T_i lies above the boiling points of liquid oxygen and nitrogen so that it can be made amenable to the

[1] Hoxton, Phys. Rev. 13, p. 438, 1919.

process by being precooled by liquid air. Again T_i of helium is above the boiling point of hydrogen (20°.5 K). Whether these gases are precooled in this way (cascade system) or by adiabatic expansion, the process they are subjected to in technical applications is the *integral Joule-Thomson effect*, i.e. an expansion from a high pressure (p_1) to a considerably lower one (p_2) with an attendant temperature drop from T_1 to T_2. These changes are still governed by eq. (4.43) or

$$\chi(p_2, T_2) - \chi(p_1, T_1) = 0. \tag{4.55}$$

We may ask under what conditions the maximum cooling is attained, (T_2 = min.), if we start from a given temperature T_1. This question is, in fact, of practical importance, because the temperature T_1 to which the system can be precooled is usually dictated by technical considerations. Let us suppose, for a moment, that the end pressure p_2 is also given (T_1 = const, p_2 = const). Then eq. (4.55) is a relation between only two variables T_2 and p_1, and the condition for T_2 = min. is obviously $dT_2/dp_1 = 0$. The total differential of the equation is

$$\left(\frac{\partial \chi_2}{\partial T_2}\right)_p dT_2 + \left(\frac{\partial \chi_1}{\partial p_1}\right)_T dp_1 = 0. \tag{4.56}$$

Hence we conclude that, in order to obtain the lowest end temperature, the pressure p_1 must be chosen so as to satisfy the condition

$$(\partial \chi_1/\partial p_1)_T = 0. \tag{4.57}$$

The fact that this condition is independent of p_2 shows that our assumption of a fixed end pressure was unnecessary. The choice of p_1 as a root of eq. (4.57) assures the maximum of cooling *for any end pressure*, provided the difference Δp is not very small. However, owing to eq. (4.45), this condition is precisely of the same form as that for the differential inversion point, which we transformed into (4.49) (with the sign of equality). *For a given* (initial) *temperature, the optimum in the integral Joule-Thomson effect occurs at the same pressure as the inversior in the differential effect.* If the substance follows the law of Van der Waals this pressure is determined by eq. (4.53), or resolving it with respect to π:

$$\pi_1 = 24\left(\sqrt{3\tau_1} - \frac{\tau_1}{2} - \frac{9}{8}\right). \tag{4.58}$$

Exercise 39. Starting from eq. (4.47), prove the relation

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p. \tag{4.59}$$

Exercise 40. Using partial differentiation (as in exercise 33) derive the relation

$$\left(\frac{\partial x}{\partial p}\right)_v = \left(\frac{\partial x}{\partial p}\right)_T + \left(\frac{\partial x}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v.$$

With the help of (3.26), (4.45), and (4.27) transform it into

$$\left(\frac{\partial x}{\partial p}\right)_v = c_v \left(\frac{\partial T}{\partial p}\right)_v + v. \tag{4.60}$$

Exercise 41. Calculate the differential inversion points, for the gases and pressures of Table 7 (excepting air), making use of formula (4.53) and of the data of Table 2 (on p. 14). Compare them with the measured values.

29. Realization of the absolute scale of temperatures. The absolute temperature T was introduced in section 4 as that which would be measured by means of an ideal thermometer filled with a perfect gas as thermometric fluid. This temperature acquired a more general significance when it was found (section 21) that the efficiency of the reversible Carnot cycle is independent of the nature of the working system and, being always the same as in the case of a perfect gas, can be very simply expressed in terms of T. This fact led, in turn, to the possibility of defining the concept of entropy by its differential $dS = dQ/T$, in which the reciprocal of the absolute temperature appears as the integrating multiplier.

The role which T plays in the analytical formulation of the second law makes it a quantity of general thermodynamical importance and gives a practical way of indirectly determining the absolute temperature, although the perfect thermometer is only an abstraction. In fact, any thermodynamical equation derived from the second law represents a relation between T and the other variables of the system to which it applies. Theoretically it is, therefore, possible to express the absolute temperature T in terms of measurable characteristics of any system of nature. On the other hand, one can read directly, under the same conditions, the arbitrary temperature t on a real thermometer and, comparing it with T, graduate this thermometer in the absolute scale. This procedure was conceived and carried out by Lord Kelvin who used, for this purpose, the equation of the Joule-Thomson process. Let us take the form (4.48) which refers to the case of small pressure differences Δp. Suppose that we have established a correspondence between the scales of T and t, so that we can regard them as functions of each other. We wish to introduce into the equation the quantities Δt, $(\partial v/\partial t)_p$, c'_p measured by means of the real thermometer. We obtain immediately, $\Delta T = \Delta t \cdot dT/dt$, $(\partial v/\partial T)_p = (\partial v/\partial t)_p \, dt/dT$; moreover, from the definition of molal

heats we have, in general, $c = Dq/dT = (Dq/dt)dt/dT = c'dt/dT$ and, in particular, $c_p = c'_p\, dt/dT$. The substitution into (4.48) gives

$$\frac{\Delta t}{\Delta p} \cdot \frac{dT}{dt} = \left[T\left(\frac{\partial v}{\partial t}\right)_p \frac{dt}{dT} - v \right] \Big/ c'_p \frac{dt}{dT},$$

whence

$$\frac{dT}{T} = \frac{(\partial v/\partial t)_p\, dt}{v + c'_p(\Delta t/\Delta p)}. \tag{4.61}$$

The right side of this expression contains only readily measurable quantities, so that the absolute temperature can be found by integrating it. In practice it is convenient to measure the temperature t with a gas thermometer filled with the same gas which is used in the Joule-Thomson process. We have then, according to (1.08), $v = v_0(1 + \alpha t)$, and this is the same v as in the denominator of (4.61), since p is there considered as constant. Further, $(\partial v/\partial t)_p = v_0\alpha$, so that the integral of the right side becomes

$$K(t) = \int_0^t \frac{\alpha dt}{1 + \alpha t + c'_p \Delta t/v_0 \Delta p}. \tag{4.62}$$

Suppose that to the point $t = 0°$ C corresponds $T = T_0$, then we can adjust the scales so (compare section 4) that to $t = 100°$ C corresponds $T = T_0 + 100$. The integral of (4.61) is, therefore,

$$\log (T/T_0) = K(t), \tag{4.63}$$

and for $t = 100°$ one obtains an expression for T_0 in terms of measurable quantities

$$T_0 = 100[\exp K(100) - 1]. \tag{4.64}$$

The number T_0 indicates how many degrees of the absolute scale the zero point of absolute temperature ($T = 0$) lies below the point of freezing water ($t = 0$). It is remarkable that the measurements of $\Delta t/\Delta p$ need not be carried out at very low temperatures, in order to obtain it, but only between $t = 0$ and $t = 100$. In this range the numerical value of the term $c'_p \Delta t/v_0 \Delta p$ is pretty small. In the case of helium, it is smaller than 0.001 in any part of the interval, so that neglecting it altogether would already give an approximation of better than 0.1%. If this is done, eq. (4.62) reduces to $K(t) = \log (1 + \alpha t)$, whence $T_0 = 1/\alpha$, as if helium were a perfect gas. With the experimental $\alpha = 0.003659$ this gives $T_0 = 273.32$, which is, in fact, pretty close to the true value. The most accurate determinations of T_0 were carried out by Roebuck (by this method [1]) and by Henning

[1] J. R. Roebuck, Proc. Am. Soc. Arts. Sci. 60, p. 537, 1925.

and Heuse (by a different one [1]). The weighted mean of their results [2] is

$$T_0 = (273.18 \pm 0.03)^\circ \text{ K},$$

where the symbol ° K indicates degrees in the absolute or *Kelvin* scale. Nevertheless, we shall have to adopt here the old value of $T_0 = 273°.1$ on which all current tables are based. A change in the definition of the zero point has far-reaching consequences and can be made only by international agreement.

As stated in the beginning of this section, any phenomenon which satisfies the following two conditions can be used for establishing the absolute temperature scale: it must be (1) expressible by a theoretical formula as a function of T, and (2) measurable in terms of a relative scale t. Temperatures in the vicinity of 0° K are being established by means of the magneto-caloric effect (compare section 136), the same effect by means of which these extremely low temperatures are reached.

Exercise 42. In the range from 0° to 100° C (at 1 atm) the Van der Waals equation gives a sufficient approximation for a rough estimate of the third term in the denominator of the integral (4.62). Calculate its maximum value in this interval from eq. (4.49) and the data of Table 2, for H_2 and N_2. Estimate the percentual error in T_0, if this term is neglected.

Exercise 43. How can the formula $(\partial u/\partial v)_T = T(\partial p/\partial T)_v - p$ be used to establish the absolute scale of temperatures? Suppose that $(\partial u/\partial v)_t$, $(\partial p/\partial t)_v$ and p can be measured as functions of the relative temperature t.

30. Statistical interpretation of the entropy concept. Matter consists of discrete particles (atoms, molecules, etc.), and the actions exercised by material systems upon one another can be traced to the effects of these ultimate parts. Thus the pressure of a gas upon a wall is due to its bombardment by the moving molecules of the gas which hit it at very short, but irregular, intervals and transfer to it varying amounts of momentum. From this point of view, the pressure is a *statistical average* which is automatically taken and presented to us by the integrating action of our measuring instrument, the manometer. The same is true with respect to other thermodynamical variables and functions. The temperature, in particular, can be brought in connection with the average of the kinetic energy which is distributed over the individual particles according to the laws of chance or the *laws of probability.*

The mathematical theory of probabilities had its origin in the analysis of games of chance. Suppose that a deck containing an

[1] F. Henning and W. Heuse, Zs. Physik 5, p. 285, 1921; W. Heuse, 37, p. 157, 1926.
[2] R. T. Birge, Phys. Rev. Suppl. 1, p. 18, 1929.

equal number of black and red cards is manufactured and shuffled so perfectly that the chance of drawing from it a black or a red card is exactly equal. In other words, if the drawing is repeated a large number of times Z, the card being returned and the deck reshuffled every time, the number of red and black cards drawn will be, relatively, the closer to $Z/2$ the larger Z is. We say then that the probability of drawing a red card is one half: $P_R = \frac{1}{2}$, and, in the same way, the probability of drawing a black card $P_B = \frac{1}{2}$. What is now the probability P_{RB} of obtaining, in two successive drawings, first a red and then a black card? There are four possible cases for the result of this double drawing: (1) red, red; (2) red, black; (3) black, red; (4) black, black. Since the chance of each of the four cases is the same, we conclude that the probability $P_{RB} = \frac{1}{4}$ or $P_{RB} = P_R P_B$. This is an example of the *multiplicative law of probabilities*. In general, the probability P_{12} of a complex event, which consists of two simple events, is equal to the product of their respective probabilities P_1, P_2

$$P_{12} = P_1 P_2. \tag{4.65}$$

The multiplicative law holds only when the simple events are *statistically independent*, meaning by this that the outcome of the first in no way influences the chances of the second.

The application of the laws of probability to the molecular structure of matter is treated in the branches of physics called statistical mechanics and kinetic theory. Here we shall give only a brief reference to some notions about the entropy which are, in part, postulated, in part, deduced in these disciplines. A striking property of the entropy is its onesidedness. In any spontaneous process of nature it can only increase, and the state of equilibrium is the state of maximum entropy (compare also next section). On the other hand, when we regard a physical system as an assembly of interacting atoms and molecules, we say that it will change in the direction of a more probable state, as to positions and energy distribution of its ultimate units: The final state will be that of the highest probability. The question arises, therefore, whether it is possible to give a definition of the probability of a state which would bring out its parallelism with the entropy and permit to follow it through in a mathematical way. This is, precisely, what is accomplished in statistical mechanics: *The probability of a state is defined there as the number of ways in which this state can be realized.* Let us illustrate this by the example of pure and mixed crystals. Consider a crystal consisting of Z_1 identical atoms in a regular arrangement. We shall discuss here the probabilities, only in so

far as they depend on the normal position of the atoms, and leave out of consideration the deviations and velocities due to their thermokinetic motions. If we could label and individually distinguish the Z_1 atoms, every permutation of them would lead to a new way of realizing the crystal, and the total number of ways would be equal to the number of possible permutations $P_{s1} = Z_1!$. This is called by Gibbs the *specific definition of the probability*. In modern statistical mechanics it is recognized, however, that it is not possible to tell the atoms apart so that all the permulations must be considered as one single realization $P_{g1} = 1$: the *generic probability definition* which was preferred by Gibbs himself. On the other hand, let us take the case of a mixed crystal, that is Z_1 atoms of one kind and Z_2 of another arranged in a joint lattice. If we assume that every distribution of atoms of the second kind between those of the first represents still the same macroscopic state of the mixed crystal, we find that the number of possible realizations is, in the specific definition, again equal to the permutation number $P_{s12} = (Z_1 + Z_2)!$. In the generic definition it is smaller because the permutations of atoms of each kind among themselves ($Z_1!$ and $Z_2!$) do not count. The previous number, therefore, must be divided by the product $Z_1!\, Z_2!$

$$P_{g12} = \frac{(Z_1 + Z_2)!}{Z_1!\, Z_2!}. \tag{4.66}$$

Let us consider the process of combining two pure crystals (Z_1 and Z_2) into a mixed crystal. The initial probability of the system, according to the multiplicative law (4.65), is P_1P_2: We see that it is increased in the process in the ratio given by the expression (4.66), no matter which of the two definitions we use. We repeat that the preceding discussion implies that all the realizations which we counted belong to the same macroscopic state of the crystal. To what extent this is the case in reality, will be considered in sections 98 and 99.

What is now the mathematical relation between the probability and the entropy function? The probability of complex systems follows the multiplicative law, the entropy the additive. We cannot, therefore, make them simply proportional. But if we take the logarithm of the probability, the difficulty is removed, since eq. (4.65) then becomes $\log P_{12} = \log P_1 + \log P_2$. In view of this, Boltzmann postulated

$$S = k \log P, \tag{4.67}$$

as a general *principle* which now bears his name. Here $k = R/n_A$ is the *Boltzmann constant* as defined by eq. (1.14). Applying this to

the above example, we find that the entropy increase in the process of producing a mixed crystal out of two pure ones is

$$\Delta S = k\,[\log\,(Z_1 + Z_2)! - \log Z_1! - \log Z_2!]. \tag{4.68}$$

As stated above, the multiplicative law of complex probabilities applies only when the simple events are statistically independent. On the other hand, the entropy of a complex system is additive, only, when the equilibrium of its constituent parts is characterized by a uniform temperature (section 22). It follows from this that the thermodynamical criterion of two statistical systems not being independent is that they come in equilibrium with different temperatures (compare footnote on p. 60).

This is not the place to enter into the applications of Boltzmann's principle. We shall only mention one or two of its immediate consequences which will be useful in interpreting and rounding out the thermodynamical treatment. We restrict ourselves to the case when the events are considered as statistically independent.

(A) There is an alternative formulation of Boltzmann's principle which we give only for two special cases as we shall not need it in its generality. (1) If the particles of a system move in a field of conservative forces, the probability of finding a particle in the space element $\Delta\tau$ is

$$P d\tau = C \exp\,(-\varepsilon_{\text{pot}}/kT) d\tau, \tag{4.69}$$

where ε_{pot} is the potential energy of the particle, when in the space element $d\tau$, and C is independent of the coordinates of the particles. (2) A similar relation exists for the total energy, its formulation is particularly simple in the quantum theory. If a system consists of identical elements (atoms, molecules, linear oscillators, etc.), each capable of assuming the quantum states 0, 1, 2, . . . with the respective energies $\varepsilon_0, \varepsilon_1, \varepsilon_2, \ldots$, the probability of finding an element in the state (j) is

$$P_j = C' \exp\,(-\varepsilon_j/kT). \tag{4.70}$$

(B) In classical statistics (when quantum restrictions do not exist and all energy levels are permissible) Boltzmann's principle leads to the *equipartition of energy*. The mean kinetic energy of an element is equal to $kT/2$ per degree of freedom:

$$\bar{\varepsilon}_{\text{kin}} = nkT/2, \tag{4.71}$$

n being the number of (translational and rotational) degrees of freedom. As to the potential energy, this law applies to it only in

the case when the forces producing it are elastic forces (i.e. are proportional to the distance).

Exercise 44. A coin is tossed three times; what are the probabilities of (1) head being up all three times, (2) head being up twice and tail once?

Exercise 45. Calculate from the formula (4.69) the relative number of molecules of air in a space element $d\tau$ of the earth atmosphere at the height h above the surface of the sea. Use a mean molecular mass (m), and, substituting $k = R/n_A$, show that one obtains in this way the barometric formula of Laplace.

CHAPTER V

THE TREND OF THERMODYNAMICAL PROCESSES TOWARDS EQUILIBRIUM

31. The direction of spontaneous processes. Let us consider a complex thermodynamical system whose parts may or may not be in equilibrium. We assume it prevented from heat exchange with the outer world by an adiabatic envelope but capable of doing work. If all its microscopic dynamical, electrical, etc., parameters were given, as well as the outer forces acting on it, its future states would be determined and predictable. Can we foresee anything about the spontaneous processes in it and their direction, knowing only its thermodynamical characteristics? The two laws of thermodynamics as stated in the preceding chapters will not lead us very far in this endeavor: the first law only states that one type of energy is convertible into another, but, as far as this principle is concerned, the conversion can go either way, provided the geometrical constraints of the system permit it. The second law tells us a little more about the direction of spontaneous processes: only such changes are permissible in which the entropy does not decrease. This excludes, at once, a large number of conceivable occurrences as incompatible with this law. Still, the second law is incomplete in that it leaves the question open whether the entropy actually will increase when conditions permit it. In fact, in the enunciations of the preceding chapter the fundamental fact is not contained that there is in every thermodynamical system a tendency towards a definite state of equilibrium.

Fortunately, the empirical evidence relating to these questions can be summarized in the form of two simple rules supplementing the first and the second law of thermodynamics. In the first place, *the internal energy U has the nature of a potential energy.* A dynamical system which is at rest, at a certain moment, will set itself in motion if its constraints permit a decrease of the potential energy. The potential energy has a tendency to diminish and to be converted into kinetic energy, so that equilibrium can ensue only when it has reached its minimum. In a similar way, *the internal energy of an isolated thermodynamical system tends to decrease* when the existing conditions give

it a chance of being converted into forms of energy of non-potential nature. U tends towards its minimum, and the system will not be in equilibrium until this minimum is reached.

$$U \rightarrow U_{\min}. \tag{5.01}$$

In the second place, *the entropy of isolated systems tends to increase.* Processes attended by an augmentation of the entropy are not only permissible, as the second law states, but one of them will necessarily take place spontaneously. Equilibrium will be reached only when S has attained its maximum

$$S \rightarrow S_{\max}. \tag{5.02}$$

This condition can be regarded as a portion of the second law, *a third part of the entropy principle*, of equal importance with the first two enunciated in section 23. We speak of it separately in this place, in order to bring out its analogy with the rule (5.01) supplementing the first law.

From this discussion follow the necessary and sufficient conditions of equilibrium of a thermodynamical system: The internal energy must have its minimum and the entropy its maximum value. It is known, from mathematics, that this will be the case if, for all virtual infinitesimal changes of state, consistent with the nature of the system, the variations δU and δS vanish:

$$\delta U = 0, \quad \delta S = 0. \tag{5.03}$$

There is a difference between the differential and the variation. The *differential* dU refers to an actual infinitesimal change of state which the system undergoes in a specified real process. In thermodynamics, the initial and the infinitely close final state must be states of equilibrium if they are to define a differential. On the other hand, the *variation* has reference to all conceivable ("virtual") changes whether they conserve the equilibrium or not. A variation may start from a state of equilibrium and lead away from it. It may even connect two (infinitely close) thermodynamically unstable states. The reason for such a definition of the variation is that we do not know in advance which virtual changes are permissible, and we wish to select, a posteriori, those which are compatible with the conditions (5.03) and with other conditions, inherent in the nature of the system and in the concept of equilibrium. It is clear from this explanation that the *virtual changes* are the more comprehensive class: every actual change is contained among the virtual changes, but the reverse is not true.

32. Variation of the internal energy. Partial molal quantities. The systems and states we are going to deal with must be capable of a thermodynamical description. We have to restrict our considerations to systems which can be divided into phases with the following properties: though, possibly, not in physical or chemical equilibrium, each phase must be uniform with respect to temperature, pressure, and composition so that it has a definite internal energy and entropy. For all virtual changes in which no matter is added to the system, holds the fundamental formula (4.07), or

$$\delta U = T\delta S - p\delta V. \tag{5.04}$$

We can choose the volume V and the entropy S as the thermodynamical variables. In addition, the system may be characterized by other parameters specifying its mass, chemical composition, etc. To fix our ideas let us assume that the system is not chemically pure but a mixture of N_1 mols of a first chemically pure component, N_2 mols of a second, and so on. The internal energy is then a function of the variables

$$U = U(S, V, N_1, N_2, \ldots N_\sigma). \tag{5.05}$$

The variation of U is the most general change which takes place while all the variables undergo virtual changes,

$$\delta U = \left(\frac{\partial U}{\partial S}\right)_{V,N} \delta S + \left(\frac{\partial U}{\partial V}\right)_{S,N} \delta V + \sum_k \left(\frac{\partial U}{\partial N_k}\right)_{S,V} \delta N_k. \tag{5.06}$$

We shall only consider virtual changes in which no matter is added to the system so that the variations δN_k represent increases of some components at the expense of other components. In this case the formulas (5.04) and (5.06) are valid simultaneously and apply to all possible virtual changes satisfying this condition. In particular, we may consider the case when the composition remains altogether unchanged, $\delta N_k = 0$ (compare, in this connection, section 39). Comparing the two equations, we find

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p. \tag{5.07}$$

The subscript N is usually omitted because the symbol of partial differentiation implies that all the other variables are to be kept constant. Substituting this into the general eq. (5.06) and subtracting (5.04), we obtain the remarkable relation

$$\sum_{k=1}^{\sigma} \left(\frac{\partial U}{\partial N_k}\right)_{S,V} \delta N_k = 0. \tag{5.08}$$

These results can be generalized for systems with several phases (provided T and p are uniform throughout), but we need not deal with this aspect of the question here since it will occupy us in section 42, in connection with the problem of equilibrium. The partials of eq. (5.08) should not be confused with the *partial molal internal energies* which are defined as follows:

$$\bar{u}_k = \left(\frac{\partial U}{\partial N_k}\right)_{p,\,T}. \tag{5.09}$$

In the case of a chemically pure substance, $U = Nu$, where the ordinary molal internal energy u is a function of temperature and pressure only and remains constant when p and T are kept constant. Therefore, $\bar{u}_k$ is a generalization of u for mixtures and solutions, becoming identical with it in the extreme case of pure substances. Another partial molal quantity worth mentioning is the *partial molal volume*. When several substances are mixed or dissolved in one another, the total volume is, generally, not additive but a complicated function of the mol numbers (compare also section 57)

$$V = V(p, T, N_1 \ldots N_\sigma).$$

The partial molal volume of each component is defined as

$$\bar{v}_k = \left(\frac{\partial V}{\partial N_k}\right)_{p,\,T}. \tag{5.10}$$

The relation of the functions $(\partial U/\partial N_k)_{S,\,V}$ to partial molal quantities will become clear in the next sections.

Exercise 46. The measurements by Wade (J. Chem. Soc. **75**, p. 254, 1899) on the volume of aqueous solutions of NaCl can be represented by the following empirical formula (due to Lewis and Randall)

$$V = 18N_1 + 16.4N_2 + 2.5N_2^2 - 1.2N_2^3,$$

where N_1 refers to water and N_2 to NaCl. Calculate the volumes of solutions with 0.1, 0.3, 0.5 mol of NaCl per 1000 g of water and the partial molal volumes of NaCl in all these cases.

Exercise 47. Prove for the perfect gas the formula

$$\left(\frac{\partial U}{\partial N}\right)_{S,\,V} = u - Ts + pv.$$

Directions. Calculate $\delta U = \delta(Nu)$ from (3.18) and eliminate δT and δv with the help of the conditions $\delta S = \delta(Ns) = 0$ and $\delta V = \delta(Nv) = 0$. For s, use the formula (4.17).

33. Construction of new characteristic functions. Further properties of the heat function. In addition to the characteristic functions U and S, we had occasion to introduce in section 17 the *heat function* defined as

$$\mathbf{X} = U + pV, \tag{5.11}$$

while its differential, in the case of a simple system, is obtained from (3.22) and (4.07),

$$d\mathbf{X} = TdS + Vdp, \tag{5.12}$$

whence in an isobaric process ($dp = 0$)

$$Q_p = \mathbf{X}_2 - \mathbf{X}_1. \tag{5.13}$$

Instead of using the variables S, V of the preceding section, we can describe the system also by the variables S, p, and use $\mathbf{X}$ as the appropriate characteristic function. The term pV in (5.11) has the effect that its differential $d(pV) = pdV + Vdp$ cancels the term $-pdV$ of (5.04) and leaves in its place Vdp. In this way the differential dp is introduced instead of dV. In mathematics the method of replacing a term ydx by the term $-xdy$ by means of subtracting the differential $d(xy)$ is called a *Legendre transformation.* It is obvious that we can construct by this expedient still two more characteristic functions from the expression (5.04), namely, subjecting to Legendre transformations the first term, or both terms simultaneously. We shall discuss these functions in the next sections and reserve the remainder of this one for a few remarks about the variation of the heat function.

As explained in the preceding section, we assume that the state of the system depends on the mol numbers N_1. N_2, . . . N_σ in addition to the thermodynamical variables:

$$\mathbf{X} = \mathbf{X}(S, p, N_1, \ldots N_\sigma). \tag{5.14}$$

We can obtain, for the variation of $\mathbf{X}$, two expressions closely analogous to those for δU in the preceding section. On the one hand, the relation (5.12) is valid also for the variations

$$\delta\mathbf{X} = T\delta S + V\delta p.$$

On the other hand, we find from (5.14)

$$\delta\mathbf{X} = \left(\frac{\partial\mathbf{X}}{\partial S}\right)_{p,N} \delta S + \left(\frac{\partial\mathbf{X}}{\partial p}\right)_{S,N} \delta p + \sum_k \left(\frac{\partial\mathbf{X}}{\partial N_k}\right)_{S,p} \delta N_k. \tag{5.15}$$

As in the preceding section, we conclude by comparing the two expressions

$$\left(\frac{\partial \mathbf{X}}{\partial S}\right)_{p,N} = T, \quad \left(\frac{\partial \mathbf{X}}{\partial p}\right)_{S,N} = V. \tag{5.16}$$

(The subscript N is usually omitted). Another form of the variation of (5.11) is $\delta \mathbf{X} - V\delta p = \delta U + p\delta V$. Hence and from (5.06) and (5.15)

$$\sum_k \left(\frac{\partial \mathbf{X}}{\partial N_k}\right)_{S,p} \delta N_k = \sum_k \left(\frac{\partial U}{\partial N_k}\right)_{S,V} \delta N_k.$$

We cannot conclude from this equation that the terms are equal individually:

$$\left(\frac{\partial \mathbf{X}}{\partial N_k}\right)_{S,p} \equiv \left(\frac{\partial U}{\partial N_k}\right)_{S,V}, \tag{5.17}$$

because the virtual changes δN_k are not independent: we have excluded changes in which matter is added to the system. However, the proof of the identity (5.17) can be easily supplied by partial differentiation. In fact, let us describe U by the coordinates S, p instead of S, V. We can effect this change of variables by substituting for V its expression in terms of S, p, N. We need not bring S in evidence since it is considered as constant, and we write instead of (5.05)

$$U = U[V(p, N), N].$$

By the rules of partial differentiation

$$\left(\frac{\partial U}{\partial N}\right)_{S,p} = \left(\frac{\partial U}{\partial N}\right)_{S,V} + \left(\frac{\partial U}{\partial V}\right)_{S,N} \cdot \left(\frac{\partial V}{\partial N}\right)_{S,p}.$$

According to (5.07), the second term on the right is $-[\partial(pV)/\partial N]_{S,p}$. Taking it to the left side, the equation becomes identical with (5.17).

Exercise 48. Consider the general form of dU based on (2.02)

$$dU = TdS - \sum_{j=1}^{n} y_j\, dX_j.$$

Show that the number of characteristic functions which can be constructed from it by Legendre transformations is $2^{n+1} - 1$.

Exercise 49. Prove that, for a perfect gas,

$$\left(\frac{\partial \mathbf{X}}{\partial N_k}\right)_{S,p} = u - Ts + pv.$$

Directions. Calculate $\delta \mathbf{X} = \delta(N\chi)$ from (3.28) and eliminate δT with the help of the conditions $\delta S = \delta(Ns) = 0$ and $\delta p = 0$. For s, use the formula (4.18).

34. The work function. We subject to a Legendre transformation the first term of the differential of the internal energy (4.07)

$$dU = TdS - DW. \tag{5.18}$$

Subtracting from it $d(TS)$, we find

$$D\Psi = -SdT - DW, \tag{5.19}$$

where

$$\Psi = U - TS. \tag{5.20}$$

The function Ψ is useful in bringing out certain properties of isothermal processes. We have, in this case, $dT = 0$ and

$$d\Psi = -DW. \tag{5.21}$$

Integrating this over a reversible process at constant temperature from the initial state (1) to the final (2),

$$\Psi_1 - \Psi_2 = -\Delta\Psi = W. \tag{5.22}$$

The work done by a system in a reversible isothermal process is equal to the decrease of the function Ψ. The case when the system remains in contact with a heat reservoir of constant temperature but the process is not conducted reversibly is sometimes, loosely, called an *irreversible isothermal process.* In this kind of a process the temperature of the system is not strictly equal to that of the reservoir and is, in fact, not strictly uniform. We have seen in section 12 that the process is less efficient and the work done in it by the system is less than in the reversible case. We can, therefore, say that $\Psi_1 - \Psi_2$ *represents the maximum work that can be obtained from the system in any isothermal process* leading from the state (1) to the state (2).

Applying eq. (5.20) to the initial and final states and taking the difference,

$$U_1 - U_2 = \Psi_1 - \Psi_2 + T(S_1 - S_2). \tag{5.23}$$

The second term on the right side is, according to eq. (4.11), equal to $-Q$, representing the heat transferred to the heat reservoir during the process. Helmholtz, who used the function Ψ a great deal, called it the *free energy* because the difference $\Psi_1 - \Psi_2$ represents that part of the decrease of the internal energy $U_1 - U_2$ in the process which is available for work while the *bound energy* $T(S_1 - S_2)$ is lost to the reservoir maintaining the constancy of temperature. However, the name cannot be regarded as very fortunate because it loses sight of the fact that there exist in nature endothermic processes in which $T(S_1 - S_2)$ is negative. In this case, work is done by the system, in

part at the expense of the heat reservoir, which supplies heat instead of receiving it. The decrease $\Psi_1 - \Psi_2$ can, therefore, be larger than $U_1 - U_2$, as was first pointed out by Gibbs. To make matters worse, in a part of the chemical literature of this country the name "free energy" is applied to a different function (namely, to Φ defined in the next section). We think it, therefore, advisable to avoid the term "free energy" altogether and shall refer in this book to the function Ψ as the *work function*. This name was introduced by R. H. Fowler [1] and is highly appropriate in view of the physical meaning of the quantity Ψ as expressed in eq. (5.21). This relation means that, *as long as the temperature is kept constant*, the elements of work used in thermodynamics are exact differentials which possess the potential Ψ.

We shall discuss the very important question, under what circumstances Ψ tends to decrease, in section 36 and shall say here only a few words about its partial derivatives. In the case of a simple system, $DW = pdV$, and the variation becomes, in accordance with (5.19),

$$\delta\Psi = -S\delta T - p\delta V. \tag{5.24}$$

The appropriate coordinates for the description of the work function are, therefore, T and V in addition to the mol numbers N_k, determining the composition of the system:

$$\Psi = \Psi(T, V, N_1, \ldots N_\sigma).$$

In analogy with the preceding sections, we find

$$\left(\frac{\partial\Psi}{\partial T}\right)_{V,N} = -S, \quad \left(\frac{\partial\Psi}{\partial V}\right)_{T,N} = -p. \tag{5.25}$$

(The subscript N is usually omitted). As to the partials with respect to N_k, it is easy to prove the identity (exercise 51)

$$\left(\frac{\partial U}{\partial N_k}\right)_{S,V} = \left(\frac{\partial\Psi}{\partial N_k}\right)_{T,V}, \tag{5.26}$$

by means of which eq. (5.08) can be expressed in terms of derivatives of the function Ψ.

It will be useful to give here the explicit expressions of the *molal work function* ψ *for* perfect and Van der Waals gases. We take the more general case of the formulas (3.19) and (4.20) when the molal heat is not considered as constant. In the case of the perfect gas,

$$\psi = \omega'(T) - RT\log v, \tag{5.27}$$

[1] R. H. Fowler, Statistical Mechanics, p. 96. 1929.

of the Van der Waals gas, according to (4.26) and (4.28),

$$\psi = \omega'(T) - \frac{a}{v} - RT\log(v - b), \tag{5.28}$$

where $\omega'(T)$ is an abbreviation for

$$\omega'(T) = \int_0^T c_v dT - T\int \frac{c_v dT}{T} + u_0 - Ts'_0. \tag{5.29}$$

Exercise 50. Prove, for the perfect and for the Van der Waals gas, the relation

$$(\partial\Psi/\partial N)_{T,V} = u - Ts + pv.$$

Directions. Calculate $\delta\Psi = \delta(N\psi)$ with $\delta T = 0$ from (5.27) and (5.28). Eliminate δv by means of the condition $\delta V = \delta(Nv) = 0$.

Exercise 51. Prove the identity (5.26) in the following way: In (5.05) replace S by a function of V, T, N, i.e. $U = U[S(T, N), N]$, and take the partial $(\partial U/\partial N)_{T,V}$ in analogy with the procedure at the end of section 33.

Exercise 52. Consider the case of a system with many degrees of freedom when the element of work has the general form (2.02): $DW = \Sigma y_k dX_k$. Write out the differential of the work function $\Psi = U - TS$ and, by applying the reciprocity relations (2.10), prove the equation

$$\left(\frac{\partial S}{\partial X_k}\right)_T = \left(\frac{\partial y_k}{\partial T}\right)_X. \tag{5.30}$$

35. The thermodynamic potential. Let us consider a system which depends on some non-mechanical (e.g. electrical, magnetical, etc.) variables, in addition to p and T. The element of work done by it can, then, be represented as $DW = pdV + DW'$, where DW' is the work done by the non-mechanical forces. Accordingly, the differential (5.04) of the internal energy takes the form

$$dU = TdS - pdV - DW'. \tag{5.31}$$

We subject the first and second term on the right side to Legendre transformations adding $-d(TS) + d(pV)$. The result is

$$d\Phi = -SdT + Vdp - DW', \tag{5.32}$$

where

$$\Phi = U - TS + pV \tag{5.33}$$

is known as the *thermodynamic potential.*

In the laboratory, processes (like chemical reactions, etc.) are very often conducted at constant temperature and constant pressure. The temperature is maintained by a suitable heat bath while the pres-

sure is that of the terrestrial atmosphere. Under these conditions ($dT = 0$, $dp = 0$), eq. (5.32) reduces to

$$d\Phi = - DW', \tag{5.34}$$

or integrating this over a reversible path (at T = const, p = const) from the initial state (1) to the final (2)

$$\Phi_1 - \Phi_2 = - \Delta\Phi = W'. \tag{5.35}$$

The non-mechanical work done by a system in a reversible isothermal, isobaric process is equal to the decrease of the function Φ. When the process is led between the same two states in an irreversible way (i.e. when the temperature and pressure are imperfectly maintained), it is more wasteful. *The difference* $\Phi_1 - \Phi_2$ *gives, therefore, the maximum of the non-mechanical work that can be obtained from the system in any process leading from state* (*1*) *to state* (*2*) of the same temperature and pressure.

The great importance of the thermodynamic potential arises from the fact (which we shall prove in the next chapter) that, in the equilibrium state of a heterogeneous system, p and, T are the same in all its phases. They are, therefore, the most convenient thermodynamical variables, and eq. (5.32) shows that Φ is the appropriate characteristic function for this choice of variables. In the special case of a simple system $DW' = 0$, and the variation becomes

$$\delta\Phi = - S\delta T + V\delta p, \tag{5.36}$$

while Φ has the expression

$$\Phi = \Phi(T, p, N_1, \ldots N_s).$$

In analogy with the preceding sections

$$\left(\frac{\partial\Phi}{\partial T}\right)_{V,N} = - S, \quad \left(\frac{\partial\Phi}{\partial p}\right)_{T,N} = V. \tag{5.37}$$

(The subscript N is usually omitted). The partial derivative with respect to N_k must be taken at constant p and T: it is, therefore, the partial molal thermodynamic potential, according to the definition of the partial molal quantities given in section 32.

$$\overline{\Phi}_k = \left(\frac{\partial\Phi}{\partial N_k}\right)_{p,T}. \tag{5.38}$$

It is easy to prove the identity (exercise 54)

$$\bar{\varphi}_k = \left(\frac{\partial \Psi}{\partial N_k}\right)_{V,\,T} \tag{5.39}$$

or from (5.17) and (5.26)

$$\bar{\varphi}_k = \left(\frac{\partial \mathbf{X}}{\partial N_k}\right)_{S,\,p} = \left(\frac{\partial U}{\partial N_k}\right)_{S,\,V} \tag{5.40}$$

We shall have occasion to use the expression for the molal thermodynamic potential of a perfect gas. From (5.33), (4.20), and (3.19)

$$\varphi = \omega(T) + RT \log p, \tag{5.41}$$

where

$$\omega(T) = \int_0^T c_p\, dT - T\int \frac{c_p\, dT}{T} + u_0 - Ts_0. \tag{5.42}$$

In the particular case $c_p = \text{const}$,

$$\omega(T) = c_p\, T(1 - \log T) + u_0 - Ts_0. \tag{5.43}$$

Exercise 53. Derive the explicit expression of φ for the Van der Waals gas:

$$\varphi = \omega(T) + RT \log\left(p + \frac{a}{v^2}\right) - \frac{2a}{v} + \frac{RT\,b}{v - b}. \tag{5.44}$$

Exercise 54. Prove the identity (5.39), making in Ψ exactly the same substitution for V which was made at the end of section 33 in U (to prove 5.17).

Exercise 55. Consider the case of a system with many degrees of freedom when the element of work has the general form (2.02): $DW = \Sigma y_k dX_k$. Write out the differential of the *generalized thermodynamic potential* $\Phi' = U - TS + \Sigma y_k X_k$, and prove, by applying the reciprocity relations (2.10), the equation

$$\left(\frac{\partial S}{\partial y_k}\right)_T = \left(\frac{\partial X_k}{\partial T}\right)_y. \tag{5.45}$$

36. The decreasing tendency of the thermodynamic potential and of the work function. We have found in eqs. (5.22) and (5.35) that work is done by a system (at $T = \text{const}$) at the expense of the work function, and non-mechanical work (at $T = \text{const}$, $p = \text{const}$) at the expense of the thermodynamic potential. The question arises, however, as to the tendency of these functions to decrease: if the differences $\Psi_1 - \Psi_2$ or $\Phi_1 - \Phi_2$ are available in a system, will they be spontaneously converted into work, and under what conditions?

Let us start our considerations from the work function $\Psi = U - TS$. It is obvious that Ψ would decrease (if possible) in a system "left to itself" or "isolated", but *remaining at constant temperature.* In fact,

we know from section 31 that the positive term U has a tendency to decrease and the negative TS to increase (in absolute value). However, in the processes which we wish to consider the systems are not isolated: in the first place, there is the heat bath by means of which the temperature is maintained; in the second, the environment may do work against it through the forces of pressure. Let us try to make the system isolated by including in it both these influences. With respect to the heat bath, this is easy since it does not do any work of either a mechanical or a non-mechanical nature. According to eqs. (5.21) and (5.34), the values of the functions Φ and Ψ characterizing the heat reservoir remain constant in view of this. We may regard it, therefore, as a part of the system without changing anything in the available differences $\Psi_1 - \Psi_2$ and $\Phi_1 - \Phi_2$, or, in other words, we may base our discussion on $\Psi = U - TS$ of the enlarged system (with inclusion of the heat bath). The conditions are simplest when other interactions with the outer world are precluded. This is the case when the *volume of the system is constant*, for instance, when it is surrounded by a rigid heat-conducting envelope and immersed in the heat bath: *when the temperature and the volume of a system are kept constant, its work function has a tendency to decrease.* Any spontaneous isothermal and isochoric process goes on until Ψ reaches its possible minimum. The necessary and sufficient condition for the starting and proceeding of a process is that the work function must be larger in the initial state than in the final ($\Psi_1 - \Psi_2 > 0$). This can be used as a criterion whether a chemical reaction will go. At constant temperature and volume the maximum possible change of Ψ is a measure of the *chemical affinity* of the substances entering into the reaction. It is to be noted that the work done by this reaction, if any, is non-mechanical work: from $dV = 0$, there follows $DW = DW'$.

The conditions are different when the *pressure* is maintained constant, instead of the volume. The practical method of accomplishing this is to subject the system to the hydrostatic pressure either of the atmospheric air, or of another medium (liquid or gas) compressed by a suitable load. If the system expands under this pressure from the initial volume V_1 to the final V_2, the work of expansion $p(V_2 - V_1)$ is converted into the potential energy of lifting the load or the air column resting on the system, and pV is a measure of this potential energy at any moment. In addition to U, having the nature of a potential energy, we have here still the item pV which tends to be converted into energy of a non-potential character. We have, therefore, to use the thermodynamic potential $\Phi = U - TS + pV$: including the heat bath into the system as in the former case, we see that this function has

a tendency to decrease (at T = const and p = const), since the two positive terms tend to decrease, the negative to increase (in absolute value). *The criterion for a process taking place* under these conditions is that the thermodynamic potential must be larger in the initial state than in the final ($\Phi_1 - \Phi_2 > 0$). This applies in particular to chemical reactions: they will continue as long as they can produce non-mechanical work. The measure of chemical affinity in a reaction conducted in an isothermal and isobaric way is the maximum non-mechanical work $W' = \Phi_1 - \Phi_2$ which can be obtained from it.

All three terms of Φ tend to decrease, but it would be wrong to conclude that they always diminish separately. The functions U, S, V are all interdependent, and the reduction of one may force the growth of another. Only the sum Φ always decreases, each individual term is only then sure not to increase when the other two remain constant. From (5.35) and (5.33)

$$W' = -\Delta\Phi = (U_1 - U_2) - T(S_1 - S_2) + p(V_1 - V_2). \quad (5.46)$$

The term $T(S_1 - S_2)$, representing the heat imparted to the heat bath, is often negative (endotermic reaction), and the third term $p(V_1 - V_2)$ is also sometimes negative (reaction with expansion).

In later chapters we shall have to consider the case when the system is in *partial equilibrium*, its phases having the same temperatures but standing under different pressures $p_1, p_2, \ldots p_\alpha$. Since U and S are additive, the thermodynamic potential has, then, the form

$$\Phi = U - TS + p_1V_1 + \ldots + p_\alpha V_\alpha. \quad (5.47)$$

It is obvious that it tends to decrease also in this case, because the terms p_jV_j are the potential energies due to the expansion of the individual phases.

37. The Gibbs-Helmholtz equation. Galvanic cells. Another form of the relation (5.46) is

$$\Delta\Phi = \mathbf{X}_2 - \mathbf{X}_1 - T(S_2 - S_1),$$

or substituting for S from eq. (5.37)

$$T\left(\frac{\partial\Delta\Phi}{\partial T}\right)_p = \Delta\Phi - \Delta\mathbf{X}. \quad (5.48)$$

This relation is known as the *Gibbs-Helmholtz* equation. It applies to any *isothermal* difference $\Delta\Phi$ as it is based only on the definitions of the functions Φ and $\mathbf{X}$. In the special case of an isothermal-isobaric

process, we have $\Delta\Phi = -W'$, and from (4.36″), $\Delta\mathbf{X} = Q_p$ (isobaric heat of reaction),

$$T\left(\frac{\partial W'}{\partial T}\right)_p = W' + Q_p. \tag{5.49}$$

The left side of the equation is identical with $T(S_2 - S_1)$ and represents the energy gained by the system from the heat reservoir, in the isothermal-isobaric process we are considering. It is interesting to note that this heat is proportional to the temperature coefficient of W'. The *Gibbs-Helmholtz* equation has many uses; as an example we mention here its application to the electromotive forces of galvanic cells. The active substance in a galvanic cell is an electrolyte whose negative ions react with the material of the positive plate, transferring their electric charges to it. At the same time, an equal number of positive ions is deposited upon the negative plate and neutralized by the (negative) current flowing to it through the outer circuit of the cell from the positive plate. According to Faraday's law, the electric charge supplied to the circuit by 1 mol of the electrolyte is σF, where F is Faraday's equivalent, (9648.9 ± 0.7) abs e-m units, and σ the valency of the ion. The electric energy w' of the current (per 1 mol of the electrolyte) is obtained multiplying this by the electromotive force E,

$$w' = \sigma F E, \tag{5.50}$$

or substituting into (5.49)

$$T\left(\frac{\partial E}{\partial T}\right)_p = E + q_p/\sigma F, \tag{5.51}$$

where q_p is the heat of reaction, referred to 1 mol. When q_p is expressed in calories and E in international volts, the numerical value of the Faraday becomes $F = 23\,046$.

Let us apply this to the Weston cell in which the electrodes consist of Cd-amalgam and of pure mercury. It contains the following substances:

$$\text{Hg-Cd} \mid \text{CdSO}_4 \text{ (solid)} \mid \text{CdSO}_4 \text{ (sat. sol.)} \mid \text{Hg}_2\text{SO}_4 \text{ (paste)} \mid \text{Hg}$$

arranged as shown in Fig. 11. The following empirical formula has been found (and internationally adopted) for the electromotive force of the Weston cell

$$E = [1.01827 - 4.06(t - 20) \times 10^{-5} - 9.5(t - 20)^2 \times 10^{-7} + (20 - t)^3 \times 10^{-8}] \text{ int volt.} \tag{5.52}$$

Equation (5.51) permits to calculate the heat of the reaction ($Cd + Hg_2SO_4 = 2Hg + CdSO_4$) in the cell. It gives, with $\sigma = 2$, $q_p = -47\,482$ cal mol^{-1}, while direct thermochemical measurements yielded $-47\,437$ cal mol^{-1}. In the Weston cell the temperature coefficient of E is negative and represents an energy loss. There are, however, other cells (see exercise 56) where it is positive, so that a part of their energy and electromotive force is supplied by the heat bath (surrounding air).

It is clear from this discussion that in a galvanic cell the heat Q_p of an exothermic reaction is converted into (electrical) work in a practically complete way. Its operation is not cyclic but can be made continuous, since the working substances can be fed in, at the positive plate, and the waste products taken out, at the negative. If the same reaction were used for heating the boiler of a cyclic heat engine (section 21), not more than the fraction $(T_1 - T_2)/T_1$ of the heat Q_p could be utilized, according to eq. (4.03). In view of this superiority, there was a great deal of speculation whether it is feasible to construct a galvanic cell working with the most common industrial fuel, coal (i.e. carbon). But it proved impossible to bring carbon into electrolytic solution.

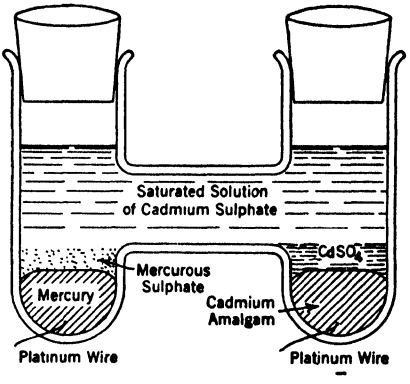


FIG. 11.—The Weston galvanic cell.

For some of the applications it is useful to integrate eq. (5.49) and to express $W' = -\Delta\Phi$ in terms of Q_p. An integrating multiplier of the equation is $1/T^2$, and the multiplication by it gives

$$[\partial(W'/T)/\partial T]_p = Q_p/T^2,$$

whence by partial integration

$$-W' = \Phi_2 - \Phi_1 = Q_p - T\int\left(\frac{\partial Q_p}{\partial T}\right)_p \frac{dT}{T}. \qquad (5.53)$$

Exercise 56. The Pb-Hg cell is constructed as follows:

Pb-amalgam | $PbSO_4$ (solid) | Na_2SO_4 (solution) | Hg_2SO_4 (solid) | Hg

Its electromotive force is

$$E = [0.96466 + 1.74(t - 25) \times 10^{-4} + 3.8(t - 25)^2 \times 10^{-7}] \text{ int volt}$$

What part of E is supplied by the heat reservoir, and what is the heat of reaction at 25° C?

Exercise 57. In the Cu-Hg cell

$$\text{Hg-Cu} \mid \text{CuSO}_4 \text{ (solid)} \mid \text{CuSO}_4 \text{ (sat. sol.)} \mid \text{Hg}_2\text{SO}_4 \text{ (paste)} \mid \text{Hg}$$

the molal heat of reaction is, at 20° C, $q_p = -\,39\,596$ cal mol^{-1}, the electromotive force $E = 0.3500$ int volt. Find the temperature coefficient of E.

Exercise 58. In the same way as (5.48) is derived for $\Delta\Phi$, derive for Φ the equation

$$T\left(\frac{\partial\Phi}{\partial T}\right)_p = \Phi - \mathbf{X} \quad \text{or} \quad \frac{\mathbf{X}}{T^2} = -\left[\frac{\partial(\Phi/T)}{\partial T}\right]_p. \tag{5.54}$$

Hence prove the relation

$$\Phi = -\,T\int \frac{\mathbf{X}}{T^2}\,dT + T\,f(p). \tag{5.55}$$

Remark. In the differentiation and integration with respect to T the pressure is regarded as constant. Therefore, the integration constant may depend on p. In (5.53) the function of p cancels out when the isobaric difference $\Phi_2 - \Phi_1$ is formed.

Exercise 59. Prove from (5.20) and (5.25) the analogous equations

$$T\left(\frac{\partial\Psi}{\partial T}\right)_V = \Psi - U, \quad \text{or} \quad \frac{U}{T^2} = -\left[\frac{\partial(\Psi/T)}{\partial T}\right]_V, \tag{5.56}$$

and

$$\Psi = -\,T\int \frac{U}{T^2}\,dT + T\,f_1(v). \tag{5.57}$$

Forming the difference $\Delta\Psi = \Psi_2 - \Psi_1$ leads to the relation

$$T\left(\frac{\partial\Delta\Psi}{\partial T}\right)_V = \Delta\Psi - \Delta U, \tag{5.58}$$

which sometimes is also given the name of a Gibbs-Helmholtz equation.

CHAPTER VI [1]

GENERAL CONDITIONS OF EQUILIBRIUM OF THERMODYNAMICAL SYSTEMS

38. The method of virtual displacements. The theory of thermodynamical equilibrium was developed by Gibbs and patterned by him after the mechanical theory of statics of Lagrange. We have explained in section 31 what virtual changes are, but it will be well to say here a few words about how they are used. Let the parameters of the system be denoted by $\xi_1, \xi_2, \ldots \xi_n$, which may include as well the thermodynamical variables as those defining the composition of the system; and let the equilibrium be determined by the condition that the variation of a certain characteristic function $F(\xi_1, \ldots \xi_n)$,

$$\delta F = \sum_{k=1}^{n} \frac{\partial F}{\partial \xi_k} \delta \xi_k = 0, \tag{6.01}$$

vanish for all virtual changes $\delta\xi_k$ consistent with the conditions of the system.

If the parameters are not subject to any further restrictions, the virtual changes are entirely *independent* of one another and can be chosen in any arbitrary way. In particular, we could choose all but one of them equal to zero ($\delta\xi_k \neq 0$, and when $i \neq k$, $\delta\xi_i = 0$). Then the condition (6.01) is reduced to $(\partial F/\partial \xi_k)\delta\xi_k = 0$, or

$$\frac{\partial F}{\partial \xi_k} = 0, \qquad (k = 1, 2, \ldots n). \tag{6.02}$$

Since $\delta\xi_k$ was selected at random, this must hold for each of the parameters. We have, therefore, n equations from which the equilibrium values of the n parameters ξ_k can be determined, and this constitutes a complete solution of the problem.

However, usually, the parameters ξ are not quite independent but subject to constraints or subsidiary conditions which take the analyti-

[1] *Suggestion to teachers.* Chapters V and VI are both somewhat abstract. It is, therefore, recommended to interpose between them sections 134, 135, and 136 of Chapter XX, which contain applications of the concepts introduced in Chapter V.

cal form of equations imposed upon them. Suppose that there exist m ($< n$) subsidiary conditions

$$\left.\begin{aligned} f_1(\xi_1, \ldots \xi_n) &= 0, \\ f_2(\xi_1, \ldots \xi_n) &= 0, \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ f_m(\xi_1, \ldots \xi_n) &= 0. \end{aligned}\right\} \tag{6.03}$$

In this case, only $n - m$ of the ξ_k are independent and can be chosen arbitrarily. The remaining m parameters are determined by these through eqs. (6.03). The same is true of the virtual changes $\delta\xi_k$: only $n - m$ of them are within our free choice. In order to find the final conditions of equilibrium, it is necessary to eliminate the m dependent virtual changes from the variation δF and to represent it as a linear form of the independent $\delta\xi_k$, only. This could be done by eliminating m of the parameters from the function F, with the help of eqs. (6.03), before taking its variation. However, this is seldom convenient, and it is preferable to take δF in the form (6.01) and to eliminate the dependent $\delta\xi_k$ from it, using a method worked out by Lagrange. The subsidiary conditions can be, also, thrown into a variational form; in fact, they apply as well to the values of the parameters ξ_k as to $\xi_k + \delta\xi_k$.

$$f_i(\xi_1 + \delta\xi_1, \ldots \xi_n + \delta\xi_n) = 0. \tag{6.04}$$

The difference between (6.04) and (6.03) is, for infinitesimal changes,

$$\sum_{k=1}^{n} \frac{\partial f_i}{\partial \xi_k} \delta\xi_k = 0, \quad (i = 1,2, \ldots m). \tag{6.05}$$

Often the subsidiary conditions are given directly in the variational form

$$\sum_{k=1}^{n} a_k(\xi_1, \ldots \xi_n)\delta\xi_k = 0, \tag{6.06}$$

which cannot always be integrated. However, it is irrelevant for the further treatment whether the form is (6.05) or (6.06). To fix our ideas we use eqs. (6.05) and multiply them, respectively, by *Lagrangean multipliers* $\lambda_i(\xi_1, \ldots \xi_n)$ and add them to eq. (6.01)

$$\sum_{k=1}^{n} \left(\frac{\partial F}{\partial \xi_k} + \lambda_1 \frac{\partial f_1}{\partial \xi_k} + \ldots + \lambda_m \frac{\partial f_m}{\partial \xi_k} \right) \delta\xi_k = 0.$$

The m functions λ_i can be chosen in such a way as to make the m first parentheses of this equation vanish

$$\frac{\partial F}{\partial \xi_k} + \lambda_1 \frac{\partial f_1}{\partial \xi_k} + \ldots + \lambda_m \frac{\partial f_m}{\partial \xi_k} = 0, \tag{6.07}$$

for $k = 1,2, \ldots m$. The remaining expression

$$\sum_{k=m+1}^{n} \left(\frac{\partial F}{\partial \xi_k} + \lambda_1 \frac{\partial f_1}{\partial \xi_k} + \ldots + \lambda_m \frac{\partial f_m}{\partial \xi_k} \right) \delta \xi_k = 0,$$

contains now only $n - m$ *independent* $\delta \xi_k$, so that the problem is reduced to the case of independent virtual changes treated above: this equation is satisfied only then when all the coefficients in parentheses vanish. The conditions (6.01) obtain, therefore, for all values of $k(= 1, 2, \ldots n)$. There are n such equations, and together with the m eqs. (6.03), we have $m + n$ relations between the variables $\xi_1, \ldots \xi_n; \lambda_1, \ldots \lambda_m$, i.e. the number necessary to determine all of them and to obtain a complete solution of the problem of equilibrium.

Exercise 60. A heavy material point moves in the field of gravity of the earth. It is constrained to remain in the curve (ellipse)

$$(\alpha x + \beta y + \gamma z)^2 + \varepsilon y^2 = 1, \qquad ax - by = 0,$$

where x, y, z are cartesian coordinates, z being the vertical. The point comes to rest when its potential energy has its minimum (z = min.) What is its position of rest? (Use Lagrangean multipliers).

Exercise 61. Make the same calculation for a point which is constrained to move in the surface

$$x^2 + (y \cos \alpha + z \sin \alpha)^2 + 2p(y \sin \alpha - z \cos \alpha) = 0.$$

39. Auxiliary constraints. Homogeneity of the thermodynamical functions. It follows from the considerations of the preceding sections that the equations of equilibrium (6.07) hold for *any* system of virtual changes $\delta \xi_k$ satisfying the main condition (6.01) and the subsidiary (6.05). In some cases, it is useful to treat the problem of equilibrium, not in its entirety, but only in part, and to select a *special* system of variations $\delta \xi_k$ compatible with those conditions. It is trivial that the requirements (6.01) and (6.05) are satisfied if all the virtual changes are taken equal to zero ($\delta \xi_k = 0$; $k = 1, 2, \ldots n$). If only some arbitrarily chosen of them are equal to naught (provided the subsidiary conditions permit it), the result is quite consistent with the general solution but represents only a part of it. In fact, in this case, the

corresponding terms of the expressions (6.01) and (6.05) vanish: the method of the Lagrangean multipliers leads, then, simply to an incomplete set of eqs. (6.07).

More generally, we can say that *it is permissible to impose upon the parameters any additional constraints which do not disturb the equilibrium of the system.* At first sight it may appear that this principle is of little practical use because, apart from such simple cases as that just mentioned, we must first know what the state of equilibrium is before we can judge whether a constraint is compatible with it or not. In practice, however, the simple cases are the most important ones, and frequently the knowledge of the nature of the system and of the physical circumstances of its equilibrium gives enough criteria to decide this question. In fact, the introduction of *auxiliary constraints* is a very useful and widely applied expedient.

In this chapter we are going to consider a system consisting of several phases, each described as well by thermodynamic variables as by the mol numbers $N_1, N_2, \ldots N_\sigma$ defining its composition (compare section 32). We shall make use of auxiliary constraints in two connections. The first application consists in breaking up the problem of equilibrium into two partial problems by first considering the case when the composition remains unchanged and dealing with the thermodynamic variables alone. Consequently, the auxiliary constraints take here the simple analytical form $\delta N_1 = \delta N_2 \ldots = \delta N_\sigma = 0$. It is obvious that this assumption is compatible with the notion of equilibrium because the most perfect equilibrium obtains then when no process at all is going on in the system. The conditions, the parameters N_k are subject to, are found separately as the second partial problem into which the treatment is broken up.

In the other application the auxiliary constraint takes a geometrical form. Let us imagine that, anywhere, in the system a thin, closed layer of its substance is removed and replaced by a rigid and adiabatic envelope. Will the presence of this envelope disturb the equilibrium? Strictly speaking, it will. The state of a substance, at any point, is influenced by all the molecules in a small radius around it (radius of molecular action). Therefore, a very thin layer of matter, immediately adjacent to the imaginary envelope, will find itself in a new condition, and this will influence the system as a whole. However, when the volume within the envelope is sufficiently large the influence of the surface layer can be neglected. In fact, the volume increases with the third power of the linear dimensions, the surface with the second, so that the influence of the surface becomes relatively less and less important as the size increases. We shall treat the properties of the

surface layer separately in Chapter XII, and we are going to assume here that all the phases of the system are so large that the surface effects can be neglected (as well at the boundary as at the surfaces of discontinuity between the phases). When this assumption is made, the equilibrium is not disturbed by the rigid envelope just mentioned, whether we think it surrounding the whole of the system or a part of it. It is inherent in the notion of a system in equilibrium that there is in it no relative motion of the parts and no heat transfer between them. The imaginary envelope will not interfere, therefore, with any actual process going on in the system. As to virtual changes, some of them are precluded or restricted, but no new virtual changes are made possible, by the presence of the envelope, which did not exist without it. According to the above argument, it represents a constraint which does not change the form of the conditions of equilibrium. This fact, immediately, leads to some physically interesting conclusions: (1) The envelope can be laid in such a way as to cut off a part of any of the phases. Therefore, the conditions of equilibrium cannot depend on the total masses and volumes of the phases but only on their *specific properties* like temperature, pressure, composition, etc. (see below). (2) It can be laid so as to include only two of the phases and exclude all the rest. Therefore, the equilibrium of two phases is determined only by their own properties and is not affected by the presence of other phases. (3) Since this is true for any pair of phases, the problem of equilibrium of several of them can be reduced to the simpler one of equilibrium between two. It also follows from this that two phases which are in equilibrium with a third are in equilibrium between them. (4) In general, a thermodynamical system is not completely defined unless it is known how it is delimited at its boundary. However, it is clear from the preceding discussion that any boundary conditions can be replaced, without loss of generality, by rigid, adiabatic walls enclosing the system. In this case, the constraints introduced by the walls are not only auxiliary but necessary as forming part of the definition of the system. In the following sections we shall use the expedient of the rigid, adiabatic envelope for all these purposes.

A further example of an auxiliary constraint in geometrical guise is a *semipermeable partition* or *semipermeable membrane*, interposed between two phases, which lets through one kind of molecules but is impenetrable to all other kinds. This device can be also regarded as a part of the definition of the system, inasmuch as it is the thermodynamical criterion for the difference or identity of molecules: two particles are different if it is possible to find a semipermeable membrane

which lets through the one but holds back the other.[1] It is, therefore, perfectly legitimate to introduce semipermeable partitions which are selective not only with respect to chemical differences of molecules but also with respect to differences in the physical (quantum) state of otherwise identical particles.[2]

The notion of *specific* (also called intensive) *properties* used above requires some amplification. It is easy to define it accurately for phases which are described by the variables p, T, N_1, N_2, . . . N_σ. Any property which does not change when all the N_k are increased in the same proportion ε (p and T remaining constant) is a specific property. For instance, the composition is best described in a specific way by the *mol fractions*

$$\left.\begin{aligned} x_k &= N_k/N, \\ N &= N_1 + N_2 + \ldots + N_\sigma. \end{aligned}\right\} \tag{6.08}$$

It follows from the definition of the mol fraction that

$$x_1 + x_2 + \ldots + x_\sigma = 1. \tag{6.08'}$$

In general, a function $F_n(N_1, \ldots N_\sigma)$ which changes in the proportion ε^n, when all the variables N_k are increased in the proportion ε,

$$F_n(\varepsilon N_1, \ldots \varepsilon N_\sigma) = \varepsilon^n F_n(N_1, \ldots N_\sigma), \tag{6.09}$$

is called, in mathematics, a *homogeneous function of the n-th degree.* It satisfies Euler's equation

$$nF_n = N_1 \frac{\partial F_n}{\partial N_1} + \ldots + N_\sigma \frac{\partial F_n}{\partial N_\sigma}, \tag{6.10}$$

which is easily derived (compare exercise 62) from the definition (6.09). Mathematically speaking, the *specific quantities* are, therefore, homogeneous functions of the degree zero in the mol numbers N_k, since they satisfy the condition

$$F_0(\varepsilon N_1, \ldots \varepsilon N_\sigma) = F_0(N_1, \ldots N_\sigma). \tag{6.11}$$

Of course, F depends also on p and T, but we shall compare only states and systems at the same temperature and pressure and need

[1] An interesting discussion of these matters will be found in a paper by L. Szillard, Zs. Physik **32**, p. 840, 1925.

[2] Einstein pointed out the paradox that a semipermeable membrane must differentiate between two particles, be the difference in their states ever so little. This difficulty disappears in the quantum theory where the states are discrete (compare: J. Von Neumann, Math. Grundlagen d. Quantentheorie, p. 197. Berlin 1932).

not bring these variables in evidence. The factor ε may have any value, and, in particular, we may put $\varepsilon = 1/N$, whence

$$F_0(N_1, \ldots N_\sigma) = F_0(x_1, \ldots x_\sigma). \tag{6.12}$$

In a specific quantity we may replace the mol numbers N_k by the mol fractions x_k without changing it.

On the other hand, the volume V, the internal energy U, and the entropy S are additive quantities. When all the mol numbers N_k are increased in the proportion ε, the mass of the whole system increases in the same proportion, without change in its composition. The quantities V, U, S are proportional to the mass and also increase in the proportion ε (p and T remaining constant). The thermodynamic potential is defined as $\Phi = U - TS + pV$ and has, obviously, the same property

$$\Phi(\varepsilon N_1, \ldots \varepsilon N_\sigma) = \varepsilon\Phi(N_1, \ldots N_\sigma). \tag{6.13}$$

The thermodynamic potential, like all the other additive functions of thermodynamics, is a *homogeneous function of the first degree.* Hence its derivative with respect to N_k, or the *partial molal thermodynamic potential,* $\overline{\varphi}_k = \partial\Phi/\partial N_k$ (compare section 35), *is a homogeneous function of the degree zero,* as is easily shown by differentiating (6.13) with respect to N_k. Therefore, Φ and $\overline{\varphi}_k$ satisfy Euler's equation (6.10) with $n = 1$ and $n = 0$.

$$\left.\begin{aligned} \Phi &= N_1\overline{\varphi}_1 + \ldots + N_\sigma\overline{\varphi}_\sigma, \\ 0 &= N_1\frac{\partial\overline{\varphi}_k}{\partial N_1} + \ldots + N_\sigma\frac{\partial\overline{\varphi}_k}{\partial N_\sigma}. \end{aligned}\right\} \tag{6.14}$$

As $\partial\overline{\varphi}_k/\partial N_i = \partial\overline{\varphi}_i/\partial N_k$, this can be also written

$$N_1\frac{\partial\overline{\varphi}_1}{\partial N_k} + \ldots + N_\sigma\frac{\partial\overline{\varphi}_\sigma}{\partial N_k} = 0. \tag{6.15}$$

Every term of this expression is a homogeneous function of the degree zero. We can, therefore, make use of the property (6.12) and replace the mol numbers by the mol fractions

$$x_1\frac{\partial\overline{\varphi}_1}{\partial x_k} + \ldots + x_\sigma\frac{\partial\overline{\varphi}_\sigma}{\partial x_k} = 0. \tag{6.16}$$

Although this relation was already given by Gibbs, it is usually called *Duhem's equation.*

Exercise 62. Prove Euler's eq. (6.10) from (6.09). (Directions. Differentiate (6.09) with respect to ε, denoting, for short, $\varepsilon N_k = \xi_k$. Then put $\varepsilon = 1, \xi_k = N_k$).

Exercise 63. Check by direct calculation the statement that Euler's equation is correct for the homogeneous (in x, y, z) function $F_n = x^a y^b z^{n-a-b}$. Therefore, it must be true for any sum of such terms of the degree n.

40. The temperatures and pressures of phases in equilibrium. Let us consider a heterogeneous system consisting of simple phases. Its total internal energy U is the sum of the internal energies $U^{(i)}$ of the individual phases

$$U = \sum_{i=1}^{\alpha} U^{(i)}. \tag{6.17}$$

In the same way, the total entropy S is additive with respect to the individual entropies $S^{(i)}$

$$S = \sum_{i=1}^{\alpha} S^{(i)}, \tag{6.18}$$

and we define as the total volume V the sum of the volumes $V^{(i)}$ of the phases

$$V = \sum_{i=1}^{\alpha} V^{(i)}. \tag{6.19}$$

We can choose $S^{(i)}$ and $V^{(i)}$ as the two thermodynamical variables characterizing the state of the phase (i). It will, further, depend on a number of parameters describing its chemical composition. In general, the phases will not be chemically pure substances but mixtures of several or many chemically pure constituents or *components*. Suppose that they contain N_1 mols of the first component, N_2 of the second, and so on, the number of components being σ. The internal energy of the phase (i) is, then, a function of the following variables

$$U^{(i)} = U^{(i)}(S^{(i)}, V^{(i)}, N_1^{(i)} \ldots N_\sigma^{(i)}), \tag{6.20}$$

although a part of the mol numbers N may be equal to zero in some of the phases. This is the form we have considered in section 31: the variation of the total internal energy U is, therefore, in accordance with eqs. (5.06) and (5.07),

$$\delta U = \sum_{i=1}^{\alpha} \left\{ T^{(i)} \delta S^{(i)} - p^{(i)} \delta V^{(i)} + \sum_{k=1}^{\sigma} \left(\frac{\partial U^{(i)}}{\partial N_k^{(i)}} \right)_{S,V} \delta N_k^{(i)} \right\} \tag{6.21}$$

Applying auxiliary constraints, as explained in the preceding section, we shall at first suppose that the mol numbers do not change

($\delta N_k^{(i)} = 0$) and shall find only the conditions controlling the thermodynamical variables.

The conditions of equilibrium are, according to eqs. (5.03): $\delta U = 0$, $\delta S = 0$. It is mathematically convenient to regard $\delta U = 0$ as the primary condition. It now takes the form

$$\delta U = \sum_{i=1}^{\alpha} (T^{(i)} \delta S^{(i)} - p^{(i)} \delta V^{(i)}) = 0. \tag{6.22}$$

The condition

$$\delta S = \sum_{i=1}^{\alpha} \delta S^{(i)} = 0 \tag{6.23}$$

we regard as subsidiary. Another subsidiary restriction is obtained if we replace the border conditions of the system by the assumption that it is surrounded by a rigid adiabatic envelope (compare the preceding section): We have then $V = \text{const}$, or

$$\delta V = \sum_{i=1}^{\alpha} \delta V^{(i)} = 0. \tag{6.24}$$

In the case when the several phases are separated by natural surfaces of discontinuity and each of them can expand, virtually, at the expense of the others, the variations $\delta S^{(i)}$, $\delta V^{(i)}$ are not subject to any other restrictions so that eqs. (6.22), (6.23), and (6.24) exhaust the problem. Multiplying eqs. (6.23) and (6.24), respectively, by λ_1 and λ_2 and adding them to (6.22)

$$\sum_{i=1}^{\alpha} [(T^{(i)} + \lambda_1) \delta S^{(i)} - (p^{(i)} - \lambda_2) \delta V^{(i)}] = 0, \tag{6.25}$$

where the $\delta S^{(i)}$ and $\delta V^{(i)}$ must be considered as independent (compare section 38):

$$T^{(i)} = -\lambda_1, \qquad p^{(i)} = \lambda_2.$$

The temperatures of all the phases are equal to the same function which has, therefore, the physical meaning of the uniform temperature T of the whole system ($\lambda_1 = -T$). In the same way, the pressures of all the phases are equal to p

$$T^{(1)} = \ldots = T^{(\alpha)} = T, \qquad p^{(1)} = \ldots = p^{(\alpha)} = p. \tag{6.26}$$

In short, *the temperature and pressure in a system in equilibrium are uniform.* However, this applies only to the case when each of the phases can change its volume. In the opposite case, when the con-

straints are such that the volume of each phase remains unchanged ($V^{(i)} = \text{const.}$), the condition (6.24) must be replaced by α separate conditions

$$\delta V^{(i)} = 0. \tag{6.27}$$

This will occur, for instance, when each of the phases is enclosed in rigid heat-conducting walls, but also in some cases which are less trivial, as we shall see in sections 107 and 127. In applying the method of Langrangean multipliers, we take eq. (6.23) with the factor λ_0 and (6.27) with the factors $\lambda^{(i)}$ and add them to eq. (6.12)

$$\sum_{i=1}^{\alpha} [(T^{(i)} + \lambda_0)\delta S^{(i)} - (p^{(i)} - \lambda^{(i)})\delta V^{(i)}] = 0, \tag{6.28}$$

whence

$$T^{(i)} = -\lambda_0 = T, \qquad p^{(i)} = \lambda^{(i)}. \tag{6.29}$$

The temperature is uniform throughout, as in the previous case, *but the pressures of the phases are all different.* It is quite obvious how these considerations are to be extended to the mixed case when the volume of some of the phases is constant while others can expand. The case when some of the phases are adiabatically enclosed and their entropies are constant ($\delta S^{(i)} = 0$) is also possible but hardly worth our consideration, since it is one of dynamical, rather than thermodynamical, equilibrium.

We have obtained a partial solution of the problem of equilibrium, with respect to the thermodynamical variables T and p, and can now turn to the other side of the problem relating to the virtual changes of the mol numbers. In order to deal with it, we shall again impose upon the system suitable constraints. We already know that, in equilibrium, the temperature T is uniform while the pressures $p^{(i)}$ of the phases may or may not be equal. We shall now consider only virtual changes in which $\delta T = 0$ and $\delta p^{(i)} = 0$. It was shown in section 36 that, under these circumstances (when the temperature and the local pressures are kept constant), the function Φ tends to decrease and equilibrium is possible only when it has reached its minimum

$$(\delta\Phi)_{p,T} = 0. \tag{6.30}$$

The total thermodynamic potential is represented by the sum over the phases

$$\Phi = \sum_{i=1}^{\alpha} \Phi^{(i)}(T, p^{(i)}, N_1^{(i)}, \ldots N_\sigma^{(i)}).$$

In forming the variation T and p are to be kept constant, whence

$$(\delta\Phi)_{p,T} = \sum_{i=1}^{\alpha} \sum_{k=1}^{\sigma} \left(\frac{\partial \Phi}{\partial N_k^{(i)}}\right)_{T,p^{(i)}} \delta N_k^{(i)}. \tag{6.31}$$

In general, the virtual changes $\delta N_k^{(i)}$ are not independent but subject to subsidiary conditions determined by the nature of the system.

Exercise 64. Consider eqs. (6.22), (6.23), and (6.24) for the case of only two phases and solve them without use of Lagranean multipliers. Show that this method can be used to obtain the general result by the reasoning of section 39.

Exercise 65. Take the case of p and T being uniform throughout the system and generalize the argument of section 32 which led to the formula (5.08) for systems with several phases. Show that this is an alternative way of obtaining the condition (6.31).

41. Number of phases in equilibrium. The phase rule. In order to derive the explicit equations of equilibrium from the condition (6.31), it is necessary to eliminate from it the dependent virtual changes $\delta N_k^{(i)}$ by means of the subsidiary conditions. It was pointed out in section 38 that this can be done either before taking the variation (6.30) of the function Φ, or after. The former procedure consists in expressing a part of the arguments $N_k^{(i)}$ of the function Φ by the remainder and so reducing their number as far as possible. We say, then, that the thermodynamical potential is expressed in terms of the mol numbers of the *independent components* of the system. To illustrate this by an example, let us take the case that N_1 mols of hydrogen (H_2) and N_2 mols of iodine (I_2) are brought into the same vessel. The two gases will partially react and form a certain amount (N_3 mols) of hydrogen iodide which will be the third constituent of the mixture but not an independent one: in the state of equilibrium N_3 is completely determined by N_1 and N_2, so that hydrogen and iodine can be taken here as the independent components. We see, moreover, from this example that the method is of no help in the treatment of concrete cases, because we must have solved the problem of equilibrium and found the expression of N_3, in terms of N_1 and N_2, before we can eliminate it from the thermodynamical potential. This is, in fact, characteristic of all thermodynamical systems: the main part of the subsidiary conditions between the virtual changes $\delta N_k^{(i)}$ are given in the variational form (6.06), and not in the integral (6.03), and often there is no practicable way of eliminating the dependent mol numbers $N_k^{(i)}$ except by means of the final solution of the problem. However, some interesting conclusions can be drawn from the theoretical possibility of this elimination: we simply suppose that the system is reduced

to its independent components, without attempting to carry out this reduction in any special case.

Generally, *those constituents of a system should be chosen as its independent components which cannot be converted into one another* by any reaction going on in it. In the above example hydrogen and iodine satisfy this requirement, but, in general, the number of independent components of a system is, by no means, identical with the number of chemical elements of which it consists. For instance, if all the phases of a system consist of water in different states of aggregation (ice, steam, liquid water), hydrogen and oxygen are not independent components, because the mol number of the one is defined by that of the other, viz. stands to it in the constant ratio 2 : 1. We have here a system of only one independent component. Strictly speaking, the number of components depends on the accuracy with which we wish to describe the system: there is always a certain amount of dissociation in steam, and, because of the different solubility of hydrogen and oxygen, the phases will not contain exactly equal mol numbers of the two elements. However, these effects are entirely negligible at ordinary temperatures. An example of a system in which the number of independent components is larger than the number of elements is presented by a mixture of hydrocarbons. There are many hydrocarbons which do not react under ordinary conditions, so that the mol numbers of hydrogen and carbon are quite insufficient for a description of such a system. The ultimate criterion for the choice is, of course, that *a virtual change of the mol number in one of the independent components should not necessitate any virtual changes in the others.*

The notion of independent components is sufficiently clear from this discussion. Suppose that their number is β and that the mol numbers of all the constituents, the independent as well as the dependent, are eliminated from the functions $\Phi^{(i)}$ and replaced by the *masses* $M_1^{(i)}, M_2^{(i)}, \ldots M_\beta^{(i)}$ of the independent components in the several phases. Equation (6.31) becomes, then (if we drop the subscripts T,p),

$$\delta\Phi = \sum_{i=1}^{\alpha} \sum_{k=1}^{\beta} \frac{\partial \Phi^{(i)}}{\partial M_k^{(i)}} \delta M_k^{(i)} = 0. \tag{6.32}$$

The only subsidiary conditions which remain are now those which apply to each independent component separately. We shall restrict ourselves here to the case that the phases are in direct contact, so that a component can pass freely from one phase into another. As was pointed out in the preceding section, the border conditions of the system as a whole can be replaced by an imaginary rigid envelope

surrounding it. This implies that the total mass of each component must remain constant. $\sum_{i=1}^{\alpha} M_k^{(i)} = \text{const}$, or taking the variation,

$$\sum_{i=1}^{\alpha} \delta M_k^{(i)} = 0, \qquad (k = 1, 2, \ldots \beta).$$

Multiplying these equations, respectively, by the Lagrangean multipliers λ_k and adding them to (6.32),

$$\sum_{i=1}^{\alpha} \sum_{k=1}^{\beta} \left(\frac{\partial \Phi^{(i)}}{\partial M_k^{(i)}} + \lambda_k \right) \delta M_k^{(i)} = 0,$$

where the virtual changes $\delta M_k^{(i)}$ are completely independent. There follows the system of equations

$$\frac{\partial \Phi^{(1)}}{\partial M_k^{(1)}} = \ldots = \frac{\partial \Phi^{(\alpha)}}{\partial M_k^{(\alpha)}} = -\lambda_k. \tag{6.33}$$

The index k goes here from 1 to β, so that this formula represents $\alpha\beta$ relations. If we eliminate from them the functions λ_k, there remain $Z_{eq} = \alpha\beta - \beta$ equations between the partials of the functions $\Phi^{(i)}$. What is, on the other hand, the number of variables on which these partials depend? It was shown in section 39 that the partials of $\Phi^{(i)}$, with respect to $N_k^{(i)}$, represent specific quantities. The reasoning used in that demonstration is in no way affected, if the masses $M_k^{(i)}$ are regarded as the arguments of these functions, instead of the mol numbers. The partials $\partial\Phi^{(i)}/\partial M_k^{(i)}$ are, therefore, homogeneous functions of the degree zero in the masses. In analogy to the mol fractions we introduce the *mass fractions*

$$\left.\begin{aligned} y_k^{(i)} &= M_k^{(i)}/M^{(i)}, \\ M^{(i)} &= M_1^{(i)} + \ldots + M_\beta^{(i)} \end{aligned}\right\} \tag{6.34}$$

and conclude from eq. (6.12) that $\partial\Phi^{(i)}/\partial M_k^{(i)}$ can be represented in terms of the variables $y_k^{(i)}$. Only $\beta - 1$ of these fractions are independent because there exists the identical relation

$$y_1^{(i)} + \ldots + y_\beta^{(i)} = 1. \tag{6.35}$$

The number of variables defining the composition of the phase (i) is, just $\beta - 1$, and the number of them in all the α phases is $\alpha\beta - \alpha$. To this must be added the two thermodynamical variables, the common temperature T and pressure p of all the phases. The total number of

variables by which the partial derivatives of the system (6.33) are determined is, therefore, $Z_{\text{var}} = \alpha\beta - \alpha + 2$.

A system of equations is only then compatible and capable of being satisfied when their number does not exceed the number of variables on which they depend ($Z_{\text{eq}} \leqq Z_{\text{var}}$). This condition restricts the number of phases which can be simultaneously in equilibrium: from $\alpha\beta - \beta \leqq \alpha\beta - \alpha + 2$ there follows

$$\alpha \leqq \beta + 2. \tag{6.36}$$

This inequality expresses the famous *phase rule* of Gibbs: *The number of phases coexisting in equilibrium cannot exceed the number of independent components by more than two.*

Let us consider the main cases that can arise. Examples of them will be treated in the following chapters. The maximum which α can reach is

$$\alpha = \beta + 2, \tag{6.37}$$

it will be attained when the number of variables is just equal to the number of equations. All the variables are then completely determined, the equilibrium can exist only at one definite temperature and one definite pressure, and the composition of all the phases is also quite definite. This state is often called the *fundamental state* of the system.

In the case

$$\alpha = \beta + 1 \tag{6.38}$$

the number of the variables exceeds that of the equations just by one: the value of one of the variables can be chosen arbitrarily, and this fixes the values of all the others. For instance, if we specify the temperature, the pressure and the compositions are completely determined by it, etc.

Similarly, when

$$\alpha = \beta, \tag{6.39}$$

two of the variables can be assigned arbitrary values: if p and T are specified, the compositions of the phases are definite.

Finally, in the cases $\alpha < \beta$, the compositions of the phases are not yet defined by the temperature and pressure. There are, then, so many cases of equilibrium possible that hardly any rules of general validity can be given.

In conclusion, it will be well to emphasize that the phase rule deals only with the number of phases in *equilibrium*. We have mentioned

water in its different states of aggregation as an example of a system with one independent component ($\beta = 1$). According to the phase rule not more than $1 + 2 = 3$ phases of it can coexist (viz. vapor, liquid water, ice), and the simultaneous equilibrium of all three is possible only in the fundamental state at a definite temperature and pressure (compare also section 48). However, everybody knows that he can throw a lump of ice into a bucket of water and that there will be, at all temperatures, water vapor on top of the system. In this case, the three phases are not in equilibrium, and, in the long run, one of them will disappear, but the coexistence without equilibrium may last hours. In applying the phase rule one must be quite sure that equilibrium is, actually, established.

42. Explicit equilibrium conditions. We return now to the description of the phases by the mol numbers of all their chemically distinct constituents and not only of the independent components. We shall make use of the notation (5.38) defining the *partial molal thermodynamic potential*

$$\overline{\varphi}_k^{(i)} = \left(\frac{\partial \Phi^{(i)}}{\partial N_k^{(i)}}\right)_{T,p} \tag{6.40}$$

It will be well to recall here that it is a generalization of the ordinary molal potential. In the special case, when the phase is chemically pure, there is only one constituent, $\Phi^{(i)} = N^{(i)}\varphi^{(i)}$, where $\varphi^{(i)}$ is independent of $N^{(i)}$. Then $\overline{\varphi}^{(i)}$ becomes identical with $\varphi^{(i)}$.

The condition (6.31) now takes the form

$$(\delta\Phi)_{p,T} = \sum_{i=1}^{\alpha}\sum_{k=1}^{\sigma} \overline{\varphi}_k^{(i)} \delta N_k^{(i)} = 0, \tag{6.41}$$

and is valid for all possible virtual changes $\delta N_k^{(i)}$ consistent with the nature of the system.

The virtual processes in the system can be reduced to two simple types. In the first place, a small amount of the constituent k can pass from a phase (1) into an adjacent phase (2). The molecular weights $\mu_k^{(1)}$ and $\mu_k^{(2)}$ of this component in the two phases need not necessarily be the same because there is the possibility of association. The mass added to the first phase is, then, $\mu_k^{(1)}\delta N_k^{(1)}$, and that added to the second $\mu_k^{(2)}\delta N_k^{(2)}$. These masses must be oppositely equal

$$\mu_k^{(1)}\delta N_k^{(1)} = -\mu_k^{(2)}\delta N_k^{(2)},$$

or

$$\delta N_k^{(1)} : \delta N_k^{(2)} = -\frac{1}{\mu_k^{(1)}} : \frac{1}{\mu_k^{(2)}} = \nu_k^{(1)} : \nu_k^{(2)}. \tag{6.42}$$

The symbols ν_k are integral numbers with the following meaning. Suppose that $-\nu_k^{(1)}$ mols of the component k are removed from phase (1): they are converted into $\nu_k^{(2)}$ mols belonging to phase (2). If no association takes place in either phase, we can put $-\nu_k^{(1)} = \nu_k^{(2)} = 1$.

There are no conditions in the system which should prevent us from putting all the other virtual changes δN_k equal to naught, in the way of an auxiliary constraint. Therefore the condition (6.41) reduces to

$$\Delta\Phi \equiv \nu_k^{(1)}\overline{\varphi}_k^{(1)} + \nu_k^{(2)}\overline{\varphi}_k^{(2)} = 0. \tag{6.43}$$

$\Delta\Phi$ can be interpreted as the change of the total thermodynamic potential which takes place in the finite virtual process of reversibly transferring $-\nu_k^{(1)}$ mols of the component k from the first phase into the second (where they are converted into $\nu_k^{(2)}$ mols). The temperature and pressure are supposed to remain constant, maintained so by a suitable arrangement of heat baths and loads. Of course, the process will be attended by the system receiving (positive or negative) heat from the heat baths and doing work against the loads.

Sometimes it is convenient to express the composition not in terms of the mol numbers $N_k^{(i)}$ but in terms of the masses $M_k^{(i)} = \mu_k^{(i)}N_k^{(i)}$ of the individual components. We shall denote the *partial specific thermodynamic potentials* (referred to unit mass)

$$\overline{\varphi}_{Mk}^{(i)} = \frac{\partial\Phi^{(i)}}{\partial M_k^{(i)}} = \frac{1}{\mu_k^{(i)}}\overline{\varphi}_k^{(i)}. \tag{6.44}$$

Because of (6.42), $\mu_k^{(1)}\nu_k^{(1)} = -\mu_k^{(2)}\nu_k^{(2)}$, and (6.43) reduces to

$$\overline{\varphi}_{Mk}^{(1)} - \overline{\varphi}_{Mk}^{(2)} = 0. \tag{6.45}$$

The second simple type of process we have to consider is a chemical reaction between several constituents of the same phase. Let us take, as an example, the equation of the reaction between hydrogen and iodine

$$2\mathrm{HI} = \mathrm{H}_2 + \mathrm{I}_2,$$

or

$$2\mathrm{HI} - \mathrm{H}_2 - \mathrm{I}_2 = 0.$$

Like the equations of all chemical reactions it is of the general type

$$\nu_1 G_1 + \nu_2 G_2 + \ldots + \nu_\sigma G_\sigma = 0, \tag{6.46}$$

where $G_1, \ldots G_\sigma$ are the chemical symbols of the different substances (components) and $\nu_1, \ldots \nu_\sigma$ the numbers of mols with which they take part in the reaction. We may observe here that the process of

transferring matter from one phase into another, as considered above, can be represented by the same sort of a symbolical equation

$$\nu_k^{(1)} G_k^{(1)} + \nu_k^{(2)} G_k^{(2)} = 0. \tag{6.47}$$

Both equations are included in the general form

$$\sum_{i=1}^{\alpha} \sum_{k=1}^{\sigma} \nu_k^{(i)} G_k^{(i)} = 0. \tag{6.48}$$

We shall usually consider a definite *direction* of the reaction, namely, that in which it is endothermic and the *heat of reaction positive.* Consequently, we shall attribute positive signs to the numbers ν_k of those components which are produced, and negative to those which are consumed, in the *endothermic* reaction.

When eq. (6.41) refers to a process of the type (6.46), the corresponding virtual changes δN_k must be taken proportional to the numvers ν_k

$$\delta N_1 : \delta N_2 : \ldots : \delta N_\sigma = \nu_1 : \nu_2 : \ldots : \nu_\sigma.$$

(The numbers ν_k and variations δN_k for the components not taking part in the reaction can be put equal to zero because of the principle of auxiliary constraints). The condition becomes

$$\Delta\Phi \equiv \nu_1 \overline{\varphi}_1 + \ldots + \nu_\sigma \overline{\varphi}_\sigma = 0. \tag{6.49}$$

As in the preceding case $\Delta\Phi$ must be interpreted as the total change of the thermodynamic potential in the finite virtual process corresponding to the transformation of $\nu_1, \ldots \nu_\sigma$ mols of the several components.

Equations (6.43) and (6.49) represent partial solutions of the problem of equilibrium. The complete solution is given by the simultaneous system of equations corresponding to all processes of these two types possible in the thermodynamical system. Both these equations are included in the general form

$$\Delta\Phi \equiv \sum_{i=1}^{\alpha} \sum_{k=1}^{\sigma} \nu_k^{(i)} \overline{\varphi}_k^{(i)} = 0, \tag{6.50}$$

in which a part of the coefficients $\nu_k^{(i)}$ are equal to those of (6.43) or (6.49) and the rest vanish. It will be useful to find the partial derivatives of $\Delta\Phi$ with respect to the pressure and temperature: from eqs. (5.37)

$$\left(\frac{\partial \Delta\Phi}{\partial p}\right)_T = \Delta V \tag{6.51}$$

and $(\partial\Delta\Phi/\partial T)_p = -\Delta S$, where ΔV and ΔS represent the changes of the total volume and the total entropy in the process. This process being isothermal (as well as isobaric), we can apply to ΔS the formula (4.11), $\Delta S = Q_p/T$, where Q_p is the isobaric heat of the reaction

$$\left(\frac{\partial\Delta\Phi}{\partial T}\right)_p = -\frac{Q_p}{T}. \tag{6.52}$$

Moreover, taking into account the condition $\Delta\Phi = 0$, we can write

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta\Phi}{RT}\right)\right]_p = -\frac{Q_p}{RT^2}. \tag{6.53}$$

Exercise 66. What is the structure of ΔV and Q_p in terms of partial molal quantities? Show that

$$\Delta V = \sum_k \sum_i \nu_k^{(i)} \bar{v}_k^{(i)}, \quad Q_p = \sum_k \sum_i \nu_k^{(i)} \bar{\chi}_k^{(i)}.$$

CHAPTER VII

PHASES OF A CHEMICALLY PURE SUBSTANCE

43. Equilibrium of two phases. If all the phases of a system consist of the same chemically pure substance, in different physical states, it contains, according to section 41, only one independent component ($\beta = 1$). The phase rule (6.36) tells us, then, that no more than three phases can be simultaneously in equilibrium. There exist substances which are known in more than three states. For instance, sulfur occurs in the vaporized, liquid, monoclinic crystalline, and rhombic crystalline states, but only three of them can coexist in equilibrium. The problem of thermodynamics in relation to pure substances is, therefore, reduced to the consideration of the equilibrium of one phase, two phases, or three phases. The properties of a single phase were sufficiently discussed in Chapters I to IV, and we shall restrict ourselves here to the cases of two and three phases, starting with the two-phase system as the simpler problem.

The only possible virtual process in such a system is that represented symbolically by eq. (6.43): $\nu^{(1)}G^{(1)} + \nu^{(2)}G^{(2)} = 0$, viz. the transformation of $-\nu^{(2)}$ mols of the second phase into $\nu^{(1)}$ of the first. It will be more convenient to define the numbers $\nu^{(1)}$ and $\nu^{(2)}$ both as *positive* and to indicate the fact that the second phase is consumed in the process by writing its equation as $\nu^{(1)}G^{(1)} - \nu^{(2)}G^{(2)}$ with

$$\nu^{(1)}/\nu^{(2)} = \mu^{(2)}/\mu^{(1)} = g, \tag{7.01}$$

instead of (6.42). It was pointed out in the preceding section that, for a pure substance, the partial thermodynamic potential and the ordinary molal are identical $\overline{\varphi} = \varphi$. The eq. (6.31) of equilibrium takes, therefore, the form

$$\Delta\Phi \equiv \nu^{(1)}\varphi^{(1)} - \nu^{(2)}\varphi^{(2)}, \tag{7.02}$$

or, in the special case when there is no association and the molecule is the same in both phases ($\nu^{(1)} = \nu^{(2)} = 1$),

$$\varphi^{(1)} = \varphi^{(2)}. \tag{7.03}$$

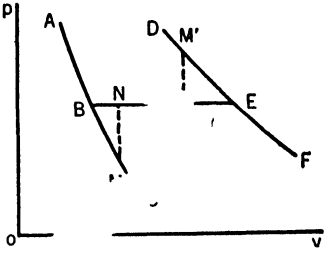
In words, the molal thermodynamical potentials in two adjacent

phases are equal. The molecular constitution of the condensed phases is not always known and, in some cases, even not well defined. For this reason, many authors refer the quantities $\varphi^{(i)}$ of all the phases to 1 mol of the vapor. In particular, this is unavoidable in the chemical literature which has to present results of measurement on all sorts of substances, including those whose molecular structure is not yet sufficiently investigated. The purpose of this book is, however, a different one: we are not so much interested in the presentation of a large amount of experimental material as in its theoretical penetration. The questions of association and dissociation play an important role in the interpretation of the experimental behavior of substances, and they can be conveniently studied if the fundamental equation of equilibrium is written in the general form (7.02). We shall, therefore, make this formula the basis of the following discussions (compare also section 60).

In general, the coefficients $\nu^{(i)}$ are integers, completely determined by the nature of the system, while the functions $\varphi^{(i)}$ depend only on the common temperature and pressure of the two phases. p and T are, therefore, the only variables which enter into eq. (7.02) or (7.03), and, if one of them is arbitrarily chosen, the other is determined by this relation. It was pointed out in section 41 that this is always the case when the number of phases is larger by one than the number of independent components ($\alpha = \beta + 1$). When the equilibrium of the liquid and the gaseous phase is considered, the temperature which corresponds to a given pressure, in virtue of the condition (7.02), is called the *boiling temperature* or the *boiling point.* Vice versa, if the temperature is regarded as given, the pressure corresponding to it is known as the *boiling pressure.* Similarly, one speaks, in the case of the coexistence of the liquid and the solid phase, of the *freezing point* and the *freezing pressure.* More general terms including all cases of a pair of pure phases are *transformation temperature* and *transformation pressure.*

Let AC and DF in Fig. 12 represent, respectively, the isothermals of a pure substance in its liquid and gaseous states. Suppose we have a single phase of it corresponding to the point A of the diagram. Keeping the temperature constant we increase the volume reversibly, thus allowing the pressure slowly to drop: the representative point of the system will move along the isothermal towards C. Let the point B correspond to the *boiling pressure* for this isothermal at which the coexistence of the liquid and the vapor phase is possible. The question arises now: will the substance, after reaching this point, remain in a single liquid phase and continue to move along the branch

B, or will it begin to vaporize at constant pressure and be converted into a two-phase system whose states are represented by the horizontal BE? What is the relative stability of the states M and N lying on a vertical and corresponding to the same volume? The results of the preceding chapter are insufficient to solve this problem because they regard the number of phases as given: the criteria given there are satisfied in both cases. To obtain an answer, we must fall back on the fundamental principles governing thermodynamical equilibrium as expounded in Chapter V. Since the processes BM and BN are both isothermal and lead to the same end volume, we have to use the criterion adapted to this case (section 36): The work function Ψ tends to decrease, and, of two states of the same temperature and volume, that with the lower Ψ is more stable. Let us now evaluate the work functions Ψ_M and Ψ_N in the states M and N by comparing them with Ψ_B in the state B. We make use of eq. (5.22) which applies to any isothermal process: $\Psi_B - \Psi_M = W_{BM}$ a



F 4.—Isothermals in equi- ium of liquid and vapor.

the right sides of the equations repr $\Psi_B - \Psi_N = W_{BN}$, where system, respectively, in the processes . the work done by the find $\Psi_N - \Psi_M = W_{BM} - W_{BN}$. In and BN. Subtracting we represented by the areas under the iiagram W_{BM} and W_{BN} are M lies lower than N, we have), BM and BN; and, since $\Psi_N < \Psi_M$: The states on the h .ic BN. We find, therefore, work function and of higher stabi E are the states of lower that the states represented by ehave mentioned in section 5 impossible but sometimes occ anch BC are not absolutely (supercooling). However, they the exceptional circumstances and the system is always read ur d to an unstable equilibrium, This reasoning can easily be cor ts over into the two-phase state. transformation pressure or y trmal o all analogous cases: at the divides into two phases. exm a pure substance, generally, cenfact s a single phase only in exceptional conditions. t is

Exercise 67. When the Van de equation applies (continuity of liquid and vapor), there are two isother processes between B and E (Fig. 1, p. 10) represented by the curve an d the st line. Applying eq. (5.21) to both of them, prove that the two shaded areas in 1 are equal.

44. The Clapeyron–Clausius equation. Equation (7.02) cannot be directly used for the calculation of transformation temperatures

because the explicit form of the functions $\varphi^{(i)}$ is known in only very few cases. However, its differential form gives a relation between easily measurable quantities. Let us consider the equilibrium of our two-phase system in two cases: at the temperatures and pressures T, p and $T + dT$, $p + dp$. The respective equations (7.02) are $\Delta\Phi(T, p) = 0$ and $\Delta\Phi(T + dT, p + dp) = 0$. According to the definition of the differential of a function, the difference between these two equations is

$$\left(\frac{\partial\Delta\Phi}{\partial T}\right)_p dT + \left(\frac{\partial\Delta\Phi}{\partial p}\right)_T dp = 0. \tag{7.04}$$

We can substitute the expressions (6.51) and (6.52) for the partial derivatives. The heat of the process (Q_p) is, in this case, the *latent heat of transformation* L (compare section 10). We find, therefore,

$$\frac{dp}{dT} = \frac{L}{T\Delta V}. \tag{7.05}$$

This relation was found by the French engineer Clapeyron before the discovery of the first law of thermodynamics (1832). Its deduction from the modern point of view is due to Clausius. It is, therefore, called the *Clapeyron-Clausius equation*. If the mass of the material transformed in the process is reduced to 1 mol of the vapor phase, we shall denote the latent heat by l, while the change of volume becomes $\Delta V_l = (\nu^{(1)}v^{(1)} - \nu^{(2)}v^{(2)})/\nu^{(}$ (difference of the molal volumes after and before the transformation referred to 1 mol of the vapor)

$$\frac{dp}{dT} = \frac{l}{T\Delta V_l}. \tag{7.06}$$

This formula has been extensively tested by experiment and found to be accurate within the limits of experimental error. As an example we may take water at the normal boiling point (373°.1): the change of volume is $\Delta V_l = 30\,186$ cm^3 for 18.015 g, $dp/dT = 27.12$ mm/deg. The conversion factor is 1 mm/deg = (1.01325/760 $\times$ 4.1852 $\times$ 10) cal deg^{-1} cm^{-3} = 3.1854 $\times 10^{-5}$ cal deg^{-1} cm^{-3}. The formula (7.06) gives, therefore, $l = 9726$ cal mol^{-1}, while the direct measurement gives $l = 9720$ cal mol^{-1}.

We give in Table 8 the normal (i.e. 1 atm) boiling points (T_B) and melting points (T_F) of the more important elementary substances together with the latent heats of vaporization (l_B) and of fusion (l_F) at these temperatures.

TABLE 8

Element	T_B	l_B (cal mol^{-1})	l_B/T_B	T_F	l_F (cal mol^{-1})
He	4.2	24.5	5.7		
Ne	27.3	416	15.3	24.5	57
A	87.5	1 540	17.6	84.0	267
Kr	121.4	2 240	18.4	104	360
Xe	164.1	3 200	19.5	133	490
H_2	20.5	220	10.7	14.0	28.4
N_2	77.3	1 370	17.7	63.3	170
O_2	90.2	1 640	18.2	54.8	105
O_3	161	3 570	22.2	22	
Cl_2	238.6	4 900	20.5	171.6	1620
Br_2	332.0	7 150	20.9	266.0	2560
I_2	457.5	10 5[illegible]	23.0	386.7	4000
Na	1153	25[illegible]	21.8	370.7	633
K	1033	20[illegible]	19.8	335.5	518
Cu	2570	11[illegible]	43.4	1356	2750
Ag	2220	[illegible]	26.8	1233.7	2630
Au	2870	[illegible]0	30.6	1336	3180
Zn	1180	[illegible]0	20.7	692.6	1690
Cd	1040	[illegible]0	24.5	594.1	1480
Hg	630.1	[illegible]0	23.0	234.3	556
Al	2070	[illegible]0	26.0	933.2	1910
Si	2870	[illegible]	14.3	1690	
Sn	2530	[illegible]	30.6	505.0	1670
Pb	1890	46 10[illegible]	24.4	600.7	1120
Bi	1720	46 100	26.8	544	2600
S	717.8	2 190	30.5	392.2	262
W	6170	223 000	36.2	3643	
Fe	3270	90 700	28.6	1808	2670
Pt	4570	167 000	36.6	2028	5250

In the case of the transformations solid → liquid and liquid → vapor, the latent heat L is positive. The volume of the vapor is, moreover, always larger than the volume of the same mass of liquid, $\Delta V > 0$, so that the boiling temperature rises with the pressure ($dT_B/dp > 0$). For instance, in the case of water we have the following conditions:

TABLE 9

t.....	0°	50°	100°	120°	200°	370°.4 C
p_B....	6.025×10^{-3}	0.1217	1.0000	1.9594	15.341	217.72 atm

On the other hand, the specific volume of the liquid phase may be either larger or smaller than that of the solid in equilibrium with it.

For instance water (at 0° C and 1 atm) has a 9% smaller volume than ordinary ice. Therefore, ΔV and dT/dp are in this case negative, as was pointed out by James Thomson (elder brother of Lord Kelvin). The melting point falls, therefore, with increasing pressure: when ice at a temperature slightly below 0° C is subjected to pressure, it is brought into a state in which its T is above the melting point. It is, therefore, converted into water but freezes again as soon as the pressure is released. This phenomenon is called *regelation*, and it accounts for the plasticity of ice which permits, among other things, the flow of glaciers. The ease of skating on ice is also usually attributed to regelation: enough water is melted under the pressure of the sharp edges of the skates to keep the ice lubricated.

In the case of vaporization, the pressures are sometimes such that the formula (7.06) can be simplified. For instance, when the vapor pressure is so low that the equation of state of perfect gases applies, with sufficient approximation, to the gas phase: $v_2 = RT/p$. Under these conditions the molal volume of the liquid phase can be neglected compared with v_2. In fact, at 100° C and 1 atm, the ratio v_2/v_1 for water (e.g.) is 1676, and at lower temperatures, when the law of perfect gases can be used, it is larger. In this way, we obtain an approximate form of eq. (7.06):

$$\frac{d \log p}{dT} = \frac{\lambda}{RT^2} \qquad (7.07)$$

which is useful for many purposes.

Exercise 68. Calculate the latent heat of water, at 100° C and 760 mm Hg, from eq. (7.07). Use the value $dp/dt = 27.12$ mm/deg. Compare the results with the exact value as given in text.

Exercise 69. Calculate the latent heat of mercury at its normal boiling point ($t_B = 357°.3$, $p = 760$ mm). Use the value $dp/dt = 13.81$ mm/deg and eq. (7.07).

Exercise 70. Calculate the coefficient dT/dp for the fusion of ice at 0° C and 1 atm, using the following data (per 1 g of the substance): $l_g = 80$ cal g^{-1}, $v_1 = 1.000$ cm^3 g^{-1}, $v_2 = 1.091$ cm^3 g^{-1}. Apply suitable conversion factor to p.

Exercise 71. Naphthalene melts at 80°.1 C, its latent heat of fusion is 4563 calories per mol, and the increase in volume on fusion is 18.7 cm^3 mol^{-1}. Find the change of the melting point with pressure.

Exercise 72. The transition point of mercuric iodide, red → yellow, is at 127°.4 C. The latent heat absorbed in the change is 150 cal mol^{-1}, and the approximate change of volume −5.4 cm^3 mol^{-1}. Find dT/dp for the transition point.

45. Temperature dependence of the latent heat. Another relation between measurable quantities can be obtained by differentiating

eq. (3.23) of section 17, $dL = d(\mathbf{X}^{(1)} - \mathbf{X}^{(2)}) = d(\nu^{(1)}\chi^{(1)} - \nu^{(2)}\chi^{(2)})$ and substituting the expressions (4.47) for $d\chi$. We find

$$dL = \Delta C_p\, dT + \left[\Delta V - T\left(\frac{\partial \Delta V}{\partial T}\right)_p\right] dp,$$

where ΔC_p and ΔV denote the changes of capacity and volume in the transformation:

$$\Delta C_p = \nu^{(1)} c_p^{(1)} - \nu^{(2)} c_p^{(2)}, \quad \Delta V = \nu^{(1)} v^{(1)} - \nu^{(2)} v^{(2)}. \tag{7.08}$$

Dividing the equation by dT and replacing dp/dT by (7.06)

$$\frac{dL}{dT} = \Delta C_p + \frac{L}{T} - L\left(\frac{\partial \log \Delta V}{\partial T}\right)_p. \tag{7.09}$$

In the special case of vaporization at comparatively low pressure we can again make the simplification of neglecting $v^{(2)}$ (of the condensed phase) and applying to $v^{(1)}$ the equation of perfect gases: $(\partial \log \Delta V/\partial T)_p = 1/T$. The relation is then reduced to

$$\frac{dL}{dT} = \Delta C_p. \tag{7.10}$$

Exercise 73. Calculate dl/dT (per 1 mol = 18.0) for boiling water (at 100° C, 1 atm) with the help of the following data: in liquid water $c_{p_2} = 18.0$ cal, in vapor $c_{p_1} = 8.8$ cal (both per 18 g, at 100° C), $\Delta V_l = 30\,186$ cm³ mol^{-1}, $(\partial \Delta V_l/\partial T)_p = 84.66$, $l = 9720$ cal mol^{-1}. Compare the results given by the two formulas (7.09) and (7.10). (The measured value is -11.0).

46. Approximate and empirical expressions for the transformation pressure. The temperature dependence of the latent heat is, usually, slight. Especially, in the case of vaporization ΔC_p in the formula (7.10) is small compared with L. As a first rough approximation one can, therefore, put $L = L_0 = \text{const}$, or $l = l_0 = \text{const}$. Substituted into eq. (7.06) this gives for the pressure of vaporization

$$\log p = -\frac{l_0}{RT} + B \tag{7.11}$$

(B being a constant), a formula due to Van der Waals, who wrote it (for liquids) in the form

$$\log \frac{p_c}{p} = a\left(\frac{T_c}{T} - 1\right), \tag{7.12}$$

which for a number of substances gives an approximate representation of the measurements even at high pressures. We shall return to this equation in the next section.

It has been found since that the formula (7.11) is insufficient for an accurate representation of the vapor pressure of liquids but can be used for that of crystalline solids. Even in this case better approximations are obtained by substituting into (7.07) the expansion $l = l_0 + l_1T + l_2T^2 + \ldots$. For instance the vapor pressure of ice between $-90°$ and $0°$ C is represented by [1]

$$\log_{10} p_{mm} = -\frac{2445.5645}{T} + 8.2312 \log_{10} T - 0.0167006T + 1.205 \times 10^{-5}T^2 - 6.757169. \quad (7.13)$$

As to the vapor pressure of liquids, the very accurate modern measurements cannot be adequately represented even by formulas with many terms.

For the dependence of the *pressure of fusion* upon temperature a theoretical formula has not yet been advanced, and one has to rely on empirical expressions. According to Simon and Glatzel [2] the following formula gives satisfactory results:

$$\log_{10}(p + a) = c \log_{10} T_F + b. \quad (7.14)$$

They give the following values for the constants (Table 10), provided the pressure is measured in $kg/cm^2 = 0.9678$ atm.

TABLE 10

Substance	a	b	c
Helium*	17	1.5544	1.236
Sodium	12 400	5.032	3.55
Potassium	3 900	−8.227	4.68
Rubidium	4 100	5.59	3.65
Cesium	2 450	8.38	4.75
Mercury	45 000	1.11	2.40
CO_2	4 000	2.564	2.64
CCl_4	3 100	1.498	2.08
$SiCl_4$	5 100	−0.459	1.39
Benzene	3 900	2.496	2.49
Chlorobenzene	5 100	1.970	2.41
Bromobenzene	5 000	2.070	2.42
Nitrobenzene	6 000	1.037	1.97
Chloroform	6 000	0.466	1.83
Bromoform	5 800	0.984	1.94
Aniline	5 500	1.913	2.33

* The data for helium are taken from Simon, Ruhemann, and Edwards, Zs. phys. Chemie (B) 2, p. 430, 1929.

[1] E. W. Washburn, Monthly Weather Review 52, p. 488, 1924.

[2] F. Simon and A. Glatzel, Zs. anorgan. Chemie 178, p. 309, 1929.

Exercise 74. Calculate the latent heat l of sublimation of ice and the difference Δc_p of specific heats (between 1 mol of vapor and 1 mol of solid), at 0° C. Use eqs. (7.13), (7.07), and (7.10).

Exercise 75. At its normal point of fusion (−38°.9 C) mercury has the molal volumes $v_1 = 14.65$ (liquid) and $v_2 = 13.90$ (solid). Its latent heat is $l = 556$ cal mol^{-1}. Check whether the formula of Simon and Glatzel is in satisfactory agreement with (7.05).

47. Vaporization as a corresponding state. It was stated in section 27 that certain groups of substances approximately satisfy what was called there the *extended law of corresponding states*. It is meant by this that within such a group the quantities $(u - u_0)/T$, s and pv/T are universal functions of the reduced variables. Since the molal thermodynamic potential is defined as $\varphi = u - Ts + pv$, the quantity $(\varphi - u_0)/T$ must also be expressible as

$$\frac{\varphi - u_0}{T} = f(\pi, \tau), \tag{7.15}$$

where f is universal for the whole group. The reduced volume does not appear as a variable, because it can be eliminated by means of the equation of state.

It must be assumed that the equations of state apply equally to the gaseous and to the liquid phase, bringing out their continuity, in the sense of section 5. Therefore, the formula (7.15) is also valid for both phases. It follows then from (7.03) that, for substances which do not associate, the boiling condition is determined by the universal equation

$$f^{(1)}(\pi, \tau) = f^{(2)}(\pi, \tau). \tag{7.16}$$

Substances boiling at corresponding pressures have corresponding boiling points. In practice the boiling point changes but little with pressure. For instance, we see from the data for water on p. 119 that, while the pressure is increased from 1 atm to 2 atm, the temperature changes only by 20° or about 5%. For all the liquids satisfying eq. (7.16) there obtain, in this respect, similar conditions. In fact, it follows from it that the ratio

$$\frac{dT}{T} : \frac{dp}{p} = \frac{d\pi}{\pi} : \frac{d\tau}{\tau}$$

must be universal. This explains the fact noticed already by Guldberg[1] that many liquids have roughly the same reduced boiling temperatures

[1] C. M. Guldberg, Zs. phys. Chem. 5, p. 374, 1890.

even when they all boil at the pressure of 1 atm, as appears from Table 11.

TABLE 11

Substance	T_c	T_B	T_B/T_c
Ether	467	308	0.66
Ethyl acetate	523	346	0.66
Ethylene chloride	561	357	0.64
Alcohol	516	351	0.68
Benzene	562	353	0.63
Hydrochloric acid	325	238	0.73
Oxygen	155	90	0.58
Carbon disulfide	545	319	0.59
Ammonia	404	234	0.58
Ethylene	282	163	0.58
Methane	191	109	0.57
Sulfuretted hydrogen.	373	211	0.57
Nitrous oxide	309	183	0.59
Stannic chloride	592	387	0.65
Water	637	373	0.59
Acetic acid	595	391	0.66

According to (4.11), the quantity l/T_B represents the entropy increase on vaporization

$$\frac{l}{T_B} = s^{(1)} - s^{(2)}.$$

It is an entropy change between corresponding states and must be, therefore, a universal function of π, τ according to (4.41). There follows that l/T_B must be the same for substances which boil at corresponding pressures. However, both l and T_B change but little with the pressure so that, in practice, l/T_B measured at any pressure of the order of 1 atm, is roughly the same for many different substances (Table 12). This fact is known as the rule of Deprez and Trouton.

The table contains of course a group of selected substances. If picked at random, the variations of Trouton's ratio are larger. Yet a very marked deviation of the ratio l_B/T_B from the average value is, usually, traceable to association. For instance, in acetic acid $l_B/T_B = 14.8$, and this is due to the abnormally high molecular weight of the vapor (97 instead of 60 corresponding to $C_2H_4O_2$). Ethyl alcohol shows the opposite deviation, $l_B/T_B = 26.8$, due to a normal vapor but partly associated liquid. Equation (7.12) of Van der Waals is

TABLE 12

Substance	t_B° C	l_B (cal)	l_B/T_B
Benzene	394.8	13 650	20.8
Chloroform	247	10 900	21.0
Aniline	434	14 920	21.1
Bromobenzene	155.9	9 350	21.0
Acetal	102.9	7 810	20.7
Toluene	109.6	7 980	20.8
Sulfuretted hydrogen.	−61.4	4 490	21.2
Stannic chloride	112	7 900	20.5
Ethyl bromide	38.4	6 500	20.9
Ethane	71.2	7 120	20.6

only a special approximate form of the general equilibrium condition between a liquid and its vapor. To the extent to which the reduced equation (7.16) is valid, the special form can claim to have universal validity. In fact Van der Waals expected the coefficient a to be a universal constant (for all substances). However, two things must be borne in mind. In the first place, (7.12) is only a rough approximation and a is, in reality, not a constant but a function of temperature. In the second place, we should expect, at best, a uniformity of a, not generally, but only within the groups of substances satisfying the law of corresponding states. The analysis of the experimental material shows that the substances of such a group can be arranged in a series so that a is nearly the same for any two successive members of the series, but it changes, systematically and considerably, from one end of the series to the other.

The emphasis on Trouton's rule, as on the law of correspondence in general, has changed in the course of time. Soon after the discovery of these regularities their importance and accuracy were being overrated. Then the pendulum swung to the other extreme: the insistence was altogether on the lack of rigor of these laws and on the numerous exceptions from them. However, as long as it is borne in mind that these rules are only rough approximations of limited range, they are interesting and useful. For instance, deviations from Trouton's rule are helpful in indicating association, as was pointed out above.

48. The fundamental or triple point. There remains to say a few words about the third case mentioned in the beginning of this chapter. It follows from the general considerations of section 41 that the coexistence of three phases is possible only at a definite temperature and pressure which jointly define the *fundamental or triple point.* In

fact, if we label the three phases by the numbers (1), (2), (3), we can apply the results of the preceding sections to each pair of them: For the equilibrium between (1) and (2), on one hand, and between (1) and (3), on the other, we have the two equations of equilibrium of the type (7.02)

$$\nu^{(1)}\varphi^{(1)} = \nu^{(2)}\varphi^{(2)}, \qquad \nu^{(1)}\varphi^{(1)} = \nu^{(3)}\varphi^{(3)},$$

the third $\nu^{(2)}\varphi^{(2)} = \nu^{(3)}\varphi^{(3)}$ being a consequence of these two. Correspondingly, of the three Clapeyron-Clausius equations following from these three relations

$$\frac{dp_{12}}{dT_{12}} = \frac{L_{12}}{T_{12}}, \qquad \frac{dp_{13}}{dT_{13}} = \frac{L_{13}}{T_{13}}, \qquad \frac{dp_{23}}{dT_{23}} = \frac{L_{23}}{T_{23}}, \tag{7.17}$$

only two are independent, while the third is a consequence of them.

If we plot the pressure of the system against its temperature, the three equations (7.17) will represent three curves OA, OB, OC (Fig. 13). All points of the p, T-plane which do not lie on one of these curves correspond to a single-phase state of the system. The points on the curves OA, OB, OC represent the equilibrium of two phases, and the point of intersection O is the triple point. As an illustration of the (p, T)-diagram, we have taken the most common case when the three phases in question are vapor, liquid, and crystalline solid. The branch OA representing equilibrium of the liquid and gaseous phases ends abruptly at the critical point A, since there is no difference between these two states at higher temperatures.[1] Suppose that we have vapor and liquid in equilibrium and slowly change the boiling pressure and temperature so as to move the representative point of the system along the curve of boiling AO towards the triple point O. When the point O is reached, a contingency may arise similar to that discussed in section 43 with respect to the expansion of a liquid. Under special conditions of great purity of the material and of very careful manipulation, the solid phase may fail to appear and the vapor-liquid combination may get into a state of supercooled and unstable equilibrium represented by the dotted continuation of the curve AO. The slightest shock may cause then a sudden crystallization.

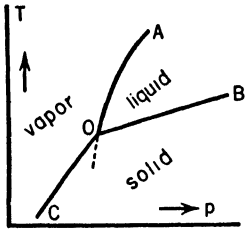


FIG. 13.—Triple point and equilibrium of solid, liquid, and vapor.

[1] With respect to attempts of extending the branch OA beyond the critical point, compare: Trautz and Ader, Phys. Zs. 35, p. 446, 711, 1934; Eucken, *ibidem*, p. 708.

The triple point of most substances lies at pressures which are low compared with the normal atmospheric. When they are heated at constant atmospheric pressure, their state changes along a vertical straight line drawn to the right of the triple point. The crystal is first converted at a certain temperature (of fusion) into a liquid; at a higher temperature the liquid is vaporized. It is different, when the pressure of the triple point is high or when the substance is heated at a low pressure: then, the vertical lies to the left of the point *O* and the crystal is directly sublimated into vapor without passing through the liquid state.

The best-known example of the coexistence of three phases is that of steam, water, and ice at $p = 4.579$ mm Hg and $t = 0.0075°$ C. However, researches by Tammann [1] and Bridgman [2] have disclosed that, in addition to the ordinary ice (I), there exist at least four other crystalline states of water (ices II, III, V, VI) which are all denser than water and observable only at very high pressures. (The existence of a modification, formerly labeled ice IV, is considered as doubtful). The table of the several triple points, as far as they have been observed, is as follows

TABLE 13

PHASES	*t*	*p*	FIG. 14
Ice I, liquid, vapor....	0°.0075 C	4.579 mm Hg	*O*
Ice I, liquid, Ice III...	−22°	2115 kg/cm	*C*
Ice III, liquid, Ice V...	−17°	3530 "	*D*
Ice V, liquid, Ice VI...	+ 0°.16	6380 "	*E*
Ice I, Ice II, Ice III...	−37°.7	2170 "	*F*
Ice II, Ice III, Ice V...	−24°.3	3510 "	*G*

A graphical representation of the measurements carried out with water in its different phases is given in Fig. 14.

An interesting situation was disclosed by Tammann's investigation of the equilibrium curves of phosphonium chloride, PH_4Cl (Fig. 15). The curve of fusion could be traced to temperatures considerably higher than the critical point of the liquid-vapor equilibrium. It seems paradoxical that the crystalline phase can be observed at temperatures at which the liquid does not exist or, rather, cannot be distinguished from the vapor. A similar behavior is shown by *carbon dioxide* (CO_2) and by *helium* (He). The curve of fusion of CO_2 was observed by

[1] G. Tammann, Ann. d. Phys. **2**, p. 422. 1900.
[2] Bridgman, Proc. Amer. Acad. **47**, p. 441, 1912.

Bridgman up to $t = 93°.5$ C and $p = 12\,000$ kg/cm², while the critical data are $t_c = 31°.4$ C, $p_c = 72.9$ atm. The case of helium is even more striking: Simon, Ruhemann, and Edwards [1] observed its curve

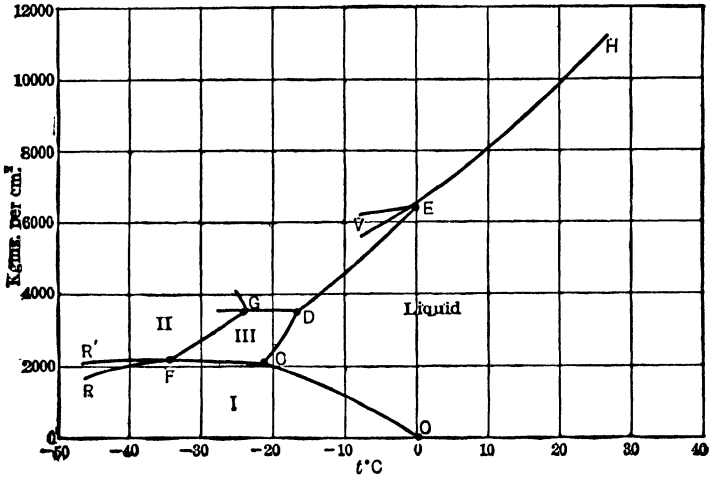


FIG. 14.—Phase equilibrium in water.

of fusion up to $T = 42°$ abs and 5600 atm, i.e. solid helium can be prepared at a temperature fully eight times as high as the critical point of liquid helium ($t_c = 5°.2$ abs, $p_c = 2.25$ atm). The question is still open whether the curve of fusion extends indefinitely to still higher temperatures or is limited, either by a solid-liquid critical point or in some other way. Its experimental investigation is very difficult as it requires the application of extremely high pressures.

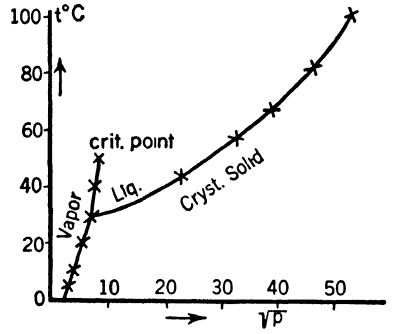


FIG. 15.—Phase equilibrium in phosphonium chloride.

49. Phase equilibrium of higher order.[2] The usual case of two phases in contact treated in section 1 may be called *equilibrium of the first order.* Influenced by observations on liquid helium, Ehrenfest[3] discussed another possible case which he called *equilibrium of the second*

[1] Simon, Ruhemann, and Edwards, Zs. phys. Chem. (B) **2**, p. 340, 1929; **6**, p. 62, 1930.

[2] This section may be skipped without loss of continuity.

[3] P. Ehrenfest, Communications Leiden, Suppl. 756, 1933.

order. It may happen that the transformation takes place without development of latent heat and without change of volume. Supposing the molecule to be the same in the two phases,

$$Q_p = \chi_2 - \chi_1 = 0, \quad \Delta V = v_2 - v_1 = 0. \tag{7.18}$$

This means that the two phases have the same molal heat function and the same molal volume. Because of the fundamental relation of equilibrium,

$$\Delta\Phi = \varphi_2 - \varphi_1 = 0, \tag{7.19}$$

they have then also the same entropy ($\Delta S = s_2 - s_1 = 0$), since $\Delta S = Q_p/T$, according to (4.11). Yet the phases are different because of their other properties (for instance, the molal heats) changing dis-

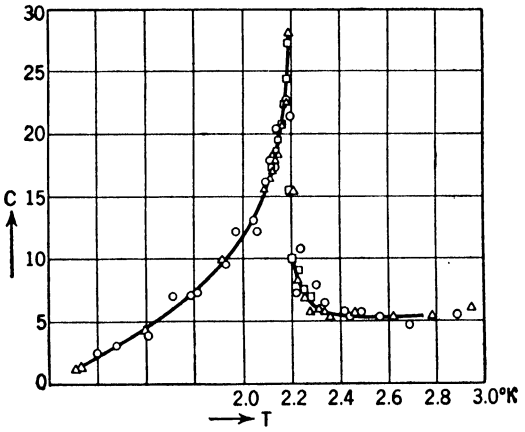


FIG. 16.—Specific heat of helium.

continuously in the transformation. This seems to happen with liquid helium at the temperature of 2°.2 K: the discontinuity in its molal heat is given in Fig. 16 as measured in Leiden [1] while changes of entropy and volume were not observed. Similar conditions are known to obtain in many other transformations: solid methane at 20°.4 K, solid oxygen at 44° K, HBr at 87° K, ammonium chloride and bromide, etc.[2] The accuracy of these observations was in no case sufficient for a conclusive proof that the conditions (7.18) were strictly satisfied, but it is interesting to follow up the theoretical implications of such a contingency.

[1] W. H. Keesom and A. P. Keesom, Comm. Leiden 222 d; W. H. Keesom and K. Clusius, 219 e; K. Clusius and A. Perlick, Zs. phys. Chemie **24**, p. 313, 1934.

[2] Compare reviews by M. Von Laue and A. Eucken, Phys. Zs. **35**, pp. 945, 954, 1934.

Taking account of (6.51) and (6.52), the conditions (7.18) can be also written in the form

$$\Delta\Phi_T = \left(\frac{\partial\Delta\Phi}{\partial T}\right)_p = 0, \quad \Delta\Phi_p = \left(\frac{\partial\Delta\Phi}{\partial p}\right)_T = 0, \tag{7.20}$$

which converts the Clausius-Clapeyron equation (7.04) into an identity. In order to obtain a relation between the differentials of temperature and pressure, Ehrenfest proceeds to differentiate these two equations.

$$\Delta\Phi_{TT}\,dT + \Delta\Phi_{pT}\,dp = 0, \quad \Delta\Phi_{Tp}\,dT + \Delta\Phi_{pp}\,dp = 0, \tag{7.21}$$

where the partial differentiation with respect to T or p is indicated by writing these variables as subscripts. He further postulates that these two relations be compatible. It should be remembered that, according to (5.37), (4.32)

$$\left.\begin{aligned} \Delta\Phi_{TT} &= -\frac{c_{p2} - c_{p1}}{T} = -\frac{\Delta C_p}{T}, \\ \Delta\Phi_{Tp} &= \left(\frac{\partial\Delta V}{\partial T}\right)_p, \quad \Delta\Phi_{pp} = \left(\frac{\partial\Delta V}{\partial p}\right)_T. \end{aligned}\right\} \tag{7.22}$$

The elimination of dp/dt from eqs. (7.21) gives Ehrenfest's relation for equilibrium of the second order

$$D \equiv \left(\frac{\partial\Delta V}{\partial T}\right)_p^2 + \frac{\Delta C_p}{T}\left(\frac{\partial\Delta V}{\partial p}\right)_T = 0. \tag{7.23}$$

Serious objections against these conclusions were raised by Keesom[1] and by Von Laue.[2] They can be brought out most clearly by a geometrical interpretation of eqs. (7.19) and (7.20). If we regard T, p, φ as cartesian coordinates of a three-dimensional space, the equations $\varphi = \varphi_1(p, T)$ and $\varphi = \varphi_2(p, T)$ represent two surfaces in this space. In the ordinary first order equilibrium the condition (7.19) is satisfied along the line of intersection of these two surfaces, as represented graphically in Fig 17*a*, which gives the trace upon the (φ, T)-plane. The relation between the transformation values of p and T, given by the Clausius-Clapeyron equation (and represented graphically in the figures of section 48), is then the projection of this line of intersection onto the plane p, T. The additional conditions (7.20) for the second order transformation mean that the two surfaces are in contact

[1] W. H. and A. P. Keesom, Physica 1, p. 161, 1933.
[2] Footnote on p. 129.

(Fig. 17*b*). Von Laue points out that in this case no transformation at all is possible. In fact, the theory of equilibrium requires $\Delta\Phi \leqq 0$ (section 36) and, therefore, the states of the system represented by the upper branches of the curves are unstable. It will be found in the more stable state (1) both above and below the temperature of the contact. Von Laue suggests, therefore, that the phases in question may have an *equilibrium of the third order*, i.e. the surfaces $\varphi = \varphi_1$

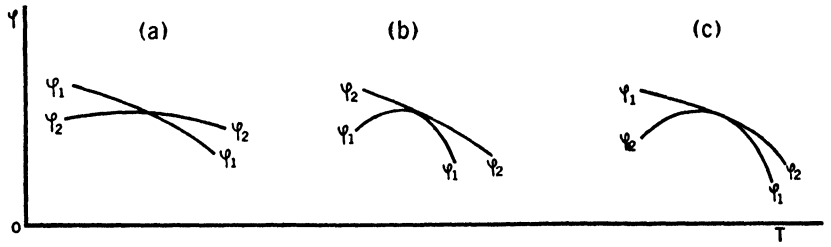


FIG. 17.—Equilibrium of first, second, and third order.

and $\varphi = \varphi_2$ have contact with penetration (Fig. 17*c*). The mathematical conditions for this are

$$\Delta\Phi_{TT} = \Delta\Phi_{pT} = \Delta\Phi_{pp} = 0, \tag{7.24}$$

in addition to (7.18) and (7.19). They represent so much of a restriction upon the parameters of the two phases that Von Laue's suggestion was not favorably received by the other workers in this field.

We think, however, that the topic should not be dismissed without a fuller investigation of the possibilities of the second order equilibrium. Ehrenfest and Von Laue make an assumption which, in our opinion, goes too far. They differentiate eqs. (7.20), implying that the contact exists along the whole line of intersection of the surfaces φ_1, φ_2 or, at least, along a finite part of it. There is nothing in the experimental observations to justify this assumption. Theoretically it is also a rather remote case, because it cannot occur, unless the properties of the two phases happen to satisfy Ehrenfest's eq. (7.23) or Von Laue's even more restrictive conditions (7.24). It is a far more common occurrence that the two surfaces are in contact in a singular point, i.e. eqs. (7.20) are satisfied just in one point whose coordinates we shall denote by p_0, T_0. What is then the value of $\Delta\Phi$ in a neighboring point, say, $p_0 + dp$, $T_0 + dT$? Expanding with respect to dp, dT to terms of the second order

$$\Delta\Phi(T_0 + dT, p_0 + dp) = \Delta\Phi(p_0, T_0) + \Delta\Phi_T dT + \Delta\Phi_p dp + \tfrac{1}{2}[\Delta\Phi_{TT} dT^2 + 2\Delta\Phi_{pT} dT dp + \Delta\Phi_{pp} dp^2] + \ldots \tag{7.25}$$

Because of the conditions (7.19) and (7.20), equilibrium in the vicinity of p, T is then determined by the condition

$$\Delta\Phi_{TT}dT^2 + 2\Delta\Phi_{pT}dTdp + \Delta\Phi_{pp}dp^2 = 0.$$

The expression D of formula (7.23) is the discriminant of this equation. When $D < 0$, the equation has no real solutions so that a change of phase is impossible. The limiting case, $D = 0$, is that of Ehrenfest's and must be excluded because of the reasons advanced by Von Laue. But when $D > 0$, the equation has two real solutions. Because of (7.22),

$$\frac{dT}{dp} = \left[\left(\frac{\partial \Delta V}{\partial T}\right)_p \pm \sqrt{D}\right]_0 \cdot \frac{T_0}{\Delta C_{p0}}. \tag{7.26}$$

Consequently, transformations are possible, if not in the point p_0, T_0 itself, in its immediate vicinity as is illustrated in the (p, T)-diagram of Fig. 18. There are *two* lines in which the phases (1) and (2)

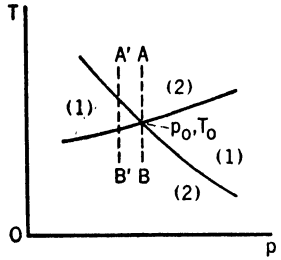


FIG. 18.—Vicinity of a point where equilibrium is of second order.

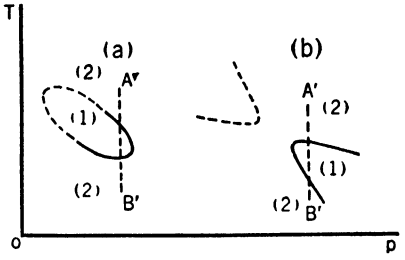


FIG. 19.—Special cases of first order equilibrium.

can coexist, and they intersect in the singular point p_0, T_0. When the substance is cooled at a pressure exactly coinciding with that of the intersection (dotted line AB), no transformation takes place. If it is cooled at a slightly different pressure (line $A'B'$) it is transformed first from the phase (2) into the phase (1) and, at a lower temperature, back again into (2). Some of the experimentally measured anomalies present features compatible with this picture: as the temperature is changed, the specific heat jumps discontinuously and, at a slightly lower temperature, jumps back to the initial value (Fig. 16). However, it would require a more detailed experimental investigation to establish the existence of this type of transformation beyond doubt in view of the following considerations.

More important than the direct application of the preceding results is the light they throw, indirectly, on transformations of the first order with small but finite latent heats and volume changes. Let p_0, T_0 be a point in which $\Delta\Phi_T$ and $\Delta\Phi_p$ are very small but finite. In the infinitesimal vicinity of the point p_0, T_0 there will hold, of course, the Clausius-Clapeyron equation. But if we consider, instead of the differentials dp, dT, small finite increments Δp, ΔT, the second order terms in (7.25) may no longer be neglected and the equation becomes

$$\Delta\Phi_T \cdot \Delta T + \Delta\Phi_p \cdot \Delta p + \tfrac{1}{2}[\Delta\Phi_{TT}(\Delta T)^2 + 2\Delta\Phi_{pT} \cdot \Delta T \cdot \Delta p + \Delta\Phi_{pp}(\Delta p)^2] = 0.$$

This represents an ellipse or a hyperbola with its vertex near the point p_0, T_0, according to whether the discriminant (D) is negative or positive (Fig. 19). The dotted parts of the curves have no reality because the approximation breaks down when Δp, ΔT become appreciable since then terms of third and higher order must be taken into account. The gist of the matter is that these p, T-lines are strongly curved. In cooling the system along the lines $A'B'$ we meet with conditions quite similar to those of Fig. 18. In fact, the transition from the first to the second order of equilibrium is a continuous one and the two cases cannot be distinguished without a complete experimental investigation of the whole region around the point p_0, T_0. Some of the cases enumerated in the beginning of this section are, probably, examples of this kind of equilibrium of the first order.[1] Another interesting illustration will be presented in section 137.

[1] The same conclusions were drawn by A. Eucken (footnote on p. 129) from the study of the experimental material.

CHAPTER VIII

MIXTURES OF PERFECT GASES

50. The thermodynamic potential of a gas mixture. An example in which the general theory of equilibrium can be completely carried through in detail is the mixture of perfect gases. This is largely due to the fact emphasized in section 4 that the pressure of such a mixture is equal to the sum of the partial pressures of the individual gases

$$p = p_1 + p_2 + \ldots + p_\sigma, \tag{8.01}$$

where $p_1, \ldots p_\sigma$ are computed for each gas as if it were filling the available volume alone and the other gases were not present. Suppose that we have in a vessel of the volume V several gaseous constituents in the respective amounts of $N_1, \ldots N_\sigma$ mols. Let their partial pressures be expressed according to eq. (1.12)

$$p_h = N_h RT/V = RT/v_h, \tag{8.02}$$

v_h being the molal volume of the gas h. In order to apply to this system the theory of Chapter VI, we must find the thermodynamic potential $\Phi = U - TS + pV$, where T and p are the temperature and the total pressure of the mixture. The physical inference from the formula (8.01) is that there is no interaction between the gases, so that the thermodynamic potential of each of them must be computed, as if it were alone in the vessel, and all these potentials must be added to obtain

$$\Phi = \sum_{h=1}^{\sigma} \Phi_h. \tag{8.03}$$

A simple and convincing way of seeing this is opened by an ideal experiment devised by Gibbs. We give the vessel containing the system the following construction (Fig. 20). The cylinder C fits tightly into the cylinder C' and can slide within it without friction. The outer ends of both cylinders are closed by tops AB and $A'B'$ impenetrable for the gases and adiabatic like the side surfaces. They have also bottoms

MN and $M'N'$ which are kept by a suitable arrangement at constant distances l from the tops while the cylinders are sliding. However, these bottoms are semipermeable membranes: The membrane $M'N'$ lets through freely the component h but is impenetrable for all the others. On the other hand, $M'N'$ is impenetrable only for h, offering no resistance to the rest of the components. The volume of each cylinder ($ABMN$ and $A'B'N'M'$) is the same and equal to V. We start our considerations from the state when the cylinder $ABMN$ is pushed completely in, so that MN touches $A'B'$ and the gas mixture fills the joint volume V. We begin now to pull out this cylinder in a reversible (infinitely slow) way. Three part volumes of the system must now be distinguished: (1) the section above $M'N'$ is filled with the pure h component because this membrane is not permeable to the other gases. (2) The middle part between $M'N'$ and MN contains all components. (3) The section below MN is free of the component h because this gas is pushed up by the membrane MN which is impermeable to it. The gas h is, therefore, present only in sections (1) and (2) (or in the upper cylinder). We have emphasized that its partial pressure p_h is independent of the presence of other gases: It will be, therefore, the same in section (1) where it is alone and in (2) where it is one of the constituents of the mixture. Only the component h exercises pressure upon the top AB and the bottom MN of the upper cylinder. The rest of the gases do not produce any pressure effects on the two surfaces: on AB, because no other component is present in the part volume (1) adjacent to it; on MN, because this membrane is completely permeable to the other gases. We see, therefore, that the forces of pressure on top and bottom are oppositely equal so that the resultant force on the whole cylinder vanishes. The process of reversibly pulling out the cylinder does not involve any work ($W = 0$), provided there are no outer forces upon the system (e.g. air-free outer space). Since the outer envelope of the system is adiabatic ($Q = 0$), the reversible process goes on without change of entropy (section 23). Moreover, it proceeds at constant internal energy and temperature. In fact, in the general eq. (3.05) of the first law, $Q = U_2 - U_1 + W$, the terms Q and W vanish leaving $U_2 = U_1$, and in the case of perfect gases, this is equivalent to $T_2 = T_1$, according to eq. (3.18) or (3.19).

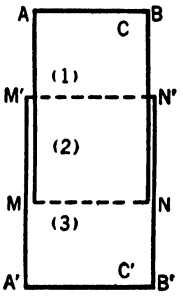


FIG. 20.—Device for unmixing gases.

Continuing the process until the membranes MN and $M'N'$ touch,

so that the middle section (2) disappears, one can entirely separate the component h from the mixture. In a similar way, the other components can be separated, one by one, so that, in the end, the system is completely unmixed and each component occupies, separately, a volume equal to V. The whole process is carried out without change of U and S. It follows from this that the internal energy and the entropy of a gas mixture are additive $U = \Sigma U_h$, $S = \Sigma S_h$, provided the entropies S_h of the individual perfect gases are computed as if each of them occupied the volume V alone. Therefore, the first two terms of the thermodynamic potential $\Phi = U - TS + pV$ are additive, while the additivity of the third follows from the relation (8.01), thus completing the proof of eq. (8.03).

If we use eq. (4.20) for the molal entropy of a perfect gas, the entropy S_h of the component h has the expression

$$S_h = N_h \left(\int \frac{c_{ph}}{T} dT - R \log p_h + s_{0h} \right),$$

and the total entropy of the mixture becomes

$$S = \sum_{h=1}^{\sigma} N_h \left(\int \frac{c_{ph} dT}{T} - R \log p_h + s_{0h} \right). \tag{8.04}$$

Sometimes it is preferable to express S in terms of the total pressure p rather than the partial pressures p_h. In order to carry out the transformation, it is convenient to use the *mol fractions* defined in section 39

$$x_h = N_h/N, \tag{8.05}$$

where $N = N_1 + \ldots + N_\sigma$ represents the total number of mols (of the different constituents) in the mixture. In the case of perfect gases, equations $p_h V = N_h RT$ and $pV = (N_1 + \ldots + N_\sigma)RT$ hold, so that $p_h/p = x_h$ or

$$p_h = x_h p. \tag{8.06}$$

Substituting this into (8.04)

$$S = \sum_{h=1}^{\sigma} N_h \left(\int \frac{c_{ph}}{T} dT - R \log p + s_{0h} - R \log x_h \right). \tag{8.07}$$

The first three terms of this expression are linear in the mol numbers N_h, while the last shows a more complicated dependence upon them.

In a similar way, there follows from eq. (5.41) for the molal thermodynamic potential

$$\bar{\varphi}_h = RT \log p_h + \omega_h(T), \tag{8.08}$$

and

$$\Phi = \sum_{h=1}^{\sigma} N_h [RT \log p_h + \omega_h(T)], \tag{8.09}$$

where

$$\omega_h(T) = \int_0^T c_{ph} dT - T \int \frac{c_{ph}}{T} dT + u_{0h} - T s_{0h}, \tag{8.10}$$

or an alternative form after the substitution of (8.06).

We denote the molal potential (8.08) by the symbol $\bar{\varphi}_h$ instead of φ_h for reasons which will become clear in the next chapter. This is entirely permissible because, in this case, the partial thermodynamic potentials of the mixture are identical with the molal of the pure components, as a consequence of the additivity expressed in eqs. (8.03) and (8.09). In fact, as determined by eq. (8.08), $\bar{\varphi}_h$ satisfies the definition (5.38) of the partial molal thermodynamic potential.

Exercise 76. Derive the expressions of the heat function **X** and the work function Ψ for mixtures of gases.

Exercise 77. Check the statement that the derivative $(\partial\Phi/\partial N_h)_{p,T}$ is identical with (8.08). In the differentiation the *total* pressure is to be kept constant.

51. The mass law. If the gases of the mixture can react chemically with one another, according to the formula (6.46), $\Sigma \nu_h G_h = 0$, the condition of equilibrium is given by eq. (6.49) or $\Sigma \nu_h \bar{\varphi}_h = 0$. Substituting for $\bar{\varphi}_h$ the expressions (8.08), we obtain

$$RT \sum_{h=1}^{\sigma} \nu_h \log p_h = -\sum_{h=1}^{\sigma} \nu_h \omega_h(T). \tag{8.11}$$

We recall that the coefficients ν_h of the components consumed in the reaction have the negative sign, of those produced in it the positive. Therefore, the physical meaning of the expressions on the right side, when (8.10) is substituted, is as follows:

$$\sum_{h=1}^{\sigma} \nu_h c_{ph} = \Delta C_p \tag{8.12}$$

represents the difference of the heat capacities (at constant pressure) of the gases produced and consumed in the reaction, or the total change of the heat capacity due to it. According to eq. (3.27),

$\int_0^T c_{ph}dT + u_{0h} = \chi_h$ is the heat function of the component h. For this reason

$$\sum_{h=1}^{\sigma} \nu_h \left(\int_0^T c_{ph}dT + u_{0h} \right) = Q_p \tag{8.13}$$

represents the total change of the heat function of the mixture $\Delta\mathbf{X}$ which is equal to the heat of reaction Q_p, as we know from eq. (3.23). The last term depending on the entropy constants of the constituents of the mixture, we shall denote by

$$\sum_{h=1}^{\sigma} \nu_h s_{0h} = R \log I. \tag{8.14}$$

We further introduce for the whole right side of eq. (8.11) the notation $RT \log K_p$, so that

$$\log K_p = \int \frac{\Delta C_p}{RT} dT - \frac{Q_p}{RT} + \log I. \tag{8.15}$$

Within the range of temperatures, where the molal heats c_{ph} can be considered as constant, this becomes

$$\log K_p = \frac{\Delta C_p}{R} \log T - \frac{Q_p}{RT} + \log I. \tag{8.16}$$

Strictly speaking, I is well defined only in this case, unless the lower limit of the integral in (8.15) is specified.

The condition of equilibrium (8.10) takes, therefore, the form

$$p_1^{\nu_1} p_2^{\nu_2} \ldots p_\sigma^{\nu_\sigma} = K_p. \tag{8.17}$$

An equivalent form is obtained by replacing the partial pressures by the molal fractions by means of eq. (8.06), $p_h = x_h p$,

$$x_1^{\nu_1} x_2^{\nu_2} \ldots x_\sigma^{\nu_\sigma} = K, \tag{8.18}$$

where $K = K_p/p^\nu$ or

$$\log K = \log I - \frac{Q_p}{RT} + \int \frac{\Delta C_p}{RT} dT - \nu \log p, \tag{8.19}$$

with the abbreviation

$$\nu = \nu_1 + \nu_2 + \ldots + \nu_\sigma. \tag{8.20}$$

The relation (8.17) between the partial pressures of the constituent gases or the equivalent eq. (8.18) between the molal fractions is known as the *mass law*. Whatever the constitution of the mixture may be,

at a definite temperature and pressure, the function $p_1^{\nu_1}p_2^{\nu_2}\ldots$ (or $x_1^{\nu_1}x_2^{\nu_2}\ldots$) is constant. The quantity K_p (respectively, K) is, therefore, called the *equilibrium constant of the reaction.*

The mass law was first deduced by the Norwegian chemists Guldberg and Waage (1867) from statistical considerations which it will be instructive to reproduce here. Let us write the equation (6.46) of the reaction in the form

$$\nu_1 G_1 + \nu_2 G_2 + \ldots \rightleftarrows \nu'_1 G'_1 + \nu'_2 G'_2 + \ldots,$$

where the symbols, on one side, refer to the substances entering the reaction and, on the other, to those resulting from it. In order that $\nu_1, \nu_2, \ldots$ molecules of the substances $G_1, G_2, \ldots$ enter the reaction, they must all meet, i.e. be simultaneously present in a small volume τ_0. What is the composite probability of such an event? The probability of one molecule of the kind G_1 being in the volume τ_0 is proportional to the total number of such molecules available, which, in its turn, is proportional to the mol number N_1. The probability of ν_1 molecules being there simultaneously is proportional to $N_1^{\nu_1}$ (according to the rules expounded in section 30), provided that the molecules are statistically independent. This statistical independence implies that there are no forces of interaction of any kind between them, and this is true only for perfect gases. Since we have to restrict ourselves to this case, we may make use of the property of perfect gases that the mol number is proportional to the partial pressure and conclude that the above probability is proportional to $p_1^{\nu_1}$. In a similar way, we find for the probability of ν_2 molecules of the second component being in the volume τ_0 the expression $p_2^{\nu_2}$, and so on. The probability of the composite event is, therefore,

$$P = \alpha\, p_1^{\nu_1} p_2^{\nu_2} \ldots,$$

where the constant of proportionality α may depend upon the properties of the system, especially its temperature and pressure. The reaction may, however, go also in the opposite direction *producing* $\nu_1, \nu_2, \ldots$ molecules of the substances $G_1, G_2, \ldots$ It is necessary for this that $\nu'_1, \nu'_2, \ldots$ molecules of the substances $G'_1, G'_2, \ldots$ enter the reaction and meet in a limited volume. The probability for this is, obviously,

$$P' = \alpha' p'_1{}^{\nu'_1} p'_2{}^{\nu'_2} \ldots$$

In the state of equilibrium the number of molecules of every kind

is stationary and the process must go as often one way as the other. The probabilities P and P' must be equal

$$\frac{p_1^{\nu_1} p_2^{\nu_2} \dots}{p'_1{}^{\nu'_1} p'_2{}^{\nu'_2} \dots} = K_p,$$

($K_p = \alpha'/\alpha$) an equation which is identical with (8.17).

The thermodynamical derivation given above is due to Gibbs (1871) and leads a good way beyond the result of Guldberg and Waage inasmuch as it contains in eqs. (8.15) and (8.19) the explicit dependence of the equilibrium constant upon p and T. It is sufficient to make one measurement at a definite pressure and temperature in order to determine the constant I. Knowing I, one can predict the equilibrium conditions for all possible states of the mixture.

Exercise 78. Find the form of the mass law (8.17) for the following reactions: $N_2 + 3H_2 - 2NH_3 = 0$; $2HBr + I_2 - 2HI - Br_2 = 0$; $2O - O_2 = 0$; $2O_3 - 3O_2 = 0$.

Exercise 79. Show that, in view of eqs. (4.36″) and (3.26), the expression (8.15) can be reduced to

$$K_p = \int \frac{Q_p}{RT^2} dT + \log I, \tag{8.21}$$

which is consistent with (6.53).

52. Examples. Degree of dissociation. We have obtained two forms of the mass law in eqs. (8.17) and (8.18). The first form is simpler inasmuch as the quantity K_p is a function of the temperature only. All the quantities on which eq. (8.17) depends are completely conserved if we add neutral gases to the mixture, because the partial pressures $p_1, \dots p_\sigma$, as well as K_p, remain unaffected by this. The second form has the advantage that it can be more readily generalized to include systems which are not perfect gas mixtures.

The most interesting question is, usually, as to the fraction of the original substance or substances transformed in the reaction. Let us discuss, for instance, the oldest reaction to which this theory was applied by Gibbs, the *dissociation of nitrogen tetroxide*

$$2NO_2 - N_2O_4 = 0. \tag{8.22}$$

The coefficients ν are in this case $\nu_{N_2O_4} = -1$, $\nu_{NO_2} = 2$, $\nu = 1$. Suppose that N_0 moles of N_2O_4 are brought into a vessel at a very low temperature when it is quite undissociated: what mol numbers shall we observe after heating the gas to the temperature T at the pressure p? If we denote by ξ the fraction of the N_2O_4 molecules which are dissociated (*degree of dissociation*) the mol number of this

component is $N_{N_2O_4} = N_0(1 - \xi)$. To every dissociated molecule there appear in the mixture two molecules of NO_2. The mol number of nitrogen dioxide is, therefore, $N_{NO_2} = 2N_0\xi$, and the sum $N = N_{N_2O_4} + N_{NO_2} = N_0(1 + \xi)$. Recalling the definition (8.05) of the mol fractions and substituting into (8.18), we find

$$\frac{4\xi^2}{1 - \xi^2} = K = K_p/p. \tag{8.23}$$

We see from this that the degree of dissociation is small when K is small, i.e. according to (8.19), at low temperatures or high pressures. Under the opposite conditions of high temperature or low pressure, ξ approaches unity.

The degree of dissociation being known, it is easy to compute the *density*, which is also accessible to direct measurement. The density of the mixture Δ, obviously, stands to the density δ of the undissociated component N_2O_4 in the inverse ratio of the numbers of molecules: $\Delta/\delta = N_0/N$, whence

$$\Delta = \delta/(1 + \xi). \tag{8.24}$$

Accurate measurements on the dissociation of nitrogen tetroxide are due to Bodenstein.[1] This gas can be regarded as approximately perfect only when the pressures are not too high and the temperatures not too low. From observations under these conditions Bodenstein derives the formula

$$\log_{10} K_p = -\frac{2692}{T} + 1.75 \log_{10} T + 0.00483T - 7.144 \times 10^{-6}T^2 + 5.943, \tag{8.25}$$

when the pressure is expressed in mm Hg. The agreement with observations can be judged from Table 14.

TABLE 14

CHEMICAL EQUILIBRIUM IN N_2O_4

T (abs).....	282°.5	285°.7	289°.5	293°.0	305°.9	323°.9
$\log_{10} K_p$ (obs.).....	1.487	1.608	1.745	1.859	2.294	2.838
$\log_{10} K_p$ (calc.)....	1.475	1.600	1.741	1.889	2.286	2.838
T (abs).....	334°.8	342°.7	352°.5	361°.9	373°.9	387°.4
$\log_{10} K_p$ (obs.).....	3.135	3.326	3.577	3.784	4.027	4.293
$\log_{10} K_p$ (calc.)....	3.135	3.341	3.577	3.794	4.032	4.323

[1] M. Bodenstein, Zs. phys. Chemie 100, p. 74, 1922.

Bodenstein's formula represents also fairly well the older measurements by Natanson.[1] Although not very accurate, they offer us examples of how the degree of dissociation varies with the pressure at constant temperature. One of the series was measured at $t = 49°.7$ C, for which temperature (8.25) gives $K_p = 643$. The normal density of N_2O_4 is $\delta = 3.180$, whence the actual density (reduced to normal) is calculated by means of eq. (8.24).

TABLE 15

DISSOCIATION OF N_2O_4

p_{mm}	$K_p/4p$	ξ	Δ (calc.)	Δ (obs.)
0		1.000	1.590	
26.80	5.997	0.926	1.651	1.663
93.75	1.715	0.795	1.772	1.788
182.69	0.880	0.684	1.897	1.894
261.37	0.615	0.615	1.969	1.963
497.75	0.323	0.494	2.129	2.144

A reaction of great practical interest is the dissociation of water vapor

$$2H_2 + O_2 - 2H_2O = 0,$$

with the coefficients $\nu_{H_2} = 2$, $\nu_{O_2} = 1$, $\nu_{H_2O} = -2$, $\nu = 1$. We suppose again that we put into the reaction vessel N_0 undissociated water molecules (at a low temperature). At a higher temperature dissociation ensues and the mol numbers of the three components become

$$N_{H_2O} = N_0(1-\xi), \quad N_{H_2} = N_0\xi, \quad N_{O_2} = \tfrac{1}{2}N_0\xi, \quad N = N_0(1+\tfrac{1}{2}\xi).$$

Equation (8.18) gives, then,

$$\frac{1}{2}\frac{\xi^2}{(1-\xi)^2(1+\frac{1}{2}\xi)} = \frac{K_p}{p}. \tag{8.26}$$

According to Siegel[2] the heat of this reaction is

$$Q_p = 113\,820 + 2.65T - 4.41 \times 10^{-4}T^2 + 1.252 \times 10^{-6}T^3 - 9.12 \times 10^{-10}T^4 + 4.36 \times 10^{-17}T^6, \tag{8.27}$$

[1] E. and L. Natanson, Ann. Physik u. Chemie 24, p. 454, 1885.

[2] W. Siegel, Zs. phys. Chemie 87, p. 641, 1914. The value of the constant −1.08 is due to Nernst and Wartenberg.

and the equilibrium constant

$$\log_{10} K_p = -\frac{24\,900}{T} + 1.335 \log_{10} T - 0.965 \times 10^{-4} T$$

$$+ 0.137 \times 10^{-6} T^2 - 0.665 \times 10^{-10} T^3 + 0.191 \times 10^{-17} T^5 - 1.08. \quad (8.28)$$

Nernst[1] gives the following comparison of observed data of the degree of ionization with those calculated from this formula (at atmospheric pressure):

TABLE 16

DISSOCIATION OF WATER VAPOR

T (abs)	100ξ (calc.)	100ξ (obs.)	T (abs)	100ξ (calc.)	100ξ (obs.)
290	4.66×10^{-26}	$4.6 - 4.8 \times 10^{-26}$	1705	0.107	0.102
700	5.4×10^{-9}	7.6×10^{-9}	2155	1.18	1.18
1300	0.0029	0.0027	2257	1.76	1.77
1397	0.0085	0.0078	2337	2.7	3.8
1480	0.0186	0.0189	2507	4.1	4.5
1500	0.0225	0.0197	2684	6.6	6.2
1561	0.0369	0.034	2731	7.4	8.2
			3092	15.4	13.0

The agreement is remarkable in view of the width of the range and of the fact that the observations were obtained by many different observers and methods.

Exercise 80. Find the equation for the degree of dissociation, analogous to (8.23) and (8.26), for the reactions: $3H_2 + N_2 = 2NH_3$, $Hg + I_2 = HgI_2$.

Exercise 81. Calculate ξ for hydrogen iodide from eq. (8.30) at the pressure $p = 100$ mm and at the temperatures of Table 17.

53. Influence of the excess of one component. Another interesting reaction is the dissociation of hydrogen iodide

$$\left.\begin{aligned} &H_2 + I_2 - 2HI = 0, \\ &\nu_{H_2} = 1, \quad \nu_{I_2} = 1, \quad \nu_{HI} = -2, \quad \nu = 0. \end{aligned}\right\} \quad (8.29)$$

The equation $\nu = 0$ means that the number of molecules is not changed in the reaction. The equilibrium constant (8.19), then, does

[1] W. Nernst, Theoretische Chemie, p. 775. 11th edition. Stuttgart 1926.

not contain p, so that the molal fractions and the degree of dissociation are entirely independent of the total pressure. Suppose we bring into a vessel (at a low temperature) N_1 mols of HI and N_2 mols of H_2 and heat the mixture to the temperature T. This assumption will permit us to study the influence of the excess of one component (H_2) upon the degree of dissociation ξ. As in the preceding case, $N_{HI} = N_1(1 - \xi)$. Each dissociated molecule of HI produces half a molecule of H_2 and I_2, respectively: therefore, $N_{I_2} = \frac{1}{2}N_1\xi$ and $N_{H_2} = \frac{1}{2}N_1\xi + N_2$, while the sum, $N = N_1 + N_2$, is independent of the degree of dissociation. The substitution into (8.17) gives

$$\frac{1}{4}\frac{\xi(\xi + 2N_2/N_1)}{(1 - \xi)^2} = K. \tag{8.30}$$

When the temperature is low, K is small and, with it, the degree of dissociation ξ. We can take then for the denominator the approximate value 1 and see that the numerical value of ξ greatly depends upon the term $2N_2/N_1$. When there is no excess hydrogen ($N_2 = 0$), we find $\xi = 2K^{\frac{1}{2}}$; on the other hand, when $2N_2/N_1$ is not small, we can neglect ξ, compared with it, obtaining $\xi = 2KN_1/N_2$, a number which is much smaller: *The excess of one of the products of dissociation seriously depresses its degree.* When K is very large (high temperatures), ξ approaches unity. As an approximation, we can substitute $\xi = 1$ in the numerator with the result $1 - \xi = (1 + 2N_2/N_1)^{\frac{1}{2}}/2K^{\frac{1}{2}}$. Qualitatively the presence of the term $2N_2/N_1$ has still a depressing influence. However, quantitatively ξ sinks appreciably below 1 only when $2N_2/N_1$ begins to approach K in its order of magnitude.

The physical reason of this depressive action is, of course, that the excess of H_2 gives to the iodine, produced in the dissociation process, a larger chance of reacting with hydrogen and of being transformed back into hydrogen iodide. This simple explanation makes it clear that we have here a general phenomenon which occurs, under similar conditions, in all cases of dissociation.

The equilibrium constant of the reaction (8.29) is well represented by the formula[1]

$$\log_{10} K = \log_{10} K_p = -\frac{540.4}{T} + 0.503 \log_{10} T - 2.350. \tag{8.31}$$

[1] Nernst, Zs. Electrochemie **18**, p. 687, 1909; K. Vogel v. Falkenstein, Zs. phys. Chemie **72**, p. 113, 1910.

Hence and from (8.30) we obtain Table 17.

TABLE 17

DISSOCIATION OF HI IN THE PRESENCE OF AN EXCESS OF H_2

T (abs)	$\log_{10} K$	$N_2/N_1 = 0$		$N_2/N_1 = 1$
		100ξ (calc.)	100ξ (obs.)	100ξ (calc.)
600	−1.856	19.1	18.9	2.6
700	−1.691	22.2	21.5	3.7
800	−1.565	24.9	24.7	4.8
1295	−1.202	33.3	32.9	9.8
1490	−1.117	35.6	37.5	11.3

The depressive action is very marked, indeed.

Exercise 82. Calculate from (8.31) with the help of (8.21) the heat of the reaction (8.29) at 1000° K. Do the same for the reaction (8.22) by means of the formula (8.25).

Exercise 83. Derive the generalization of the formula (8.26) when there is an excess of H_2, and estimate its depressive influence.

54. Influence of neutral gases. In the absence of neutral gases the mol fraction of each component is given by the expression

$$x_h = N_h/(N_1 + \ldots + N_\sigma). \tag{8.32}$$

On the other hand, if there are in the mixture other gases than those taking part in the reaction and the sum of the mol numbers of these neutral gases is N_0, the molal pressure of the same component becomes

$$x'_h = N_h/(N_0 + N_1 + \ldots + N_\sigma). \tag{8.33}$$

Comparing these two relations we find

$$x'_h = x_h(N_1 + \ldots + N_\sigma)/(N_0 + N_1 + \ldots + N_\sigma). \tag{8.34}$$

The expression of the mass law in the presence of neutral gases is in accordance with eq. (8.17)

$$x'_1{}^{\nu_1} \ldots x'_\sigma{}^{\nu_\sigma} = K,$$

or substituting (8.34)

$$x_1{}^{\nu_1} \ldots x_\sigma{}^{\nu_\sigma} = K\left(\frac{N_0 + \ldots + N_\sigma}{N_1 + \ldots + N_\sigma}\right)^{\nu}. \tag{8.35}$$

The addition of neutral gases at p = const has, therefore, the same effect as an increase of the equilibrium constant. This influence is opposite to that of the excess of an active component because to a larger constant K corresponds a higher degree of dissociation. *The presence of neutral gases in general advances the degree of dissociation,* provided that the total pressure p remains the same. Of course, in the particular case $\nu = 0$, neutral gases have no effect.

We see from the definition (8.19) of the function K that the same result could be achieved by reducing the total pressure p of the mixture in the proportion $(N_1 + \ldots + N_\sigma)/(N_0 + \ldots + N_\sigma)$. In a certain sense, the influence of the neutral gases is, therefore, only apparent. It comes from the fact that we refer the effect to constant total pressure to which both the active and the neutral gases contribute, so that the partial pressures of the active components are reduced in precisely the same proportion. This corresponds to the usual experimental conditions in which the total pressure p is the fundamental datum. If the question were put as to the degree of ionization in a box of constant volume, the introduction of additional neutral gases into that box would have no influence whatever on it.

Exercise 84. What is the increase of volume of the gas mixture in a reaction in which the sum of the mol numbers increases by ν? Use the equation of perfect gases (1.18) and check that the result is consistent with (6.51).

55. Mutual influence of two simultaneous reactions. Suppose that we mix at a low temperature N_1 mols of hydrogen iodide (HI) and N_2 mols of hydrogen bromide (HBr) and slowly heat the mixture. What will be its composition at a temperature T? In addition to the reaction (8.29), there can take place also the reaction of dissociation of hydrogen bromide

$$\left.\begin{aligned} &\mathrm{H_2} + \mathrm{Br_2} - 2\mathrm{HBr} = 0, \\ &\nu_{\mathrm{H_2}} = 1, \quad \nu_{\mathrm{Br_2}} = 1, \quad \nu_{\mathrm{HBr}} = -2, \quad \nu = 1. \end{aligned}\right\} \tag{8.36}$$

Accordingly there must be simultaneously satisfied two equations of the type (8.18)

$$\frac{x_{\mathrm{H_2}}\, x_{\mathrm{I_2}}}{x^2_{\mathrm{HI}}} = K_1, \qquad \frac{x_{\mathrm{H_2}}\, x_{\mathrm{Br_2}}}{x^2_{\mathrm{HBr}}} = K_2. \tag{8.37}$$

We can use the expressions of section 53 for the mol numbers of HI and of $\mathrm{I_2}$, in terms of the degree of dissociation ξ_1 of hydrogen iodide: $N_{\mathrm{HI}} = N_1(1 - \xi_1)$, $N_{\mathrm{I_2}} = \frac{1}{2}N_1\xi_1$. Similarly we can write (denoting the degree of dissociation of HBr by ξ_2): $N_{\mathrm{HBr}} = N_2(1 - \xi_2)$, $N_{\mathrm{Br_2}} = \frac{1}{2}N_2\xi_2$, since the two reactions are precisely of the same type.

As to the mol number of hydrogen, it comes from two sources: each dissociated molecule of both HI and HBr produces half a molecule of H_2, whence $N_{H_2} = \frac{1}{2}(N_1\xi_1 + N_2\xi_2)$. Substituting into (8.05) and (8.37)

$$\frac{1}{4}\frac{\xi_1(\xi_1 + \xi_2 N_2/N_1)}{(1-\xi_1)^2} = K_1, \qquad \frac{1}{4}\frac{\xi_2(\xi_2 + \xi_1 N_1/N_2)}{(1-\xi_2)^2} = K_2.$$

It is apparent from these equations that the mutual influence of the two reactions results in the decrease of the degrees of ionization of both HI and HBr. The reason of this is easy to understand: either of the reactions liberates hydrogen and creates an excess of this component for the other process, exercising upon it a depressive action (compare section 53). In general, there exists still another mutual influence: If the total pressure is kept constant, the presence of the second gas (and of the products of its dissociation) decreases the partial pressure of the first and, in this way, produces the same effect of enhancing the dissociation as a neutral gas. We have already said in the preceding section that this effect is trivial: Therefore, we have selected here two reactions in which it does not exist because they are not pressure sensitive. They permit us to study the mutual depressive influence in its pure form.

The equilibrium constant of the dissociation of HBr can be represented as follows

$$\log_{10} K_2 = -\frac{5223}{T} + 0.553 \log_{10} T - 2.72. \qquad (8.38)$$

At temperatures below 2000° K, ξ_2 is, therefore, very much smaller than ξ_1. If N_1 and N_2 are of the same order of magnitude, the dissociation of HI is not appreciably affected by the presence of HBr, and the values of ξ_1 remain the same as in Table 17. On the other hand, the dissociation of HBr is greatly depressed, as is illustrated by Table 18.

TABLE 18

DISSOCIATION OF HBr IN THE PRESENCE OF HI

T (abs)	$\log_{10} K_2$	$N_1 = 0$	$N_1 = N_2$
		$100\xi_2$	$100\xi_2$
600	−9.889	0.002	1.8×10^{-6}
1000	−6.284	0.14	3.4×10^{-4}
1490	−4.470	1.16	0.12

Exercise 85. N_0 mols of HI are brought in a vessel and heated to a high temperature where the reactions (8.29) and $2I - I_2 = 0$ must be taken into account simultaneously. Denote the degree of dissociation of HI by ξ_1 and that of I_2 by ξ_2. The equilibrium constant for the dissociation of I_2 is (Bodenstein, Zs. Electrochem. **22**, p. 338, 1916):

$$K_p = -\frac{7550}{T} + 1.75 \log_{10} T - 4.09 \times 10^{-4} T + 4.726 \times 10^{-8} T^2 - 0.440.$$

Calculate ξ_2 under the above conditions and in pure I_2 at the temperature 2000° K.

CHAPTER IX

DILUTE SOLUTIONS

56. The concept of a solution. We call a *solution* any homogeneous system which consists of two or more chemically pure substances, no matter whether it is solid, liquid, or gaseous. Solutions must be distinguished from chemical compounds, on one hand, and (in general) from mixtures, on the other. A *chemical compound* consists of molecules of only one kind; therefore, the masses of the constituents of which it is formed stand in a definite ratio. From the point of view of the phase rule (section 41) it is a system with one single independent component or a pure substance: if the amount of one constituent is given, those of all the others are uniquely determined by it. It is quite different with the solution; the molecules or atoms of the constituents do not lose their individuality in it, and their amounts can assume any arbitrary ratio, within certain limits. The composition of the solutions being continuously variable, they must be regarded as homogeneous systems with several independent components.

The difference from *mixtures* is most clearly brought out in the case of solid solutions. We know, at present, that a solid is always crystalline, and we say that two substances are mutually soluble, in the solid state, when they form a joint crystalline lattice, or a mixed crystal in which the lattice points are occupied, in part, by atoms (or molecules) of the one substance, in part, of the other. The solubility of solids is an exception, although several pairs of metals are known which are mutually soluble in all proportions, e.g. Ag—Au, Ag—Pd, Co—Ni, Cu—Ni, Cu—Pd, Au—Pt, Bi—Sb, etc. The metals of each pair are of a closely analogous chemical nature belonging to the same group of the periodic system (or sometimes to two adjacent groups). Of non-elementary solids which are mutually soluble in all proportions we could mention AgCl—NaCl, $PbBr_2$—$PbCl_2$, $SnCl_2$—$PbCl_2$, etc. More common is the case of limited solubility: the crystalline structure of a metal is preserved if a fraction of the lattice points (up to a certain limit) is replaced by atoms of another metal, usually from the same or the adjacent group of the natural system. The lattice cannot accommodate more than the limiting fraction without breaking down. Such cases are Cu—Ag, Au—Ni,

Bi—Pb, Sn—Pb, etc. Of course, limited mutual solubility occurs also with pairs of solids of a non-metallic nature: KNO_3—$NaNO_3$, KNO_3—$TiNO_3$, etc. All other cases, viz. those in which the constituents of an alloy do not form a joint crystal, must be classed as mixtures. For instance, the microscopical examination of Ag—Pb alloys shows that they are agglomerations of tiny crystals of pure silver and pure lead. Similar conditions prevail with most other alloys (e.g. Bi—Cd, Pb—Sb, also KCl—AgCl, ice—AgCl, etc.). We have seen in section 39 that, as far as the thermodynamical applications and conclusions are concerned, the size of the phases is immaterial; therefore, an alloy or other mixture of this sort must be regarded as a system of two or more coexisting phases, even if these phases are of microscopical dimensions. Unlike a mixture, a true solution is homogeneous and represents a single phase.

The conditions in a liquid solution are similar. A liquid can, in general, dissolve other liquids, solids, or gases, the true solution being homogeneous and characterized by a uniform distribution over its whole volume of the molecules or atoms of all the constituents. In the case of liquids mutual solubility is not an exception but a common phenomenon. At the same time there are numerous pairs of liquids which exhibit in certain ranges of temperature a complete (e.g. water—carbon tetrachloride) or a limited (water—ether, water—phenol, etc.) mutual insolubility. The true or molecular solutions must be distinguished from the mixtures which in the case of liquids are called suspensions, emulsions, and colloidal solutions. Like the solid mixtures they are inhomogeneous and represent two or more phases intermixed in a finer or coarser degree of dispersion.

In the case of gases, the difference between a solution and a mixture disappears, since all gases are mutually soluble or miscible, without restriction, forming a homogeneous system in which the molecules of all constituents are uniformly distributed.

The process of forming a solution is accompanied by mechanical and thermal effects which show that there is a certain degree of interaction between the molecules of the different constituents. When we dissolve ethyl alcohol and water in equal parts, there is a considerable contraction, the volume of the solution being about 5% smaller than the sum of the volumes of the free components (compare section 32). At the same time, a certain amount of " heat of solution " is developed, because the internal energy of the solution is not equal to the sum of the internal energies of the alcohol and water forming it. Both effects are characteristic of the general case although their numerical values vary widely, so that the heat of solution may be

either positive or negative. There are certain pairs of liquids known (e.g. benzene-toluene) which form solutions with very little diminution of volume and development of heat. This usually occurs in the case of a close chemical resemblance of the constituents so that the interaction between atoms of different kinds is nearly the same as that between atoms of the same kind. We can, therefore, imagine, as an ideal case, a solution in which the volumes, as well as the internal energies, are strictly additive and no change occurs in these quantities when the solution is formed. Following G. N. Lewis[1] we shall call it a *perfect solution*: although the perfect solution may not occur in nature in its pure form, it is a useful fiction as it will help us to bring out, theoretically, some typical properties of real solutions.

57. Dilute solutions. One of the components of a solution, usually the most plentiful is called the *solvent*, the others the *solutes*. In this chapter we shall discuss the case when the mol number of the solvent N_0 is much larger than those of the solutes ($N_1, N_2, \ldots N_\sigma$). The thermodynamical properties of every system are determined by the characteristic functions, especially by the thermodynamic potential which, in turn, depends on the internal energy and the volume. A theoretical treatment of the problem requires, therefore, some knowledge about the analytical structure of the functions U and V, particularly with respect to their dependence upon the mol numbers N_k of the components. We have seen in section 39 that the functions U, V, S, Φ are homogeneous of the first degree with respect to the mol numbers. There obtains, therefore, the equation analogous to (6.13)

$$\varepsilon U(p, T, N_0, \ldots N_\sigma) = U(p, T, \varepsilon N_0, \ldots \varepsilon N_\sigma).$$

Taking for ε the special value $\varepsilon = 1/N_0$, we find

$$\frac{U}{N_0} = f\left(p, T, \frac{N_1}{N_0}, \ldots, \frac{N_\sigma}{N_0}\right). \tag{9.01}$$

This equation (and a similar one for V/N_0) is quite general and does not contain any restrictive assumptions. However, we shall introduce now a restriction limiting the generality of the function f, in that *we assume that it can be expanded into a convergent multiple power series with respect to the ratios* $N_1/N_0, \ldots N_\sigma/N_0$.

$$\frac{U}{N_0} = u_0 + \frac{N_1}{N_0} u_1 + \ldots + \frac{N_\sigma}{N_0} u_\sigma + \frac{1}{2}\left(\frac{N_1^2}{N_0^2} u_{11} + 2\frac{N_1 N_2}{N_0^2} u_{12} + \ldots\right) + \ldots. \tag{9.02}$$

[1] G. N. Lewis, J. Am. Chem. Soc. 30, p. 668, 1908.

We do not claim that this condition is always satisfied, and we shall treat in section 115 a notable exception to it. However, the large majority of solutions do conform to eq. (9.02), and the present chapter will be devoted to this case. The coefficients u_h, u_{hi}, . . . of the expression (9.02) are functions of p and T independent of the mol numbers. In the analogous expansion of V/N_0 we denote the coefficients by v_h, v_{hi}, etc.

We call the solution *dilute* if, within the desired accuracy, the terms of second and higher order of the expansion can be neglected so that U and V are expressed by the linear forms

$$\left.\begin{aligned} U &= N_0 u_0 + N_1 u_1 + \ldots + N_\sigma u_\sigma, \\ V &= N_0 v_0 + N_1 v_1 + \ldots + N_\sigma v_\sigma. \end{aligned}\right\} \tag{9.03}$$

These equations contain, of course, the limiting case of the pure solvent ($N_1 = \ldots = N_\sigma = 0$), when they take the form $U = N_0 u_0$, $V = N_0 v_0$. The physical meaning of the coefficients u_0, v_0 is, therefore, the *molal internal energy* and the *molal volume* of the *pure solvent.* The mol number N_0, representing the solvent, cannot be put equal to zero: therefore, the simplest form of the equations in which N_h does not vanish is $U = N_0 u_0 + N_h u_h$. It corresponds to a solution of only the component (h) in the solvent. Consequently, we can say that the coefficients u_h must depend on the properties both of the solute h and of the solvent. They may be called the molal energy and volume of the solute *in the solution*, but they will be, in general, different from the same quantities characterizing the solute in its free state. When another mol of the solvent is added to the dilute solution (9.03), its internal energy and volume become

$$U' = (N_0 + 1)u_0 + N_1 u_1 + \ldots + N_\sigma u_\sigma,$$

$$V' = (N_0 + 1)v_0 + N_1 v_1 + \ldots + N_\sigma v_\sigma,$$

so that $U' = U + u_0$, $V' = V + v_0$. These are exactly the same values which the solution and the extra mol of the solvent have before they are brought together: there is no development of heat of solution and no change of volume when the solution is diluted still further. This additivity would not obtain if the second order terms of eq. (9.02) had to be taken into consideration: it can be taken as the *experimental criterion of the diluteness* of a solution.

According to the definition of *perfect solutions* given at the end of the preceding section, the expressions (9.03) apply also to them. However, these solutions need not be dilute and the distinction between solvent and solutes disappears in them. Any of the compo-

nents can be regarded as the solvent and, therefore, all the coefficients u_h, v_h are identical with the molal internal energies and volumes of the pure components. This fact guarantees the additivity of the functions U and V which is the essential characteristic of a perfect solution.

58. Entropy of dilute and perfect solutions. The differential of the entropy is defined by the second law of thermodynamics as $dS = (dU + pdV)/T$. The differentials dU and dV are taken *for a definite composition of the system*, so that the mol numbers N_h must be regarded as constants with respect to the differentiation. Substituting the expressions (9.03), we obtain

$$dS = \frac{1}{T}\sum_{h=0}^{\sigma} N_h(du_h + pdv_h) = \sum_{h=0}^{\sigma} N_h ds_h, \tag{9.04}$$

if we denote, for short, $ds_h = (du_h + pdv_h)/T$. With respect to s_h we must repeat what was said in the preceding section with respect to u_h, v_h. The quantities s_h are functions of pressure and temperature and may be called the molal entropies of the components while *in the solution*. They coincide with the molal entropies in the pure state only for the solvent and for the components of perfect solutions, and are different from them in all other cases.

The total entropy S, obtained by integrating eq. (9.04), will contain a constant of integration C, which is constant only in so far as it is independent of the variables p, T. However, it may depend on the mol numbers N_h (which are not variables as far as the integration is concerned), and it can be interpreted as *the entropy of mixing the components*

$$S = \sum_{h=0}^{\sigma} N_h\, s_h(p, T) + C(N_0, N_1, \ldots N_\sigma). \tag{9.05}$$

This expression is entirely independent of the state of aggregation of the system and applies to solid and liquid solutions and to gas mixtures. If we had a complete knowledge of the equations of state and of the energies involved, including the continuity of the states, we could give the explicit analytical form of the functions $s_h(p, T)$ covering all cases: to go from one state of aggregation to another, it would be sufficient to change the value of the arguments p and T, as we do it in an inaccurate way, limited to pure substances, in the Van der Waals theory. These considerations show us that the form of the function $C(N_0, \ldots N_\sigma)$ determined for one state of the system will be valid for all other states. We did find, however, the expression of the entropy of a mixture of perfect gases: If we admit that all substances

of nature have a finite vapor pressure, be it in some cases ever so small, there is the theoretical possibility of vaporizing any solution into a mixture of gases. Moreover, by reducing the pressure, these gases can be made to obey, with any degree of approximation, the laws of perfect gases. It follows from this argument that the expression (8.07) of the entropy of a mixture of perfect gases is only a special case of the formula (9.05) and must have the same analytical structure. This is, in fact, borne out by comparing them: there are in (8.07) terms linear in the mol numbers N_h which correspond to the sum in eq. (9.05), and terms containing the factors $\log x_h = \log (N_h/N)$. The totality of the latter terms must, obviously, be identified with the function C

$$C(N_0, N_1, \ldots N_\sigma) = -R\sum_{h=0}^{\sigma} N_h \log x_h. \tag{9.06}$$

The possibility of this identification rests, entirely, on the hypothesis made in the preceding section that the functions U and V can be represented as the power series (9.02) and do not contain logarithmic terms. This assumption about the analytical form of U and V is, for the purposes of the present theory, equivalent to the conclusions which we shall deduce from it in the following sections, especially to Henry's law. Van't Hoff who originated the theory of dilute solutions based it on the validity of Henry's law. We prefer the above formulation (which is due to Planck) because, on the one hand, it is more general, being capable of extension by taking into consideration higher powers of the series (9.02). On the other hand, it paves the way to the understanding of the reasons why in certain dilute solutions the laws deduced in this chapter are not satisfied (section 115).

59. General conditions of equilibrium. Equations (9.03) for the internal energy and volume, together with the entropy formula (9.05), (9.06), are sufficient to obtain the expression of the thermodynamic potential $\Phi = U - TS + pV$, viz.

$$\Phi = \sum_{h=0}^{\sigma} N_h(\varphi_h + RT \log x_h), \tag{9.07}$$

the quantities φ_h being defined as

$$\varphi_h = u_h - Ts_h + pv_h, \tag{9.08}$$

they are functions of p and T, independent of the mol numbers N_h. Being built up from the functions u_h, s_h, v_h, they have the properties which we have pointed out as pertaining to these quantities. We may call them the molal thermodynamic potentials of the components *in*

the solution. However, they are identical with the potentials of the pure substances only in the cases of the components in perfect solutions and of the solvent in dilute ones. In the case of solutes in dilute solutions they depend also on the properties of the solvent and are, therefore, different from the potentials of the same substances in their free state.

The form (9.07) of the thermodynamic potential applies not only to dilute and perfect solutions but also to mixtures of perfect gases and to single phases of chemically pure substances. In fact, the comparison with the expression (8.09) shows that, in the case of perfect gases, φ_h must be defined as

$$\varphi_h = \overline{\varphi}_h - RT \log x_h = RT \log p + \omega_h(T). \tag{9.09}$$

It differs from $\overline{\varphi}_h$ of (8.08) in that p is substituted instead of the partial pressure p_h. On the other hand, a chemically pure substance, can be regarded as the limiting case of a solution without solutes ($x_0 = 1$, $\log x_0 = 0$). We can, therefore, apply our formulas to a heterogeneous system consisting of any number (α) of phases in equilibrium, each having one of these four characters: dilute solution, perfect solution, mixture of gases, pure substance. If we designate the phase by an upper index j, the total thermodynamic potential of the system will be

$$\Phi = \sum_{j=1}^{\alpha} \sum_{h=0}^{\sigma} N_h^{(j)} [\varphi_h^{(j)} + RT \log x_h^{(j)}]. \tag{9.10}$$

The comparison with the general expression (6.14) shows that the partial thermodynamic potentials are generally $\overline{\varphi}_h^{(j)} = \varphi_h^{(j)} + RT \log x_h^{(j)}$. We can apply to the last equation the general theory of equilibrium of section 42. The most general process possible in the system is given by eq. (6.48)

$$\sum_{j=1}^{\alpha} \sum_{h=0}^{\sigma} \nu_h^{(j)} G_h^{(j)} = 0. \tag{9.11}$$

The equation of equilibrium corresponding to it is, according to (6.50),

$$\Delta\Phi \equiv RT \left[\sum_{j=1}^{\alpha} \sum_{h=0}^{\sigma} \nu_h^{(j)} \log x_h^{(j)} - \log K \right] = 0, \tag{9.12}$$

or

$$\sum_{j=1}^{\alpha} \sum_{h=0}^{\sigma} \nu_h^{(j)} \log x_h^{(j)} = \log K, \tag{9.13}$$

where the *equilibrium constant* K is an abbreviation defined by

$$\log K = -\frac{1}{RT}\sum_{j=1}^{\alpha}\sum_{h=0}^{\sigma}\nu_h^{(j)}\varphi_h^{(j)}, \tag{9.14}$$

which, in the particular case of a mixture of perfect gases, can be reduced to the form (8.19), as we shall see below. In application to dilute solutions the formula (9.13) is due to Van't Hoff.

The left side of eq. (9.13) does not explicitly depend on temperature and pressure, while K is a function of p and T only, being independent of the mol numbers. An indication as to the form of the functional dependence of the equilibrium constant upon p and T is contained in eqs. (6.51) and (6.53) which give the partial derivatives of $\Delta\Phi$ with respect to T and p. Differentiating the expression (9.12) partially, we find

$$\left(\frac{\partial \log K}{\partial p}\right)_T = -\frac{\Delta V}{RT}, \tag{9.15}$$

$$\left(\frac{\partial \log K}{\partial T}\right)_p = \frac{Q_p}{RT^2}, \tag{9.16}$$

where ΔV and Q_p are the change of volume and the heat of reaction in the process characterized by eq. (9.11).

These equations are often called *rules of displacement of equilibrium*, inasmuch as a change in the equilibrium constant leads to a displacement in the mol fractions of the components, according to eq. (9.13). The first of them expresses the following fact:

When a system is compressed at constant temperature, the equilibrium is displaced in the direction of a decrease of volume. I.e. the less voluminous components are enhanced at the expense of the more voluminous.

The other equation contains the rule:

When a system is heated at constant pressure the equilibrium is displaced in the direction of heat absorption. I.e. the components of higher heat function are enhanced at the expense of those of lower. This rule was first pointed out by Van t'Hoff and called by him *the principle of mobile equilibrium.*

Exercise 86. From the definitions (9.08), (9.04), (9.03) of the quantities φ_h, s_h, u_h, v_h check the statement that they satisfy the same differential relations as the corresponding functions *in the free state* of the substances, in particular that they obey eqs. (5.37). Having ascertained this, express ΔV and Q_p in terms of v_h and s_h from (9.15), (9.16), and (9.14).

60. Nernst's distribution law. Let us consider the particular case when the process (9.11) consists in the transfer of $\nu_h^{(2)}$ mols of the component h from the phase (2) into the phase (1), where they may form a different number of mols $\nu_h^{(1)}$, owing to association or dissociation. It will simplify matters and lessen the chances of misapprehension if we define both $\nu_h^{(1)}$ and $\nu_h^{(2)}$ as positive and recognize the fact that the phase (2) undergoes a loss by writing

$$\nu_h^{(1)} G_h^{(1)} - \nu_h^{(2)} G_h^{(2)} = 0,$$

and

$$\nu_h^{(1)} \log x_h^{(1)} - \nu_h^{(2)} \log x_h^{(2)} = \log K_h = -[\nu_h^{(1)} \varphi_h^{(1)} - \nu_h^{(2)} \varphi_h^{(2)}]/RT. \quad (9.17)$$

Moreover, we shall often drop the superscript (2) to simplify writing. With the abbreviation,

$$g_h = \nu_h^{(1)}/\nu_h^{(2)} = \mu_h^{(2)}/\mu_h^{(1)}, \quad (9.18)$$

denoting, according to (6.42), the ratio of molecular weights, this becomes

$$\log [(x_h^{(1)})^{g_h}/x_h^{(2)}] = (\log K_h)/\nu_h^{(2)} = -[g_h \varphi_h^{(1)} - \varphi_h^{(2)}]/RT. \quad (9.19)$$

In particular, when the process takes place without change of molecule, we have $\nu_h^{(1)} = \nu_h^{(2)} = g_h = 1$ and

$$\log(x_h^{(1)}/x_h^{(2)}) = \log K_h = -(\varphi_h^{(1)} - \varphi_h^{(2)})/RT. \quad (9.20)$$

In many textbooks these equations are given only in the simpler form (9.20). Indeed, this can be justified on the following grounds. Even if the vapor of the component h has a different, say dissociated, molecule, the dissociation is theoretically never complete: according to Chapter VIII, there must exist a certain fraction of undissociated molecules, be it ever so small. Equation (9.20) gives then the equilibrium of the solution with the undissociated portion of the vapor and permits to determine its mol fraction, whereas the mol fraction of the main (dissociated) part of the component h can be obtained, in a secondary way, by using the theory of Chapter VIII. However, the more general eq. (9.19) is preferable from the practical point of view, as it gives directly the equilibrium with either of the two fractions. It permits one to describe by a single formula a much wider variety of observational results, a fact which more than compensates for its slightly more complicated form.

Equations (9.19) *and* (9.20) *are the fundamental relations in the theory of equilibrium* of phases of dilute and perfect solutions. A num-

ber of important laws can be derived from them. The second equation can be written in the form

$$x_h^{(1)}/x_h^{(2)} = K_h. \tag{9.21}$$

The ratio of the molal fractions of any component in two phases is a function of temperature and pressure only, provided the molecule of the component is the same in both phases. Suppose, for instance, that the phases (1) and (2) mainly consist of two solvents spread one on top of the other (as would be the case with water and carbon tetrachloride). Let the same solute h be dissolved in both solvents: the quotient $x_h^{(1)}/x_h^{(2)}$ is then called the *coefficient of distribution* in the two phases. We see from eq. (9.21) that the coefficient of distribution is independent of the concentration of the solute in either phase, a law first pointed out by Nernst in 1891.

The experimental data are, usually, expressed not in mol fractions but in mols of the solute per 1000 cm^3 of the solution, denoted by A_h. Because of the dilution, A_h can be regarded as proportional to x_h; therefore, the ratio $K' = A_h^{(1)}/A_h^{(2)}$ must be also constant. As an illustration we may take iodine (I_2) dissolved in carbon tetrachloride (2) and in water (1) at 25° C.[1]

TABLE 19

DISTRIBUTION RATIOES

$A^{(2)}$	0.02	0.04	0.06	0.08	0.09	0.10
$K' \pm 0.5$....	85.1	85.2	85.4	86.0	86.4	87.5

In the general case, when the molecular weight of the solute is different in the two solvents, eq. (9.19) gives

$$(x^{(1)})^g/x^{(2)} = K^{1/\nu^{(2)}}. \tag{9.22}$$

For instance, benzoic acid has in benzene (1) a molecular weight twice as high as in water ($\nu^{(1)} = 1$, $\nu^{(2)} = 2$, $g = \frac{1}{2}$). Another example is trichloroacetic acid ($C_2HCl_3O_2$) dissolved in water (2) and in ethyl ether (1) at 25° C. The measured data are as in Table 20.[2]

TABLE 20

$A^{(1)}$.....	0.001	0.005	0.010	0.015
$A^{(2)}$.....	0.0021	0.0048	0.0068	0.0083
$(A^{(1)})^{\frac{1}{2}}/A^{(2)}$	15.0	14.7	14.7	14.7

[1] Washburn and Strachan, J. Am. Chem. Soc. **35**, p. 681, 1913; Linhart, *ibidem*, **40**, p. 158, 1918.

[2] Smith, J. Phys. Chemistry **25**, pp. 605, 616, 1921.

It appears from this that $g = \frac{1}{2}$ or $\mu^{(1)} = 2\mu^{(2)}$. The molecule is normal in the aqueous solution but has twice the normal weight in ether as a solvent. The results are only rarely as clean cut as this: in many solvents the association is partial, resulting in an effective molecular weight which is a non-integral multiple of the normal.

Exercise 87. The following values were measured in the case of Br_2 dissolved in bromoform (1) and in water (2) at $t = 25°$ C.

$A^{(1)} =$	0.125	0.25	0.50	0.75	1.00
$100 \times A^{(2)} =$	0.193	0.382	0.750	1.11	1.47.

Show that the distribution law is approximately satisfied.

61. Influence of a neutral atmosphere on the vapor pressure. We label the condensed phase (2) and the atmosphere above it (1), and we assume that the gases of the atmosphere are but little dissolved in the condensed phase so that it can be considered as pure ($x_h^{(2)} = 1$), with a sufficient approximation. The fundamental eq. (9.19), applied to the vaporization of the condensed substance, gives

$$\log x_h^{(1)} = [\varphi_h^{(2)}/g_h - \varphi_h^{(1)}]/RT. \tag{9.23}$$

The potential $\varphi_h^{(1)}$ relating to the vapor has the form (9.09) and contains the term $RT \log p$ which can be brought to the left side and combined with $x_h^{(1)}$. Noticing that $x_h^{(1)} p = p_h^{(1)}$ (the partial pressure of the vapor in the atmosphere), we have

$$\log p_h^{(1)} = [\varphi_h^{(2)}/g_h - \omega_h(T)]/RT, \tag{9.24}$$

where $\omega_h(T)$ is the remaining part of $\varphi_h^{(1)}$ and a function of the temperature only.

The terms on the right depend only on the properties of the component h and not on the rest of the atmosphere. In the case when the condensed phase is in equilibrium with its pure vapor, the left side goes over into $\log p^{(1)}$ (where $p^{(1)}$ is the total pressure) while the right side remains the same. We see, therefore, that *the atmosphere does not influence the vapor pressure*: the partial vapor pressure in the atmosphere is identical with the total vapor pressure in its absence.

62. Henry's law. In this section we shall apply the fundamental formulas (9.19) and (9.20) to the equilibrium of a liquid and a gaseous phase labeled, respectively, (2) and (1). The question we shall ask here is about the mol fraction $x_h^{(2)}$ of a dissolved component (gas) in the condensed phase if its partial pressure in the adjacent atmsophere is given. We may say that the condensed phase (2) is here *preferred* inasmuch as we are particularly interested in what occurs in it. It

will be well to *bring the preferred phase into prominence* by dropping the superscript (2) relating to it: we shall write, therefore, x_h instead of $x_h^{(2)}$. The process to be considered is the transfer of ν_h mols of the component h from the liquid solution into the gaseous phase where they may form $\nu_h^{(1)}$ mols (because of dis- or association).

By approximation we can neglect the change (in the process) of the volume of the condensed phase by comparison with that of the vapor. The quantity ΔV in eq. (9.15) denotes, then, simply the increase of volume of the gaseous phase due to $\nu_h^{(1)}$ additional mols of the component h. According to eq. (1.18), this volume, before the beginning of the process, is $V = (N_0^{(1)} + \ldots + N_\sigma^{(1)})RT/p$; after it takes place, the mol number $N_h^{(1)}$ is increased by $\nu_h^{(1)}$, the difference is, therefore,

$$\Delta V = \nu_h^{(1)} RT/p. \tag{9.25}$$

Of course, we suppose that $N_h^{(1)}$ is very large compared with $\nu_h^{(1)}$ so that there is no appreciable change in concentration during the process. (Or else the mol number changes are not the integers ν_h themselves but infinitesimal numbers δN_h, proportional to ν_h, as in section 42). From the substitution into eq. (9.15)

$$\left(\frac{\partial \log K}{\partial p}\right)_T = -\frac{\nu_h^{(1)}}{p}, \tag{9.26}$$

a relation which can be integrated. Since T is regarded as a constant in the partial derivative, the constant of integration with respect to p will be independent of p but, in general, not of the temperature T:

$$\log K = -\nu_h^{(1)} \log p + \nu_h^{(1)} \log k_h(T), \tag{9.27}$$

where the second term represents the constant (or, rather, function of T).

Applying this to the special case of eq. (9.20), with $\nu_h^{(1)} = 1$, we find

$$\frac{x_h}{x_h^{(1)}} = \frac{p}{k_h}. \tag{9.28}$$

If we denote by $p_h^{(1)}$ the partial pressure of the component h in the gaseous phase, we can write $x_h^{(1)} = p_h^{(1)}/p$, according to eq. (8.06), whence

$$x_h = p_h^{(1)}/k_h. \tag{9.29}$$

When the mol fraction of a component in a liquid (dilute or perfect) *solution is varied* at constant temperature, *the partial pressure of its vapor varies in the same proportion*, and vice versa. In particular, we can obtain from this equation some information about the solubility

of permanent gases in water and in other liquids: with neglect of quantities of the second order in N_h/N_0, the amount of the gas absorbed by the solvent is proportional to $x_h^{(1)}$ and, therefore, proportional to the partial pressure of the gas in the atmosphere over the solution. This law was established empirically by the English chemist William Henry (1803) and, accordingly, is known as *Henry's law.*

The amount of the absorbed gas (denoted $\alpha_h p_h$) is usually expressed in terms of the volume which it would occupy at 0° C and 760 mm Hg. The quantity α_h is then called *Bunsen's coefficient of absorption* (if p is given in mm Hg). The constancy of the coefficient α can be judged from the following data referring to the absorption of nitrogen (N_2) in water at 25° C.[1]

TABLE 21

HENRY'S LAW

p_{N_2} (mm)	270	300	400	500	601.6	700	800	830
$10^3\alpha_{N_2}$	14.38	14.37	14.31	14.26	14.20	14.28	14.36	14.38

The trend of the dependence of k_h upon T can be deduced from eq. (9.16). Substituting the expression (9.27) into it, we find

$$\nu_h^{(1)} \frac{d \log k_h}{dT} = \frac{Q}{RT^2}. \tag{9.30}$$

The latent heat Q of driving out an absorbed gas from the solution is positive. Therefore, k_h increases as the temperature is raised, so that solvents absorb gases and vapors better when they are cold than when they are heated. As an example we give the values of k for (argon-free) nitrogen dissolved in water.[2]

TABLE 22

t° C	0	5	10	15	20	25	30	35	40	45	50
$k \times 10^{-7}$	4.08	4.57	5.07	5.55	6.00	6.43	6.85	7.23	7.61	7.99	8.37

In the general case, when the possibility of association (or dissociation) is taken into account, eqs. (9.19) and (9.27) give

$$(x_h^{(1)})^{\varphi_h}/x_h = (k_h/p)^{\varphi_h}; \quad p_h^{(1)}/x_h^{1/\varphi_h} = k_h. \tag{9.31}$$

A case in point is the solubility of hydrogen in molten copper (at $t = 1123$° C). Let M be the mass of hydrogen, in mg, dissolved in 100 g of copper.[3]

[1] Drucker and Moles, Zs. phys. Chemie **75**, p. 405, 1911.

[2] I. C. T. from measurements by Fox (Trans. Faraday Soc. **5**, p. 68, 1909).

[3] A. Sieverts and W. Krumbhaar, Zs. phys. Chemie **74**, p. 294, 1910.

TABLE 23

p (mm)....	281	403	606	775	883	971	1046
M.....	0.380	0.443	0.549	0.610	0.680	0.705	0.745
$p^{\frac{1}{2}}/M$	43.5	44.2	43.7	45.1	45.1	45.3	44.2

Hence $g = \frac{1}{2}$ or $\mu = \frac{1}{2}\mu^{(1)}$: the hydrogen dissolved in copper must be atomic. The constancy of $p^{\frac{1}{2}}/M$ has been ascertained for other gases dissolved in molten metals (O_2 in Ag, H_2 in Ni and Fe, etc.). It is in keeping with this that *the absorption increases with temperature.* According to (9.30) this means that the process of driving the gas out of the metal is exothermic.

In many organic solvents we find association of the gas molecules. However, it is usually incomplete, leading to irrational values of g_h.

Exercise 88. From the data about nitrogen in water and from eq. (9.30) calculate the approximate heat of solution Q. (Per 1 mol, $\nu_h^{(1)} = 1$).

Exercise 89. Suppose that the same gaseous phase (1) is adjacent to two condensed solvents. Equation (9.31) is then valid for either of the solvents. Show that the two relations so obtained are compatible with Nernst's law of distribution for the two condensed phases.

63. Raoult's law. The symbol p in eq. (9.31) represents the joint pressure of the liquid solution and of its vapor. According to our discussion in section 41, it is completely determined when the composition of the system and its temperature are given. It is called, therefore, the *boiling pressure* of the solution under these conditions. Equation (9.31) is true for every component: let us apply it to the solvent ($h = 0$) of a dilute solution. (As in the preceding section the condensed phase is " preferred," we shall emphasize it by dropping its superscript 2 while reserving the superscript 1 for the vapor phase).

$$\frac{{x_0}^{1/g_0}}{x_0^{(1)}} = \frac{p}{k_0}, \qquad (g_0 = \mu_0/\mu_0^{(1)}). \tag{9.32}$$

This relation holds for every composition and, in particular, for the limiting case of the pure solvent characterized by $N_1 = \ldots = N_\sigma = 0$ and $x_0 = x_0^{(1)} = 1$. The pressure corresponding to this limiting case is, then, the boiling pressure p_0 of the pure solvent. We can write, therefore, $1 = p_0/k_0$ or $p_0 = k_0$, whence

$$\frac{p}{p_0} = \frac{{x_0}^{1/g_0}}{x_0^{(1)}}. \tag{9.33}$$

This relation takes a very simple form when the solutes are nonvolatile (e.g. most salts) so that their partial pressures in the vapor

are negligible. The gaseous phase can, then, be regarded as pure ($x_0^{(1)} = 1$)

$$p/p_0 = x_0^{1/g_0}. \tag{9.34}$$

On the other hand, the mol fraction $x_0 = N_0/N$ can be represented as $1 - (N_1 + \ldots + N_\sigma)/N$, or by approximation

$$x_0 = 1 - (N_1 + \ldots + N_\sigma)/N_0. \tag{9.35}$$

Whence, within the accuracy of the present theory which neglects terms of the second order in N_h/N_0:

$$\frac{p - p_0}{p_0} = -\frac{1}{g_0}\frac{N_1 + \ldots + N_\sigma}{N_0}. \tag{9.36}$$

The presence of non-volatile solutes lowers the vapor pressure of a liquid. This fact was known to the chemists of the eighteenth century. In 1847 it was noticed by Babo that the relative lowering, $(p - p_0)/p_0$, is independent of the temperature. A few years later (1858) Wüllner found it to be roughly proportional to the concentration of the solution, and his observations were amplified by Ostwald. However, the most extensive investigation of this subject is due to Raoult (1886–1887), who established experimentally the law (9.36) according to which the relative lowering of pressure is determined solely by the mol fractions of the dissolved salts, being quite independent of the nature of the solvent and of the solutes. In earlier work (1878) Raoult also formulated the laws according to which the boiling and melting temperatures are changed by the presence of solutes. They form the subject of the next section.

In the case of a single solute (1) eq. (9.36) can be written in either of the two alternative forms

$$k_x = \frac{p_0 - p}{x_1 p_0} = \frac{1}{g_0}, \qquad k_m = 100\,\frac{p_0 - p}{m_1 p_0} = \frac{\mu_0^{(1)}}{10}, \tag{9.37}$$

where m_1 represents the *number of mols of the solute in 1000 g of the solvent*, called its *molality*. The second form follows from the first by substituting $x_1 = N_1/N_0$ and noticing that in 1000 g of the solvent $\mu_0 N_0 = 1000$ and $N_1 = m_1$. In the case of aqueous solutions $\mu_0^{(1)} = 18$: the quantity k_m should, therefore, be numerically equal to 1.80. However, in the tabulated data N_1 is, of necessity, not the actual mol number of the solute (which is usually unknown) but "the gram-formula weight", i.e. the mol number as it would be if the solute were neither dissociated, associated, nor hydrated. The measured values

of k_m at low concentrations are for many substances close to 1.8, as appears from Table 24.

TABLE 24

LOWERING OF THE BOILING PRESSURE

Solute	m_1	k_m	Solute	m_1	k_m
H_3PO_4.....	0.1	1.80	Citric acid.....	1.0	1.90
Mannitol.....	0.1	1.775	$Pb(C_2H_3O_2)_2$.....	1.0	1.87
Sucrose.....	0.1–0.3	1.82	H_3AsO_4.....	1.0	1.93
Glycerol.....	0.5	1.78			

In general, electrolytic solutes have tabulated coefficients k_m larger than 1.8 because they are often dissociated. Integral and half-integral multiples of 1.8 ($K_2S_2O_3$ 3.65, Na_2WO_4 3.64, $Ba(NO_3)_2$ 3.55, etc.) are fairly common in them. On the other hand, organic solutes show mostly values of k_m under 1.8, and this may be due to association.

For non-aqueous solutions, the data are usually given in the first form (9.37). When $g_0 = 1$ (the solvent does not associate), the formula requires $k_x = 1$. This requirement is satisfied in a large number of cases, provided the concentration is sufficiently low, and even for values of x, from 0.05 to 0.10, it is often still approximately fulfilled.

TABLE 25

LOWERING OF THE BOILING PRESSURE

Solvent	Solute	x_1	k_x
Benzene	Naphthalene	0.005	1.02
Ethyl alcohol	Benzil	0.001	0.99
Mercury *	Ag	0.0025	1.01
"	Tl	0.05	1.05
"	Zn	0.10	0.93
"	Au	0.05	0.55

*Hildebrand and Eastman, J. Am. Chem. Soc. **37**, p. 2452, 1915.

Of course, here too, examples of association (and dissociation) of the solute are not missing, as is indicated by the figure 0.55 relating to gold: this metal must have in mercury the molecule Au_2.

Exercise 90. In the last column of the following table are listed the measured values of the relative lowering of vapor pressure $(p_0 - p)/p_0$ *per* 1 *g of solute in* 1000 *g of solvent.*

SOLVENT	SOLUTE	$\mu_0^{(1)}$	t	$10^4(p_0 - p)/p_0$
Water	Mannitol	18	20° C	0.978
"	Glycerol	18	0°	1.935
Br_2	BrI	179.8		8.70
Benzene	Naphthalene	78.05		4.92
Ethyl alcohol	Benzil	46.05	15°	2.14

Calculate the approximate molecular weights of the solutes from formula (9.37). The accuracy is not very high.

64. Influence of solutes on the temperature and pressure of transformations. Let the temperature and pressure of equilibrium of two phases of the *pure solvent* be T_0, p_0. If small amounts of solutes are added to the two phases, the equilibrium temperature and pressure will be slightly changed, assuming the new values T, p but little different from T_0, p_0. The function $\log K$ depends only on p and T, and we can expand it into the double Taylor series

$$\log K(p, T) = \log K(p_0, T_0) + (p - p_0)\left(\frac{\partial \log K}{\partial p}\right)_0 + (T - T_0)\left(\frac{\partial \log K}{\partial T}\right)_0 + \cdots$$

neglecting terms of higher order.

Equation (9.17) applied to the solvent ($h = 0$) gives

$$\nu_0^{(1)} \log x_0^{(1)} - \nu_0^{(2)} \log x_0^{(2)} = \log K(p, T).$$

When the solvent is pure in both phases, the mol fr[illegible] .62
$x_0^{(1)} = x_0^{(2)} = 1$ and the left side vanishes, so that log [illegible] .79
For the partials of log K we can substitute from eqs. (9.[illegible] 0.34
0.55

$$\nu_0^{(1)} \log x_0^{(1)} - \nu_0^{(2)} \log x_0^{(2)} = -(p - p_0)\frac{\Delta V}{RT_0} + (T \quad \text{lar weights of}$$

T_0^2/l_0 of eq. (9.43) from these data the acid ($\mu_0 = 60.03$).

We shall restrict ourselves to the foll by the physiologist vaporization of a liquid solution (2) cont on a semipermeable utes. Second, freezing of a liquid soluti through the solvent not soluble in the solid solvent. In bot and is denoted by P. in our formulas, will be pure ($x_0^{(1)} = 1$ er part of a cylindrical or freeze out while the solutes remain i For simplicity, we phase is the *preferred* one, in the sens we shall bring it into prominence by dr

$x_0^{(2)} = x_0$ we write, as in the preceding section, $1-(N_1+\ldots+N_\sigma)/N_0$, whence

$$\log x_0 = -(N_1 + \ldots + N_\sigma)/N_0, \quad \log x_0^{(1)} = 0. \qquad (9.40)$$

As we know from the theory of the phase rule (section 41), only one of the two variables T and p can be chosen arbitrarily when the composition of the liquid phase is given. We have, therefore, to distinguish two cases in analyzing eq. (9.39).

(1) We set arbitrarily $T = T_0$ and find the difference of the vapor pressures of the solution and of the pure solvent, *at the same temperature* T_0,

$$p - p_0 = -\nu_0 \frac{RT_0}{\Delta V} \frac{N_1 + \ldots + N_\sigma}{N_0}. \qquad (9.41)$$

The sign of the difference $p - p_0$ is opposite to that of the change of volume ΔV in the transformation. In the case of vaporization, we can use for ΔV the expression (9.25) and obtain with (9.18) the equation

$$\frac{p - p_0}{p_0} = -\frac{1}{g_0} \frac{N_1 + \ldots + N_\sigma}{N_0}, \qquad (9.42)$$

($g_0 = \nu_0^{(1)}/\nu_0$) which is identical with (9.36).

(2) We set $p = p_0$ and obtain the difference of the boiling points
f the solution and of the pure solvent, *at the same pressure* p_0. The
(acc ning of the heat of reaction Q_p is here the latent heat of vaporizing
Th freezing ν_0 mols of the pure solvent; we shall denote it $Q_p = \nu_0 l_0$,
arating is the latent heat referred *to* 1 *mol of the liquid phase.*
in the
nitely sl
the solve

$$T - T_0 = \frac{RT_0^2}{l_0} \frac{N_1 + \ldots + N_\sigma}{N_0}. \qquad (9.43)$$

where ΔV
1 mol of th
$p\Delta V \cdot dN_0$, p l
the solution wi
its contact with
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its original position,
p_0 is $-RTg_0 dN_0 \log$
that dN_0 mols of the li
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remainder of the expe
corresponds to 1 mol of
the change of volu

of vaporization the latent heat is positive, in that of
There exists, therefore, an *elevation of the boiling*
ting point, both due to the solutes. As
is much larger in absolute value, the
derably less than the melting point.
ne quantities N_k in formula (9.43) repre-
numbers (taking into account association,
nd not the gram-formula weights. The
computed for every solvent. Usually,
ol of solute in 1000 g of solvent (normal
numerical values for several solvents

TABLE 26

	T_B	B.P. elevation	T_M	M.P. lowering
Water	373°1	0°521 C	273°1	− 1°86 C
Ethyl ether	307.6	2.18	.....	− 1.79
Ethyl alcohol	351.6	1.17		
Benzene	353.35	2.62	278.5	− 5.10
Chloroform	334.3	3.82	209.6	− 4.80
Acetone	329.2	1.76		
Acetic acid	391.2	3.11	289.7	− 3.90
Aniline	457.5	3.61	266.1	− 5.87
Phenol	455	3.54	314	− 7.4
Nitrobenzene	484.0	5.73	278.8	− 7.0

This effect offers a convenient and powerful method for the determination of unknown molecular weights of solutes which was of great help in the development of our chemical knowledge. The theoretical treatment of these phenomena was due to Van t'Hoff.

Exercise 91. In the last column of the following table are given the measured boiling-point elevations corresponding to a concentration c of the solute *in* g *per* 1000 g *of solvent* given in the third column

SOLVENT	SOLUTE	c (g/1000 g)	$T - T_B$
Ethyl alcohol	I_2	25.4	0°121
Benzene	I_2	12.7	0.13?
Acetone	$HgCl_2$	54.3	0.?
Aniline	Benzil	105.0	?
Phenol	Benzil	21.0	
Acetic acid	Picric acid	11.45	

Calculate from Table 26 the opproximate mo' the solutes.

Exercise 92. What is the relation between t' and the data of Table 26 which refer to molaliti latent heats for water ($\mu_0 = 18$), benzene ($\mu_0 =$

65. Osmotic pressure. It was dis Pfeffer (1877) that solutes exercise a membrane which is impenetrable to t freely. This pressure is called *osmoti* Suppose that the liquid solution fills vessel (Fig. 21) closed above by the

shall assume (at first) that the solutes are non-volatile so that the vapor, in the upper part of the vessel, is free from them; later we shall drop this restriction. Suppose that we have in the vessel a second piston consisting of a semipermeable membrane of the sort just mentioned whose initial position coincides with the plane border surface MN between the liquid and the gaseous phases. We push this piston a little down, in a reversible isothermal way, to the new position $M'N'$, the volume between the planes $M'N'$ and MN being dV. As a result, there will remain only pure solvent above the membrane $M'N'$: It is a process for recovering a certain amount of solvent, say dN_0 mols, from the solution. Since the volume V of the solution is a function of $N_0, N_1, \ldots N_\sigma$, while only N_0 changes, we have

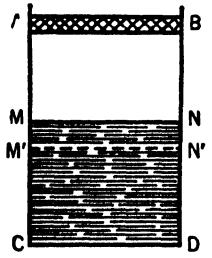

FIG. 21.—Calculation of osmotic pressure.

$$dV = (\partial V/\partial N_0)dN_0 = \bar{v}_0 dN_0,$$

where $\bar{v}_0$ is the *partial molal volume* of the solvent (compare section 32). In pushing the membrane down, work must be done against the forces of osmotic pressure P to the extent

$$DW = -PdV = -P\bar{v}_0 dN_0, \tag{9.44}$$

rding to section 7).

ere is, however, another reversible and isothermal way of sep- N_0 mols of the solvent from the solution. This can be done wing two steps: (1) By moving the upper piston up, infi- and at constant temperature, we vaporize dN_0 mols of The change of volume of the system is, then, $\Delta V \cdot dN_0$, s the change corresponding to the vaporization of . . In this expansion the system does the work r pressure of the solution. (2) We cover ly impermeable membrane. Having lost the vapor is superheated at the pressure p $> p$). As we push the piston down into done till the pressure assumes the value ccording to eq. (3.32), and considering spond to $g_0 dN_0$ mols of the gas. From the pressure stays constant, and the k is $-p_0 \Delta V_0 dN_0$, where ΔV_0 again vent. If it is permissible to neglect id, compared with that of the vapor,

and to use for the gaseous phase the laws of perfect gases, $p\Delta V = p_0\Delta V_0$: the total work done in both steps of the process becomes

$$DW' = -\, RTg_0\, dN_0 \log (p_0/p). \tag{9.45}$$

In the beginning and the end of this process the system is precisely in the same state as in the other method of separation carried out with the semipermeable membrane. Moreover, both processes are isothermal, therefore, $DW' = DW$, since both elements of work are equal to the change of the function Ψ between the initial and the final states (compare section 34). Equating the expressions (9.44) and (9.45), we obtain

$$P = \frac{g_0 RT}{\bar{v}_0} \log \frac{p_0}{p}. \tag{9.46}$$

We have assumed, for simplicity, that the solutes are non-volatile. However, this restriction is not essential and can easily be dropped: we need only imagine from the start a semipermeable membrane (opaque to the solutes) at the surface of the solution. This device permits us to have the pure vapor of the solvent in equilibrium with a solution containing volatile solutes, since the vapors of the solutes cannot penetrate the membrane. We can apply the reasoning leading to eq. (9.46) to the general case. This equation remains valid with the slight change that for p must be substituted the partial pressure of the solvent in the gaseous phase $px_0^{(1)}$:

$$P = \frac{g_0 RT}{\bar{v}_0} \log \frac{p_0}{px_0^{(1)}}. \tag{9.47}$$

The osmotic pressure depends on the ratio of the partial vapor pressures of the solvent, in its pure state and in the solution, being proportional to the logarithm of that ratio.

Equation (9.44) permits another interpretation of the osmotic pressure: It has the form (2.02) of the element of work in the case of generalized forces. The differential dN_0 represents the change in mol number of the solution due to the removal of solvent. $P\bar{v}_0$ is, therefore, the force with which the solution resists (because of the negative sign) such a removal. In other words, it can also be regarded as a tension or suction pulling the solvent back into the solution across the semipermeable membrane. Pfeffer's method of measuring the osmotic pressure is based on this interpretation (Fig. 22): A glass tube, whose lower end is closed by a semipermeable membrane MN (made of cop-

per ferrocyanide), is partially immersed in a beaker filled with pure water. When cane sugar is added to the water inside the tube, the solution in it rises because it sucks in water from the beaker. The rise stops when the pressure of the column AB is exactly equal to the force of suction, i.e. to the osmotic pressure P. This pressure is by no means small: In the case of more concentrated solutions, it is better to connect the tube with a manometer because the column becomes inconveniently high. In fact, pressures up to 268 atm have been measured in sugar solutions. The following familiar demonstration experiment shows how powerful the osmotic pressure can be. A part of an ox bladder is formed into a bag, filled with a strong aqueous solution of ethyl alcohol, and tightly sealed. The bladder is semipermeable in that it holds back alcohol but lets through water. When the bag is immersed in a water-filled vessel, the water is drawn into it with such force that the bladder cannot stand the strain and bursts within a short time.

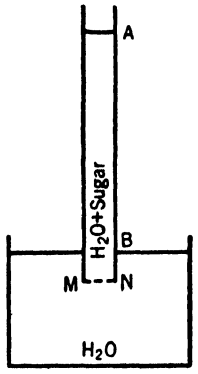

FIG. 22.—Measurement of osmotic pressure.

Let us turn to the general case when there are solutes on both sides of the membrane permeable only for the solvent. Both solutions exercise, then, a sucking action upon the solvent, and the resultant is a tension equal to the difference of the osmotic pressures, directed towards the side of higher concentration. Two solutions of the same osmotic pressure leave the solvent in equilibrium and are called *isosmotic* or *isotonic*. On these facts is based a method for determining the osmotic pressure within living cells, whose integuments are natural semipermeable membranes. When a living cell is placed in an aqueous salt solution of higher osmotic pressure than its own, it begins to lose water and to shrink. When the osmotic pressure of the medium is lower, it swells. Only in solutions approximately isosmotic with its interior does it retain, under the microscope, its size and general appearance. By this method of finding a solution isosmotic with them, the osmotic pressures in many physiological cells have been determined. In plant cells they are sometimes as high as 14 atm. In general, the vegetable and animal cells are nearly isosmotic with the natural saps and animal fluids in which they live. For instance the red corpuscles of the human blood and most other cells of the human body have the same osmotic pressure as the normal blood serum, which in turn is isosmotic with a solution consisting of 0.156 mol of NaCl per 1000 g of water. The harmful effect of certain diseases is believed to be due to

the fact that they upset the osmotic equilibrium of the body fluids and cause a destruction of cells similar to the breaking of the ox bladder in the above-mentioned experiment.

66. Van t'Hoff's equation for osmotic pressure. The expression for osmotic pressure (9.47) takes a simple form in the case of dilute and perfect solutions. On one hand, the partial molal volume then becomes identical with the ordinary molal volume of the solvent: $\bar{v}_0 = v_0$. On the other, we may substitute for $p_0/px_0^{(1)}$ from (9.33) and obtain

$$P = -\frac{RT}{v_0} \log x_0, \tag{9.48}$$

an expression which is valid both for volatile and non-volatile solutes.

If the solution is *dilute*, $\log x_0$ takes the form (9.40) and the volume $N_0 v_0$ of the solvent can be replaced by the volume V of the solution ($V = N_0 v_0$), whence

$$PV = (N_1 + \ldots + N_\sigma)RT. \tag{9.49}$$

This is *Van t'Hoff's equation* for osmotic pressure, which is formally identical with eq. (1.18) for a mixture of perfect gases. By specialization, we can obtain from it the partial osmotic pressures of the individual solutes: if only the component h is present in the solution,

$$P_h V = N_h RT, \quad \text{or} \quad P_h = x_h RT/v_0. \tag{9.50}$$

It follows from (9.49) that the partial osmotic pressures are additive $P = P_1 + \ldots + P_\sigma$. In other words, *the solutes in a dilute solution behave like perfect gases.*

The experimental data are usually expressed in terms of the *molality*, i.e. mol number of the solute per 1000 g of the solvent, which is denoted by m_h. For aqueous solutions, this reduces to $N_0 v_0 = 1000$ cm^3 and, together with eq. (9.50), gives $P_h = RTm_h/1000$, or numerically for 0° C,

$$P_h = 22.4\, m_h \text{ atm}. \tag{9.51}$$

A solution of the molality $m = 1$ is called *normal.* We see that the normal solution has a theoretical osmotic pressure of 22.4 atm. If the molality is computed from the gram-formula weight, eq. (9.51) can give a correct result only barring association, dissociation, and hydration. A few of the experimental values for dilute aqueous solutions (directly measured with copper ferrocyanide semipermeable membranes) are given in Table 27. The values of m_1 listed in this table are *not* corrected for association, etc.

TABLE 27

OSMOTIC PRESSURES

Solute	m_1	P (atm)	P/m_1
Amygdaline	0.0219	0.474	21.7
Antipyrine	0.0530	1.18	22.3
Resorcinol	0.0097	0 199	20.5
Saccharin	0.0029	0 070	24.3
Glucose	0.555	13.2	23.8
Mannitol	0.549	13.1	23.9

When the solution is not dilute we have to fall back on the general eq. (9.48). For aqueous solutions, $v_0 = 18.015$ and the coefficient has the numerical value (at 0° C)

$$P = -\ 2865 \log_{10} x_0 \text{ atm.} \tag{9.52}$$

This formula can be tested for sucrose.[1] It is known that sucrose forms a hydrate, each molecule attaching five molecules of water. The molality of pure water is $1000/18.015 = 55.51$; consequently, in the sucrose solution it is $m_0 = 55.51 - 5m_1$ and $1/x_0 = 1 + m_1/(55.51 - 5m_1)$. The values thus obtained are listed in Table 28.

TABLE 28

OSMOTIC PRESSURE OF SUCROSE

m_1	0.1	0.3	0.6	1.0	2.0	3.0	4.0
P (calc.)	2.24	6.90	14.12	24.4	53.5	89.0	132.5
P (obs.)	2.25	6.91	14.22	24.76	54.9	90.0	129.5

The agreement is surprisingly good and shows that the sucrose solution can be regarded as perfect, as far as this calculation is concerned.

In a *perfect solution* the difference between solvent and solute disappears. It is better, therefore, to avoid the word "solvent" and to speak instead of the "component 0" without making any restrictions as to its mol number. For a binary solution the interpretation of the preceding section can, then, be stated as follows: the partial osmotic pressure P_1 represents the force with which *the other component* 0 is held in the solution (and vice versa). According to (9.48) it is proportional to the logarithm of the mol number of that component. If we gradually remove it from the solution, by the mechanism of

[1] Lord Berkeley and Hartley, Proc. Roy. Soc. (A) 92, p. 477, 1916; H. L. Callendar, Proc. Roy. Soc. (A) 80, p. 466, 1908.

Fig. 21 or by some other method, the difficulty of the removal continually increases and becomes prohibitive in the end, because the last traces are held with an infinite force.

This impossibility of removing the last vestiges of any component from a phase is quite general, as can be seen, in the simplest way, directly from the fundamental equation (9.17) which applies to this case as the solution is then certainly dilute with respect to this component. Log K is, by its definition (9.14), a finite number: therefore, $x_h^{(1)}$ cannot become zero. Otherwise the left side of eq. (9.17) would become infinite, unless $x_h^{(2)}$ were zero at the same time. This means that a component cannot be completely absent from one phase of a system if it has a finite concentration in another phase. All parts of our earth have been in direct or indirect interaction for immense periods of time. Consequently, every sample of terrestrial material must contain minute quantities of all known substances, and an absolutely complete purification of it is impossible. However, the second interpretation of the osmotic pressure here used should not obscure the fact that it is not an abstraction, but, in every way, a *real pressure* like that of a gas. After all, the only tangible thing about any pressure is that it is able to resist the motion of a piston or to set it in motion, and there is no difference between the osmotic and the ordinary pressure in this respect. We shall gain some insight into the deeper nature of the osmotic pressure in section 146 but shall bring out in this chapter the analogies between dilute solutions and perfect gases. We have already seen that the osmotic pressure has a tendency towards uniformity: if the concentration of a solution is non-uniform, the local differences of osmotic pressure set up diffusion currents which make it uniform (barring gravitational fields, compare section 108). In this process some mass of the solute (h) may be transferred from a place with the osmotic pressure P_h to one with P'_h (in an isothermal way). The work done in this transfer must have in a dilute solution the same expression (3.32) as in a perfect gas, in view of the identity of the equations of state. Thus we obtain (per mol of the solute)

$$w = RT \log (P_h/P'_h) = RT \log (x_h/x'_h). \tag{9.53}$$

Exercise 93. What are the osmotic pressures of the following solutions, supposing that they satisfy the formula (9.51): (*a*) antipyrine ($C_{11}H_{12}N_2O$, $\mu = 188.11$) 10 g in 1000 g of water; (*b*) saccharin ($C_7H_5NO_3S$, $\mu = 183.11$), 2 g in 1000 g of water; (*c*) glucose ($C_6H_{12}O_6$, $\mu = 180.09$) 100 g in 1000 g of water?

Exercise 94. What are the osmotic pressures of sucrose solutions ($C_{12}H_{22}O_{11}$, $\mu = 342.17$), according to the formula (9.52) and taking into account hydration as in Table 28: (*a*) 250 g, (*b*) 500 g, (*c*) 1000 g in 1000 g of water?

Exercise 95. Calculate numerically from eq. (9.53) the work (in calories) that must be expended to reduce the mol fraction of a solvent in the ratio 1:10, at 20° C.

67. Saturated solutions. Solubility. In general, a solvent can take up only a limited amount of a solute at a given temperature. For instance, when we gradually add a salt or other solid solute to water, it dissolves at first, increasing the strength of the solution. However, when a certain limiting concentration is reached, further additions do not go into the solution but form a solid precipitate at the bottom of the vessel. Such a solution is called *saturated*, and the solute in it is in equilibrium with its solid crystalline phase. The behavior of liquid solutes is analogous, but we shall restrict ourselves in this section to solids, postponing the discussion of liquids until the next chapter.

The mol fraction x_s of the solute in the saturated state is sometimes called its *solubility*. More often, however, *the solubility is defined as the molality m_s of the solute in the saturated solution.* If we denote by m_0 the molality of the solvent ($m_0 = 1000/\mu_0$),

$$x_s = m_s/(m_0 + m_s). \tag{9.54}$$

(For water $m_0 = 55.51$). The solubilities of some of the more common solutes in water, at 0° C, are as follows:

TABLE 29

SOLUBILITIES

Solute	m_s	Solute	m_s	Solute	m_s
NaCl.....	6.10	$KClO_3$.....	0.270	$CuSO_4$.....	0.88
$NaHCO_3$.....	0.82	$CaCl_2$.....	5.35	$FeSO_4$.....	1.030
NaOH.....	10.50	$Ca(OH)_2$.....	0.0239	Sucrose.....	5.36
KCl.....	3.76	$CaSO_4$.....	0.01292	Lactose.....	0.345
KOH.....	17.3	$AgNO_3$.....	6.65	Maltose.....	1.70

It should be mentioned that the table is meant to illustrate merely the general notion of saturation. The substances listed in it are for the most part " strong electrolytes ", they do not obey quantitatively the theory of dilute solutions of this section but need a correction which will be given in section 115. Moreover, the numbers m_s listed in it present the " gram-formula weights " of the undissociated and unhydrated solutes.

Returning to the theory, we shall assume that the solvent is not soluble in the solute (as is the case with most solids) so that the excess of the solute represents a pure phase ($x_h^{(1)} = 1$). In applying to this case of equilibrium the fundamental eq. (9.17), we label the excess solute (1) and drop the superscript for the liquid solution

$$-\nu_h \log x_{sh} = \log K. \tag{9.55}$$

Both phases are here condensed, so that the change of volume in the process of solution is small and may be neglected in the first approximation ($\Delta V = 0$). According to eq. (9.15), this means that K is independent of the pressure and is a function of the temperature alone: $K = K(T)$. At the same time the heat, $Q_p = Q_V$, developed in the process is entirely due to the difference of the internal energies in the two states $Q_p = \Delta U$ because, within this approximation, the work done by the system is negligible. If we denote by Δu_h the difference of internal energies per 1 mol of solute, $Q_p = \nu_h \Delta u_h$, and we find, from eq. (9.16)

$$\frac{d \log x_{sh}}{dT} = \frac{\Delta u_h}{RT^2}, \tag{9.56}$$

or substituting for x_h the expression (9.50), we obtain

$$\frac{d \log P_h}{dT} = \frac{\Delta u_h + RT}{RT^2} = \frac{l_h}{RT^2}. \tag{9.57}$$

This relation is formally identical with the approximation (7.07) of the Clapeyron-Clausius equation. The process of solution of a salt is completely analogous to the process of vaporization, and the osmotic pressure P_h of the saturated solute corresponds to the boiling pressure p_B of the vapor. In fact, the quantity l_h in eq. (9.57) has the same structure as the heat of vaporization: According to (3.21) and (3.24), $l = \Delta u + p\Delta v$, or, when the volume of the condensed phase is neglected and the vapor regarded as a perfect gas, $l = \Delta u + RT$.

The heat of solution Δu_h is almost invariably positive. Therefore, we conclude from eq. (9.56) that *the solubility of a salt increases with temperature*, unlike the solubility of a gas (compare section 62). Our assumption that the volume does not change is only a first approximation, in reality ΔV has, usually, a very small but finite value. Consequently the effect of added pressure consists in a very slight increase or decrease of solubility.

Exercise 96. The solubility of many aqueous solutes is well represented by the formula

$$\log_{10}\frac{1}{x} = \frac{0.05223A}{T} + B.$$

	Formic Acid	Acetic Acid	Glycerol	Mannitol
Range..	7°.0 to 8°.4 C	−27 to 10	−1.3 to 18	40 to 100
A.....	12 090	14 980	17 150	2142
B.....	−2.243	−2.70	−3.078	−2.102

Calculate from (9.56) the approximate heat of solution Δu_h within the range, assuming that there is no dissociation or hydration.

68. Chemical equilibrium of solutes. We suppose that *chemical reactions* are possible between the components of a dilute solution, according to eq. (6.46)

$$\nu_0 G_0 + \nu_1 G_1 + \ldots + \nu_\sigma G_\sigma = 0. \tag{9.58}$$

The general equation of equilibrium (9.12) takes then the form

$$\nu_0 \log x_0 + \nu_1 \log x_1 + \ldots + \nu_\sigma \log x_\sigma = \log K. \tag{9.59}$$

Since we restrict ourselves to dilute solutions, the volume is practically determined by the amount of the solvent, and its change in the reaction (9.58) is very small. As in the preceding section, we conclude from this that K is very little dependent on the volume and with a good approximation can be regarded as a function of the temperature alone, $K = K(T)$. Moreover, we can replace $x_h = N_h/N$ by N_h/N_0, because the difference would amount only to terms of the second order in the expression (9.59) which are systematically neglected in the theory of dilute solutions. In application to the solvent, this means that we can replace x_0 by 1, obtaining from the last equation

$$x_1^{\nu_1} x_2^{\nu_2} \ldots x_\sigma^{\nu_\sigma} = K(T), \tag{9.60}$$

without regard to whether the solvent takes part in the reaction or not. Because of the relations (9.50) this is equivalent to

$$P_1^{\nu_1} P_2^{\nu_2} \ldots P_\sigma^{\nu_\sigma} = K_P(T) = K\left(\frac{RT}{v_0}\right)^{\nu}, \tag{9.61}$$

$$(\nu = \nu_1 + \nu_2 + \ldots + \nu_\sigma).$$

This equation is formally identical with eq. (8.17) for a mixture of perfect gases. However, the conditions under which the equilibrium takes place are different in the two cases: The mixture of perfect gases is usually observed at a given pressure p which is an important factor

in determining the partial pressures p_h, when only the mol numbers are known. On the other hand, the partial osmotic pressures P_h of the solutes are completely determined by $N_h/N_0 = m_h/m_0$ and have nothing to do with the pressure. This is brought out clearly, if we write the condition in the third form, resulting from (9.60)

$$m_1^{\nu_1} m_2^{\nu_2} \ldots m_\sigma^{\nu_\sigma} = K_m = K(T) \cdot m_0^{\nu} \tag{9.62}$$

(We recall that m_0 is the molality of the solvent: $m_0 = 1000/\mu_0$). The relation between the molalities depends only on the temperature and on the atomic weight of the solvent.

As in the case of gases, the most interesting question is the determination of the degree of dissociation. Let us take as an example the same reaction (8.22) which we discussed in section 52, the dissociation of nitrogen tetroxide (dissolved in chloroform). The expressions for the numbers ν_h and N_h remain the same as those given there. Substituting them into (9.60), we obtain for the degrees of dissociation ξ

$$\frac{4\xi^2}{1 - \xi^2} = K \frac{m_0}{m_1}, \tag{9.63}$$

where m_1 is the molality of N_2O_4 originally dissolved.

Measurements on the dissociation of N_2O_4 in chloroform were carried out by Cundall.[1] Lewis and Randall[2] give the following table calculated from his data (for 0° C).

TABLE 30

CHEMICAL EQUILIBIRUM OF NITROGEN TETROXIDE

$x_{N_2O_4}$	x_{NO_2}	$10^8 K$
0.018	0.00010	49
0.037	0.00012	35
0.050	0.00015	43
0.066	0.00019	52
0.125	0.00029	66

The constancy of K is not very good owing, perhaps, to the insufficient accuracy of the colorimetric determinations of x_{NO_2}. Of course, the degree of dissociation is quite different from that which gaseous nitrogen tetroxide has under the same conditions: K_P comes out here about 2.00×10^{-4} atm, while (8.25) gives 0.020 atm for the gas reaction at 0° C. This is not surprising since the heats of reaction are

[1] Cundall, J. Chem. Soc. 59, 1076, 1891; 67, p. 794, 1895.

[2] Lewis and Randall, Thermodynamics, p. 303, New York, 1923.

very different in the two cases: in the chloroform solution there must be added the difference of the *heats of solution* of the two components.

For very high dilutions ($m_1/m_0 \ll 1$), ξ approaches unity. This is a general property of dilute solutions, as we can readily see from eq. (9.64): Whenever the dissociation leads to an increase in the number of molecules ($\nu > 0$), dilution (i. e. increasing N_0) has the same effect as increasing K (compare section 52). It advances the dissociation which becomes complete in the limiting case of extreme dilution.

This influence of the relative amount of the solvent upon the degree of dissociation is the analogue of the effect of neutral gases upon a gas mixture discussed in section 54. The addition of neutral solutes has, according to eqs. (9.61) and (9.62), no appreciable effect upon the equilibrium. The reason for this is that in a dilute solution the quantity of a solute is, necessarily, small and its contribution to the available volume negligible. On the other hand, the remarks made in the sections 53 and 55 about the depressing influence of the excess of one active component and about the mutual interdependence of two simultaneous reactions remain fully valid in the case of solutions.

Exercise 97. Calculate the factors RT/v_0 and m_0 entering into K_P and K_m for the following solvents: water ($\mu_0 = 18$, density $d = 1.00$), chloroform ($\mu_0 = 119.38$, $d = 1.526$), ethyl ether ($\mu_0 = 74.08$, $d = 0.736$), benzene ($\mu_0 = 78.05$ $d = 0.900$).

Exercise 98. Carbonic acid and acetic acid in aqueous solutions dissociate into ions according to the following equations:

$$H^+ + HCO_3^- - H_2CO_3\,(aq) = 0, \qquad K_m = 1.84 \times 10^{-6},$$

$$H^+ + C_2H_3O_2^- - C_2H_4O_2\,(aq) = 0, \qquad K_m = 3.50 \times 10^{-7}.$$

Calculate the degrees of dissociation for the molalities m_1 (of the acid originally dissolved) 0.001, 0.01, 0.05, 0.10, 0.20.

Exercise 98′. Show that the equation of equilibrium (9.62) can be also written in the form

$$N_1^{\nu_1} N_2^{\nu_2} \ldots . N_\sigma^{\nu_\sigma} = K(T) \cdot N_0^{\nu} \qquad (9.64)$$

CHAPTER X

EQUILIBRIUM OF BINARY SYSTEMS [1]

69. General remarks. The character of the equilibrium between different phases of a system with two independent components (*binary systems*) is of great importance in chemistry and metallurgy. A vast body of experimental data, pertaining to it, has been accumulated in these branches of science. The role of thermodynamics is to help in the explanation and classification of this material by enumerating the theoretically possible types of equilibrium. Of necessity, much of the information derived from thermodynamics is qualitative: The problem consists in treating the equilibrium between solid, liquid, and gaseous binary solutions (in the sense of section 56), but we do not possess the theoretical knowledge of the condensed phases which would be necessary for a quantitative treatment, viz. the equations of state and the energy expressions for the solid and liquid state. Fortunately there exist, if not real, at least ideal systems in which the theory can be completely carried through, namely, the simplified models which we called *perfect* solutions in section 56.

The essence of this approximation is that the interactions of the components are taken into account only in so far as they affect the mutual solubility. Apart from this, each component is treated as if it were alone. We propose, therefore, to work out, for every type of equilibrium, the formulas and curves pertaining to the case of perfect solutions. Comparing them with the experimental curves, we shall see that this model is not oversimplified and gives a good account of the main features of real systems, giving examples of every type of diagram that occurs in experiments.

According to the discussion of section 41, the maximum number of phases which can be simultaneously in equilibrium exceeds by two the number of independent components: for binary systems it is 4. Four phases can coexist only at the " quadruple point " for which all the variables of the system (viz. temperature, pressure, and composition of the phases) are perfectly determinate. In the case of the

[1] This chapter may be skipped without loss of continuity.

coexistence of three phases the system has one degree of freedom; i.e. one of the variables can be chosen arbitrarily. For experimental reasons, this is, usually, the pressure: when p is given, the whole system is determined, so that equilibrium can take place only at one definite temperature and for definite compositions of all the three phases. The most interesting case is, however, that of the *coexistence of two phases*, because it was shown in the general theory of Chapter VI that the other cases can be reduced to it. Then, two of the variables can be chosen at random: for instance, we can prescribe the temperature and the composition of one phase, so that equilibrium is possible at only one definite pressure. Or else, we can select arbitrarily the pressure and the composition of one of the phases, and so completely determine the equilibrium temperature.

The parameter which determines the composition of a phase is the mol fraction of either component. If we indicate the components by the subscripts 1 and 2, and the phase by the superscript (j), we find from the definition (8.05) of the mol fraction

$$x_1^{(j)} + x_2^{(j)} = 1. \tag{10.01}$$

In most of the applications of this chapter we shall suppose that the components do not interact chemically. In this case, there is no difference between the independent components and the actual constituents.

A few remarks about ternary systems will be made in section 75.

70. Vapor pressure of binary systems at constant temperature. The available experimental data have reference to the equilibrium of liquid binary solutions and their vapors, because the vapor pressures of solid solutions are too low to be conveniently measurable. Therefore, we shall now restrict ourselves to the liquid-gaseous equilibrium and we shall further assume that, in the liquid phase, the components are mutually soluble in all proportions. We shall indicate the mol numbers of the two components, in the liquid phase, by x_1, x_2 and, in the vapor, by x'_1, x'_2, and shall apply the relations derived in the preceding chapter for perfect solutions.

In a perfect solution either component can be regarded as the solvent and obeys Raoult's law. If the molecules remain unchanged in the process of vaporization, this law must be used in the form (9.33), with $g_0 = 1$,

$$px'_1 = p_{B1}\, x_1, \quad px'_2 = p_{B2}\, x_2, \tag{10.02}$$

where p_{B1} and p_{B2} denote the boiling pressures of the two components

in their pure state. Adding these two equations and taking into account the relations (10.01) we find

$$p = p_{B1}\, x_1 + p_{B2}(1 - x_1). \tag{10.03}$$

The plot of the pressure against the mol number x_1 in the liquid phase is a straight line (Fig. 23).

We can express the pressure also in terms of x'_1, the mol number in the gaseous phase. Dividing the eqs. (10.02) by p_{B1}, p_{B2} respectively, and then adding them,

$$p = \frac{p_{B1} p_{B2}}{p_{B2}\, x'_1 + p_{B1}(1 - x'_1)}. \tag{10.04}$$

This corresponds to the curve of hyperbolic character labeled " vapor " in Fig. 23. This figure represents the so-called *px-diagram*:

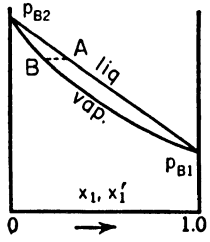

FIG. 23.

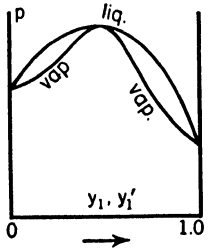

FIG. 24.

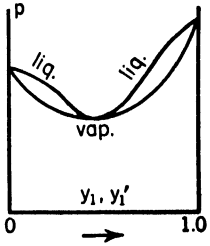

FIG. 25.

Boiling pressure as a function of composition.

when the composition and pressure of the liquid phase are given by the point A (on the " liquidus " curve), the constitution of the vapor in equilibrium with it is obtained by drawing a horizontal to the point B of intersection with the "vapor" curve.

When we turn to the experimental *px*-diagrams of pairs of organic and inorganic liquids, such a large proportion of them is found to be of the general type of Fig. 23 that it is justifiable to call it the *normal type*. It is true, the representation is not quantitative in that the " liquidus " locus geometricus is, generally, not straight but also curved. But it is typical in that both curves are monotonic and the vapor pressure of the solution intermediate to the boiling pressures of the pure components. Especially, pairs of chemically closely related substances (benzene-toluene, hexane-octane, methyl and ethyl alcohol, etc.) belong to this type. We have mentioned in section 56 that such pairs must be expected to approximate the behavior of perfect solutions.

However, there exist two other types of (p, x)-diagrams which are illustrated by the Figs. 24 and 25. We shall call them the p_{max}-type and the p_{min}-type. It is often somewhat uncertain what the molecular weight in the liquid phase is. Therefore, the pressure is usually plotted not against the mol fraction but against the mass fraction

$$y_1 = M_1/(M_1 + M_2) = x_1/(x_1 + \mu_2 x_2/\mu_1), \qquad (10.05)$$

M_1, M_2 being the masses of the two components and μ_1, μ_2 their molecular weights. This way of plotting has also some theoretical advantages as we shall see in section 74.

Our simplified model (the perfect solutions) permits us to predict a behavior of this kind in certain cases, viz. when the molecular weights of the components are different in the liquid and gaseous states. The generalization (9.33) of Raoult's equation must, then, be used, and this leads, instead of (10.03), to the equation

$$p = p_{B1}\, x_1^{1/g_1} + p_{B2}(1 - x_1)^{1/g_2}, \qquad (10.06)$$

where $g_1 = \mu_1/\mu'_1$ and $g_2 = \mu_2/\mu'_2$. It is to be expected that the case, when both components are subject to association or dissociation of molecules, is a rare one. It will be sufficient, therefore, to assume that only the exponent g_1 is different from 1, while $g_2 = 1$. It is easy to see that, under this assumption, the slope dp/dx_1 will, in general, go to zero for a value of x_1 between 0 and 1, provided the boiling pressures p_{B1} and p_{B2} are of the same order of magnitude. This means that the pressure reaches in this interval an extreme; whether it is a maximum or a minimum depends upon the sign of the second derivative $d^2p/dx_1^2 = (1 - g_1)g_1^{-2}p_{B1}x_1^{(1-2g_1)/g_1}$. In the case of association in the liquid phase $g_1 > 1$, and the sign is negative; in the case of dissociation, $g_1 < 1$, and it is positive. We should, therefore, expect the p_{max}-type when the molecules of one of the liquid components are associated, and the p_{min}-type when they are dissociated.

On the whole, these expectations are borne out by the facts: It is known that hydroxylated liquids have a tendency towards association when mixed with another liquid which is free of the hydroxyl group. Upon looking through the list of systems showing the p_{max}-type, we find that it consists largely (although not exclusively) of such pairs of liquids. On the other hand, aqueous solutions of HI, HBr, HCl, HF which are considerably dissociated belong to the p_{min}-type. However, there is another cause which may produce these kinds of px-diagrams: the existence of chemical compounds of the two components. If the vapor pressure of the compound is higher than of either pure component,

the px-curve must have a maximum, if it is lower, a minimum. The reason why the two curves in the Figs. 24 and 25 have a *joint* maximum or minimum will become clear in section 74.

This theory has an important practical application in the process of *distillation*. In the normal pressure curve (Fig. 26) there corresponds to the composition A of the liquid the composition B of the vapor; that is, the vapor is richer in the component (2) with the higher boiling pressure. Prolonged boiling at constant temperature, therefore, causes the liquid to become poorer in this component so that its representative point moves downward towards p_{B1}. If the purpose of distillation is to drive out the more volatile component, one has only to continue boiling and, eventually, the liquid will consist of the practically pure component (1). On the other hand, the procedure is different when it is desired to prepare the pure component (2). Starting again from the state A, we let the solution boil for a time and collect its vapor which has the constitution B. Condensing this vapor we obtain a liquid of the same constitution represented in our diagram by the point C. Boiling this fraction (at the same temperature) gives a vapor of the composition D, etc. By such steps it is possible to approach closely the point p_{B2} representing the pure volatile component. It is clear that pressure curves of the $p_{\min}$-type (Fig. 25) preclude the success of the first kind of distillation, and curves of the $p_{\max}$-type (Fig. 24) that of the second. The best-known example is the water-ethyl alcohol solution having a maximum at 4.43% water by weight so that the purification stops with 95.57% alcohol (about 194° proof). Distillers have learned, in recent years, to get around this maximum by adding a third component to the solution.

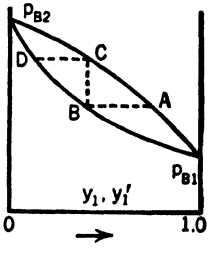

FIG. 26.—Distillation.

71. Temperature of transformation at constant pressure. When the pressure is kept constant, the temperature of equilibrium of two binary phases is completely determined by the composition of one of them. To treat this case theoretically for perfect solutions, we have to fall back again upon the fundamental eqs. (9.17) or (9.22), but to evaluate the equilibrium constant K in a way somewhat different from that of the preceding section. We can apply to the first component the eq. (9.16) in the form

$$\left(\frac{\partial \log K_1}{\partial T}\right)_p = \frac{l_1}{RT^2}, \qquad (10.07)$$

where l_1 is the latent heat of transformation referred to 1 mol of the first component in the primed phase ($\nu'_1 = 1$, ν_1 either integral or fractional).

We have pointed out in section 45 that the latent heat is a rather slowly varying function of T which can be regarded as constant in the first approximation. This approximation is amply sufficient for the purpose of the present investigation because we have already introduced an element of inaccuracy by supposing the phases to be perfect solutions. Integrating, we find therefore

$$\log K_1 = - l_1/RT + C_1(p), \tag{10.08}$$

and a similar relation with the subscripts 2, for the second component. In the particular case, when the second component is absent ($x_1 = x'_1 = 1$), we find from (9.17) $\log K_1 = 0$, and at the same time the temperature of equilibrium is the transformation temperature T_{01} of the pure first substance. This serves to determine the constant as $C_1(p) = l_1/RT_{01}$. There follows

$$\left.\begin{aligned} K_1 &= \exp \frac{l_1}{R}\left(\frac{1}{T_{01}} - \frac{1}{T}\right), \\ K_2 &= \exp \frac{l_2}{R}\left(\frac{1}{T_{02}} - \frac{1}{T}\right). \end{aligned}\right\} \tag{10.09}$$

On the other hand, the fundamental equations take the form (9.22), with $\nu'_1 = \nu'_2 = 1$,

$$(x'_1/K_1)^{1/\nu_1} = x_1, \quad (x'_2/K_2)^{1/\nu_2} = x_2. \tag{10.10}$$

We shall treat in this section the case when the *components* in both phases are *mutually soluble in all proportions*. Both components are then present in either phase, and eqs. (10.10) must be treated as simultaneous. The relations (10.01) permit us to eliminate all the variables but x_1. In particular, when there is no association in either component ($\nu_1 = \nu_2 = 1$),

$$x_1 = \frac{1 - K_2}{K_1 - K_2}. \tag{10.11}$$

This equation and $x'_1 = K_1 x_1$ resulting from (10.10) give the explicit expressions of the compositions of both phases (x_1 and x'_1) as functions of temperature. They apply to all cases of two-phase equilibrium, of which the more important (because of the accumulated experimental material) are liquid-vapor and solid-liquid. The graphical representation of these formulas leads to the so-called (Tx)-

diagram (or Ty-diagram, if the temperature of transformation is plotted against the *mass fraction* y). As an example we give in Fig. 27 the yT-curves computed with the help of our equations for the solid liquid equilibrium of an alloy of platinum ($T_{01} = 2032°$, $l_1 = 5270$ cal mol^{-1}) and gold ($T_{02} = 1338°$, $l_2 = 3140$ cal mol^{-1}) as dashed lines. For comparison the experimental curves are drawn as solid lines. The agreement is by no means quantitative, but the general trend is well accounted for by the theory. It will be noticed that *the order of the curves is inverted by comparison with Fig.* 23, the curve giving the composition of the phase, stable at higher temperatures, lying above the other. Apart from this, there is a complete analogy between the cases of constant temperature (preceding section) and constant pressure inasmuch as there exist, in addition to the "normal" or monotonic type of Fig. 27, also T_{max}- and T_{min}-types of curves (of the same shape as those of Figs. 24 and 25). They are, especially, a frequent occurrence in the liquid-vapor equilibrium of binary systems composed of organic substances. It would be easy to generalize our formulas for the case of any numbers ν and to show that association or dissociation in the liquid phase leads to these types. However, this is unnecessary because in section 74 we shall give the general proof that conditions which produce the p_{max}-type of the px-diagram also cause the T_{min}-type of the Tx-graph. In the same relation to each other stand the p_{min}-and T_{max}-types. We can, therefore, refer, with respect to the influence of association and dissociation, to the discussion at the end of the preceding section.

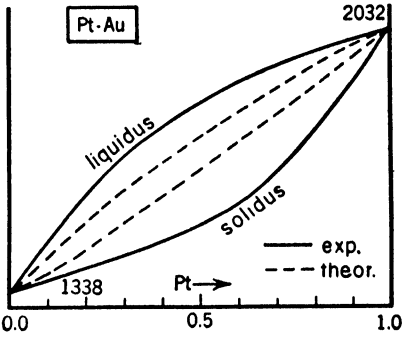

FIG. 27.—Temperature of fusion as a function of composition.

Curves of T_{min}-type occur also in the equilibrium of binary metal alloys with their melts, especially, when one of the components belongs to the ferromagnetic group. We did not find in literature any discussion of the causes responsible for the minimum, but the prevailing tacit assumption seems to be that it is due to the existence of intermetallic compounds. It should be mentioned, however, that in the case of Co-Mn alloys, a close investigation in Tammann's laboratory revealed that compounds of these metals do not exist.[1] In view of

[1] Hiege, Zs. anorgan. Chemie **83**, p. 253, 1913.

this, we calculated from our formulas the Ty-curves (Fig. 29) which would result on the assumption that Co ($T_{02} = 1762°$, $l_2 = 3950$ cal mol^{-1}) has in the solid state a diatomic molecule when in alloy with Mn ($T_{01} = 1523°$, $l_1 = 3560$ cal mol^{-1}). Comparing the theoretical curves with the experimental Ty-diagram (Fig. 28) by Hiege,[1] we see that the minimum occurs at the right mass fraction (30% Co) but at a temperature which is some 80° lower than that measured. Although this discrepancy lies well within the limits of the theoretical inaccuracies, we do not feel that the evidence is strong enough to prove positively the existence of association, especially as it is not quite clear what this would mean in terms of the lattice structure of the alloy.

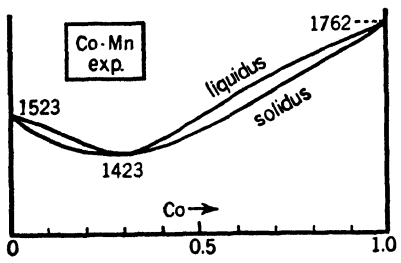

FIG. 28.

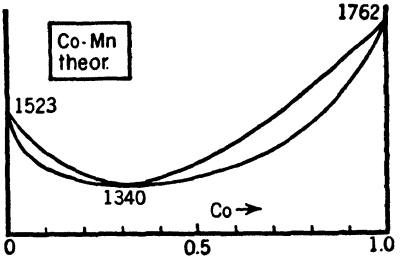

FIG. 29.

Temperature of fusion as a function of composition.

But we do wish to point out that there lies here a problem which, presumably, could be settled by experimental (X-ray) methods.

72. Case of mutually insoluble components. Let us suppose that in one of the phases the components are mutually insoluble. This can be illustrated by many examples of which we mention only a few: (1) *Aqueous solution of a salt which is insoluble in ice.* When the liquid solution is cooled, either a part of the salt is precipitated or a part of the water congealed, conditional upon the concentration of the solution. There are, therefore, two cases of two phase equilibriums: liquid solution—solid salt and liquid solution—pure ice. (2) *Molten alloy of two metals which do not form mixed crystals.* Upon cooling, either of the metals can freeze out partially, according to the composition of the liquid phase. (3) *Mixture of the vapors of two immiscible liquids.* As the temperature is lowered, either one or the other liquid condenses.

In all these cases we have equilibria of two kinds of pure substances with the (liquid or gaseous) solution. If we suppose that the pressure p is kept constant, eqs. (10.09) and (10.10) of the preceding section

[1] Hiege, *loc. cit.*

still apply, but we must put in them $x_1 = 1$ or $x_2 = 1$, the condition that the unprimed phase is pure. Equations (10.10) become

$$x'_1 = K_1, \qquad x'_2 = (1 - x'_1) = K_2, \tag{10.12}$$

and they are no longer simultaneous but refer separately to the two possible kinds of equilibrium.

To make this quite clear, we shall consider a special example, the molten alloy of cadmium ($T_{01} = 596°$, $l_1 = 1245$ cal) and bismuth ($T_{02} = 546°$, $l_2 = 2110$ cal). The first of eqs. (10.12) gives then the composition of the liquid phase when it is in equilibrium with solid bismuth; the second, when it is in contact with solid cadmium. Com-

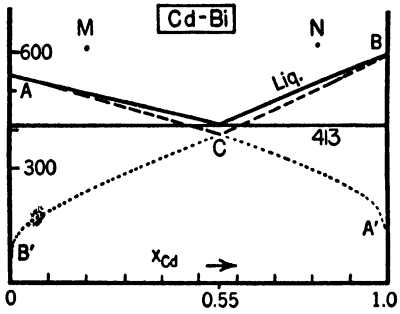

FIG. 30.—Solid lines experimental, dashed and dotted curves theoretical.

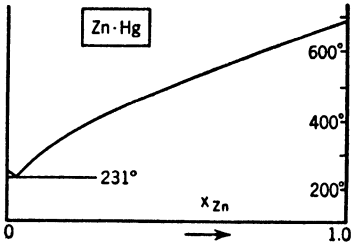

FIG. 31.—Experimental liquidus curve.

puting K_1 and K_2 from eqs. (10.9), we find, for the first case, the theoretical curve of AA' of Fig. 30; for the second, the curve BB'. Let us start from a composition (x'_1) and temperature (T) of the liquid alloy represented by the point M. When this system is slowly cooled, the representative point first moves down vertically, until it hits the curve AA'. From then on, bismuth begins to freeze out; accordingly, the cadmium concentration of the liquid phase increases and, as the cooling proceeds, the representative point moves along the equilibrium curve toward the point C. In a similar way, when we start from the point N, the state of the cooled system first strikes the curve BB' and then begins to move along it to the left. In no case, however, does the representative point move beyond the intersection C of the two curves. The point C is a triple point in which the liquid phase is in equilibrium both with bismuth and with cadmium. As soon as it is reached both components begin to freeze out simultaneously, forming a microcrystalline mixture of the two solid phases (pure bismuth and pure cadmium). The point C corresponds, therefore, to the lowest

temperature at which the alloy can be maintained in a liquid state at the given pressure p: for this reason, it is called the *eutectic point* (eutectic = Greek for readily melting). The dotted parts of the curves AA' and BB' have no physical reality as far as the system under consideration is concerned. For comparison we give the experimental Tx-diagram of the cadmium-bismuth alloy[1] (solid curves in the same Fig. 30): considering the crude approximation of the formulas (10.09), the agreement must be regarded as very good. The theoretical eutectic point lies at the same concentration as the experimental ($x = 0.55$) but about 25° too low.

This example is quite characteristic. The microcrystalline mixture into which the liquid phase congeals at the eutectic point is called, in the case of metallic components, the *eutectic alloy*. It has, usually, the same content of the two components as the liquid, but this may be said to be accidental, in the sense that it is due to the kinematics of the freezing process. As we know from section 39, the equilibrium conditions do not depend on the extension of the phases. Therefore, the eutectic liquid should be in equilibrium with the solid phases taken in any proportion. This is, in fact, observed and indicated in Fig. 30 by the horizontal line passing through the empirical eutectic point. In the case of aqueous solutions of salts, the eutectic congelations were formerly called *cryohydrates*.

It is worth pointing out that, as long as the solution can be regarded as perfect, each of the two curves given by eqs. (10.12) depends on the properties of one component only and is quite independent of the other. In application to our example (Cd–Bi) this means that the curve AA' of cadmium has exactly the same shape and position, no matter what the other component is. In order to measure a large part of it and to bring out its curvature, we must choose, as the second component, a metal with a low boiling point, e.g. mercury. Unfortunately the Tx-diagram for Cd–Hg was not available, and to illustrate this point we give in Fig. 31 the diagram for zinc-mercury. When we consider a mixture of vapors of two immiscible liquids in equilibrium with one of the pure liquid phases, the corresponding curve gives us the equilibrium of this pure phase with its own vapor. The partial vapor pressure of this component is, therefore, exactly the same as if the other component were absent.

73. Case of partial mutual solubility. Other complications. In order to complete our discussion of binary equilibrium, we shall give here a brief schematic résumé of the conditions which are to be expected in the case of partial solubility in some of the phases. To fix our ideas

[1] Petrenko and Fedorov, Zs. anorg. Chemie 6, p. 212, 1914.

let us consider the case of two metals which form mixed crystals of two kinds. The bulk of the kind α consists of the first metal while the content of the second is smaller and can vary continuously from nothing to a certain limit. In the kind β the conditions are reversed: the second metal dominates and the proportion of the first has a continuous range with a relatively small upper limit. Crystals of intermediate composition do not exist. There are, therefore, two cases of solid-liquid equilibrium: coexistence of the liquid alloy of the two metals with the mixed crystal α and with the mixed crystal β.

As long as the mol numbers of the second metal (x_2, x'_2) are small in both phases, they can change continuously and the conditions are exactly the same, in this range, as in the case of complete solubility (section 71). Assuming, by way of an approximation, that the solution is perfect, we can describe the equilibrium between the liquid alloy and the crystal α mathematically by the formulas (10.09), (10.10), and (10.11). The graphical representation is, therefore, also analogous to the corresponding range of Fig. 27. Two curves diverge from the boiling point A of the pure first component (Fig. 32), the one giving the mol number x'_1 in the liquid phase, the other x_1 in the crystal α; points of the two curves lying on the same horizontal are in equilibrium. However, these curves do not extend across the whole diagram but stop when x_1 reaches its limiting value. This fact has a bearing on the interpretation of the constants T_{01}, T_{02} of eqs. (10.9): For the same reason as in section 71 we conclude that T_{01} is the melting point of the pure first metal. However, we cannot identify T_{02} with the melting point of the second because it is not permissible to extrapolate our curves until this metal is pure. It is better to denote this constant by T'_{02}, and to bear in mind that its numerical value cannot be predicted from any general considerations. It can be larger or smaller than T_{01}: When $T'_{02} > T_{01}$ the two equilibrium curves go from the point A upwards; when $T'_{02} < T_{01}$, they go downwards. Similar conditions prevail in the other case of equilibrium (the coexistence of the liquid phase with the mixed crystal β), when the mol numbers x_1, x'_1 are small. The two equilibrium curves diverge from the melting point B (temperature T_{02}) of the pure second component and are again represented by eqs. (10.9), (10.10), and (10.11) with the new constants T'_{01}, T_{02}. They go up or down from the point B depending upon the numerical value of the ratio T'_{01}/T_{02}. We have, therefore, to distinguish three cases: (1) The equilibrium curves go downward on both sides, from the point A and from the point B. (2) They go downward on one side and upward on the other. (3) They go upward on both sides.

The first case, illustrated by Fig. 32, is the most common. Suppose we slowly cool the system, starting from a state represented by the pair of points NN'. Some α crystal freezes out consisting mainly of the first component; the remaining liquid therefore becomes richer in the second component. The representative points move down along the branches AD and AC, so that later-freezing crystalline fractions are of lower x_1. This continues until the eutectic point C is reached marking the intersection between the "liquidus" curves AC and BC. In this state the liquid alloy is simultaneously in equilibrium with the mixed crystals α and β. As in the case of the preceding section, the alloy freezes completely when the temperature is lowered further. The only difference is that it forms a microcrystalline mix-

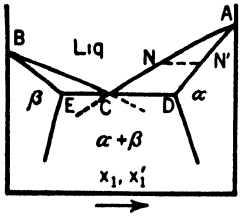

FIG. 32.

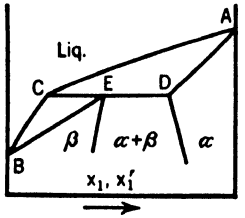

FIG. 33.

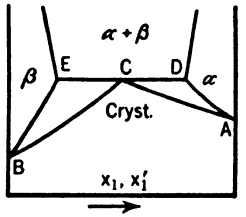

FIG. 34.

Equilibrium in case of partial mutual solubility.

ture, not of the two pure substances, but of the two mixed crystals α and β, having the composition indicated by the points D and E. This is the end of the motion along the branches AD, AC, and their dotted continuation below the line DE has no physical reality. The mixed crystals represented by the points D and E are not only in equilibrium with the eutectic liquid alloy C but also with each other. The question may be put, therefore, as to the equilibrium of the two crystalline phases at temperatures below the eutetic. The answer is given by the two schematic lines going downward from D and E: Points of them lying on the same horizontals are in equilibrium. It is an empirical fact that these lines slope away from each other.

The second case is represented by Fig. 33, which is self-explanatory because the notations in it are the same as in Fig. 32. We have used the example of two metals only to fix our ideas. All we have said applies, mutatis mutandis, to the equilibrium of two partially miscible liquids with their vapor, and to similar cases. The cases illustrated by the Figs. 32 and 33 are, in fact, as characteristic of mixed crystals as of the binary equilibrium of liquids and vapors. However, the third case represented by Fig. 34 applies only to a rather unusual system:

Two substances form, in the solid phase, a mixed crystal in all proportions, but, upon being melted, they are partially miscible liquids. At temperatures lower than the eutectic (C) the crystal melts either into the solution α or the solution β (depending upon its composition), at the eutectic point into a turbid emulsion of the two solutions.

It goes without saying that the conditions considered here include the limiting case when the first component is partially soluble in the second but does not admit the second as a solute and crystallizes (condenses or melts) in its pure state. The point D in the above figures lies then on the vertical $x_1 = 1$ passing through A.

We have enumerated in this chapter the types of binary equilibrium which can be expected when the components do not form chemical

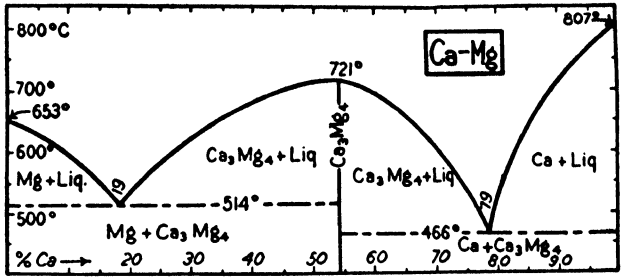

FIG. 35.—Liquidus curve.

compounds. The presence of chemical compounds does not add much new to the discussion, from the conceptual point of view, but makes the curves look more complicated. One example will be sufficient to illustrate this: In Fig. 35 we give the Tx-diagram for the melting of Ca-Mg alloys.[1] These two metals form the compound Ca_3Mg_4; there are three solid phases (pure Ca, pure Mg, Ca_3Mg_4) which happen to be insoluble in one another. At 721° C we have the equilibrium of the liquid and solid phase of the compound. The diagram is divided by this point into two halves: The left representing a binary system composed of the compound and magnesium, the right of the compound and calcium.

74. Maxima and minima of the equilibrium curves. We have seen in the preceding sections that the treatment of binary systems, as if their phases were perfect solutions, gives a good qualitative account of all the observed phenomena. It is even probable that the not very large quantitative discrepancies are due, primarily, to the crudity of our approximation in putting $l = \text{const}$ (section 71) and only in rare cases to the inadequacy of the description in terms of

[1] I.C.T. based on Baar, Zs. anorg. Chemie 70, p. 352, 1911.

perfect solutions. In particular, we could account for the appearance of maxima and minima in the equilibrium diagrams. However, it will be useful to give here a theorem (due to Gibbs) relating to these maxima and minima which is free from any assumption as to the nature of the system.

Let us denote by Φ, M_1, M_2 the thermodynamical potential and the masses of the two components in the first phase, by Φ', M'_1, M'_2 the same quantities in the second. We shall use the equations of equilibrium between the two phases in the form (6.33)

$$\Delta_1\Phi \equiv \frac{\partial\Phi}{\partial M_1} - \frac{\partial\Phi'}{\partial M'_1} = 0, \quad \Delta_2\Phi \equiv \frac{\partial\Phi}{\partial M_2} - \frac{\partial\Phi'}{\partial M'_2} = 0. \tag{10.13}$$

It was pointed out in sections 39 and 41 that Φ is a homogeneous function of the first degree in the mol numbers N_1, N_2 and the masses M_1, M_2. Consequently, the quotient $\Phi/(M_1 + M_2)$ is a homogeneous function of the degree zero; in other words, it depends only on the ratio M_1/M_2. In particular, we can represent it as a function ζ of the mass fraction (10.05), and a similar conclusion holds with respect to the other phase:

$$\Phi = (M_1 + M_2)\,\zeta(y_1), \quad \Phi' = (M'_1 + M'_2)\,\zeta'(y'_1), \tag{10.14}$$

and by partial differentiation

$$\frac{\partial\Phi}{\partial M_1} = \zeta(y_1) + (1 - y_1)\frac{d\zeta}{dy_1}, \qquad \frac{\partial\Phi}{\partial M_2} = \zeta(y_1) - y_1\frac{d\zeta}{dy_1}. \tag{10.15}$$

These expressions are quite general, no matter whether the components form chemical compounds or not. The variables entering into eqs. (10.13) are, therefore, y_1, y'_1, p, T. We give to these variables increments dy_1, dy'_1, dp, dT in such a way that the two phases remain in equilibrium, i.e. eqs. (10.13) continue to hold. We can, therefore, take their total differentials

$$\frac{\partial\Delta\Phi}{\partial y_1}dy_1 + \frac{\partial\Delta\Phi}{\partial y'_1}dy'_1 + \frac{\partial\Delta\Phi}{\partial p}dp + \frac{\partial\Delta\Phi}{\partial T}dT = 0, \text{ etc.}$$

The partials with respect to p and T are given by the formulas (6.51) and (6.52), while those with respect to y_1, y'_1 follow from eqs. (10.15)

$$\left.\begin{aligned} (1-y_1)\frac{d^2\zeta}{dy_1^2}dy_1 - (1-y'_1)\frac{d^2\zeta'}{dy'^2_1}dy'_1 + \Delta V_1 dp - \frac{l_{g1}}{T}dT = 0, \\ -y_1\frac{d^2\zeta}{dy_1^2}dy_1 + \quad y'_1\frac{d^2\zeta'}{dy'^2_1}dy'_1 + \Delta V_2 dp - \frac{l_{g2}}{T}dT = 0, \end{aligned}\right\} \tag{10.16}$$

where ΔV_1, ΔV_2 are the increases of the volume of the system and l_{g1}, l_{g2} the latent heats contingent upon the respective transfers of one gram of the first or second component from the unprimed to the primed phase. We can eliminate dy'_1 by multiplying the first equation by y'_1, the second by $(1 - y'_1)$ and adding

$$(y'_1 - y_1)\frac{d^2\zeta}{dy_1^2}dy_1 + A'dp - B'dT = 0,$$

with the abbreviations

$$A' = y'_1\Delta V_1 + y'_2\Delta V_2, \quad B' = (y'_1 l_{g1} + y'_2 l_{g2})/T. \tag{10.17}$$

We have now to distinguish two cases: (*a*) the *py*-diagram, at constant temperature ($dT = 0$),

$$\frac{dp}{dy_1} = -\frac{y'_1 - y_1}{A'}\frac{d^2\zeta}{dy_1^2}; \tag{10.18}$$

(*b*) the *Ty*-graph, at constant pressure ($dp = 0$),

$$\frac{dT}{dy_1} = \frac{y'_1 - y_1}{B'}\frac{d^2\zeta}{dy_1^2}. \tag{10.19}$$

Obviously, the maximum or minimum of the *py*- and *Ty*-curves are at the places where the derivatives dp/dy_1 and dT/dy_1 vanish. Since A', B' do not become infinite and $d^2\zeta/dy_1^2$ is not known ever to be equal to zero, this condition reduces to

$$y'_1 = y_1. \tag{10.20}$$

The maxima and minima occur in the py- and Ty-curves at the same concentrations, namely, when the mass fractions in the two phases are equal. From the partial symmetry of eqs. (10.16) with respect to y_1, y'_1 it is clear that the conditions $dp/dy'_1 = 0$ and $dT/dy'_1 = 0$ also reduce to the same eq. (10.20). This accounts for the fact that *the two curves* (liquidus and solidus, or liquid and vapor) *have always a joint maximum or minimum.*

Whether the condition (10.20) leads to a maximum or to a minimum depends on the sign of the second derivative. The second differentiation gives in the two cases (with $y'_1 - y_1 = 0$)

$$(a) \quad \frac{d^2p}{dy_1^2} = -\frac{1}{A'}\frac{d^2\zeta}{dy_1^2}, \qquad (b) \quad \frac{d^2T}{dy_1^2} = \frac{1}{B'}\frac{d^2\zeta}{dy_1^2}.$$

The quantities A' and B' can be considered as positive. In fact, B' always *is* positive, since our notations are chosen so as to make the

primed phase that of the higher heat a function (i.e. giving the positive sign to the latent heats l_1, l_2). The changes of volume ΔV_1, and ΔV_2 are always positive in the case of liquid-vapor equilibrium, and positive with rare exceptions in the case of solid-liquid. The second derivatives d^2p/dy_1^2 and d^2T/dy_1^2 have, therefore, generally opposite signs. *To a maximum in the py-curve there corresponds a minimum in the Ty-curve, and vice versa*, as has already been mentioned in section 71. It is well to point out that all these conclusions apply, *independently of the physical cause of the maximum or minimum type of curves*, whether they are due to association, compound formation, or other effects.

75. Remark on ternary systems. In a ternary system each phase consists of three (independent) components G_1, G_2, G_3 with the mol fractions x_1, x_2, x_3 (or mass fractions y_1, y_2, y_3) satisfying the condition

$$x_1 + x_2 + x_3 = 1. \tag{10.21}$$

The scope of this book does not permit us to enter into the very extensive theory of these systems. All we wish to do here is to explain the type of diagrams used in connection with them, in order to enable the reader, to understand the graphical material relating to ternary equilibrium. The triple of numbers x_1, x_2, x_3 can be interpreted as a point within the area of an equilateral triangle. In fact, it is known from geometry that the sum of the distances of any internal point P from the three sides ($PA_1 + PA_2 + PA_3$, in Fig. 36) is equal to the height of the triangle. If we choose the height as equal to unity, we may identify the distances with the mass fractions ($PA_1 = x_1$, $PA_2 = x_2$, $PA_3 = x_3$) because the relation (10.21) is then satisfied. Every composition of the phase can, then, be represented by a point of the triangle; and vice versa, every point within it corresponds to a possible composition. The mol fractions $x_1 = PA_1$ of the component G_1 are, usually, marked on the side G_1G_2, so that one must draw the (dotted) line *normal to* PA_1, in order to read y_1 in the point b_1. For instance in our Fig. 36, x_1 has the value of about 0.34. In a similar way the values of x_2 (and x_3) are listed on the sides G_2G_3 (and G_3G_1) and can be read by drawing (dotted) lines normal to PA_2 (and to PA_3) to the points b_2 (and b_3).

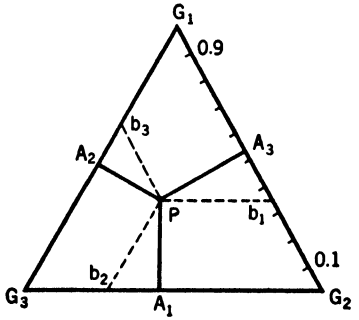

FIG. 36.—Graphical representation of the composition of ternary systems.

When two ternary phases (primed and unprimed) are in equilibrium, the condition (6.43) must be satisfied for each of the three components

$$\nu_k \overline{\varphi}_k(p,T, x_1, x_2) + \nu'_k \overline{\varphi}'_k(p,T, x'_1, x'_2) = 0, \quad (k = 1, 2, 3)$$

because the mol fraction x_3 (resp. x'_3) should not be regarded as a separate variable as it is completely determined by eq. (10.21).

Two of the variables, x'_1, x'_2 or x_1, x_2, can be eliminated from these three equations. If the *pressure is*, moreover, *considered as constant*, this leaves

$$T = T(x_1, x_2) \quad \text{or} \quad T = T'(x'_1, x'_2), \tag{10.22}$$

the equilibrium temperature expressed in terms of the mol numbers of either phase. These equations depend on three variables (T, x_1, x_2

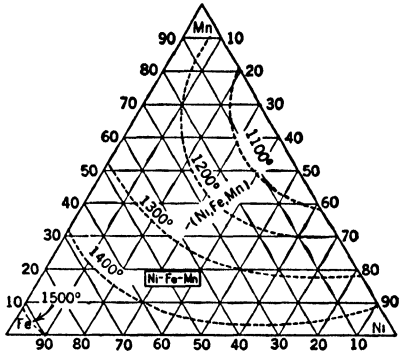

FIG. 37.—Isothermals of liquidus surface. (Temperature in ° C).

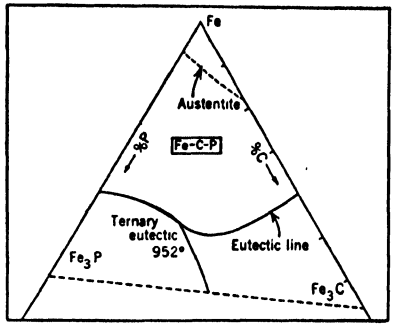

FIG. 38.—Eutectic lines. (Temperature in ° C).

or T, x'_1, x'_2) and can be represented graphically only in a three-dimensional space. For instance, we could interpret the third dimension, normal to the plane of the triangle in Fig. 37, as the temperature T. Equations (10.22) represent, then, two surfaces lying above the triangle. If the equilibrium is between a solid and a liquid phase, they are called, in analogy with the curves of Fig. 28, the *solidus* and the *liquidus surface.*

Naturally, one can represent in a plane drawing only the " levels " of these surfaces, i.e. their intersections with the planes of constant temperature, T = const. As an example we give in Fig. 37[1] the isothermal levels of the liquidus surface for the system Ni-Fe-Mn (dotted lines, the coordinates in this figure are not mol fractions but mass fractions y'_1, y'_2, y'_3). In the solid state, these three metals are

[1] I.C.T. based on Parravano, Gaz. Chim. Ital. **42** II, p. 367, 1912.

mutually soluble in all proportions: therefore, there exists only one solid phase with which the melt is in equilibrium and the liquidus surface extends over the whole of the triangle. This is not the general case: if the solid components are mutually insoluble or partially soluble, there may exist at the same temperature three (or even more) different solid phases. This case is analogous to those of Figs. 30 and 32 for binary systems. As we have there *two* separate liquidus curves corresponding to the equilibrium of the melt with the two solid phases, so here the area of the triangle (Fig. 38)[1] is divided into *three* regions and in each region we have a separate liquidus surface. The three liquidus surfaces are analytically represented by three different equations $T = T'(y'_1, y'_2)$ and each corresponds to the equilibrium of the melt with one of the three solid phases. The lines of intersection of two of these surfaces (eutectic lines) represent the states in which the melt is in equilibrium with two solid phases simultaneously (Fig. 38). In the point where all three intersect (ternary eutectic point) the melt is in equilibrium with all three solid phases. There may arise further complications in the number and shape of the equilibrium surfaces when the components are able to form chemical compounds.

[1] I.C.T. based on Goerens, Metallurgie **6**, p. 537, 1909; Stead, Iron, Steel Inst. **91**, p. 140, 1915.

CHAPTER XI

FUGACITIES AND ACTIVITIES [1]

76. Definition of fugacity. It was shown in section 42 that chemical and physical equilibrium depends on the partial thermodynamic potentials

$$\overline{\varphi}_h^{(i)} = \left(\frac{\partial \Phi^{(i)}}{\partial N_h^{(i)}}\right)_{p,T}. \tag{11.01}$$

We have reviewed, in Chapters VII to X, the cases in which some theoretical knowledge of the functions $\overline{\varphi}$ permits the making of complete or partial predictions about the details of the equilibrium. However, in the large majority of cases such knowledge is lacking or insufficient, and the only resource is to combine the experimental and the theoretical methods: to measure and record the partial potentials from one group of observations and to use these data for the prediction of another set of phenomena. A large amount of experimental material has been collected and published in the chemical literature. However, the chemists usually record not the partial thermodynamic potential $\overline{\varphi}$ itself but another function f which stands to it in the simple relation

$$f = f_0(T) \exp(\overline{\varphi}/RT) \tag{11.02}$$

or

$$\overline{\varphi} = RT[\log f - \log f_0(T)]. \tag{11.03}$$

The quantity f was introduced by G. N. Lewis [2] and is called the *fugacity* or *absolute activity*. $f_0(T)$ is an auxiliary function of temperature only, which is defined by the following requirement: in the gaseous phase, the fugacity approaches more and more the pressure, as the density is decreased, and becomes identical with it ($f = p$) in the limit $V = \infty$.

The thermodynamic potentials of perfect and of Van der Waals gases were given by the formulas (5.41) and (5.44). In order to satisfy the above requirement we have to put in both cases $f_0(T) = -\omega(T)/RT$. For the *perfect gas* we obtain

$$f = p, \tag{11.04}$$

[1] This chapter can be skipped without loss of continuity.

[2] G. N. Lewis, Proc. Am. Acad. 37, p. 49, 1901; Zs. physik. Chemie, 38, p. 205, 1901.

at all temperatures; for the Van der Waals gas we find

$$\log f = \log\left(p + \frac{a}{v^2}\right) + \frac{2a}{v} - \frac{RTb}{v - b}. \tag{11.05}$$

Once f is defined in the gaseous phase, it is definite also in the condensed phases because (barring associations) the thermodynamic potentials (and, therefore, the fugacities) are equal in equilibrium. More generally, we have for two different conditions of the systems (1) and (2), at the same temperature,

$$\bar{\varphi}_2 - \bar{\varphi}_1 = RT \log \frac{f_2}{f_1}. \tag{11.06}$$

In general, analytical expressions for f are lacking and, even in systems with one independent component, only the partial of $\log f$ with respect to p can be given explicitly from (5.37)

$$\left(\frac{\partial \log f}{\partial p}\right)_T = \frac{v}{RT}. \tag{11.07}$$

The measurement of $\bar{\varphi}$ can be easily carried out in pure substances (systems with one independent component): in this case $\bar{\varphi} = \varphi = u - Ts + pv$, where each of the three terms can be directly measured. As an example we give in Table 31 the fugacity of liquid water at various temperatures and pressures.[1]

TABLE 31

FUGACITY OF LIQUID WATER

p(atm)	Activity a			Fugacity f		
	25° C	37°.5	50°	25° C	37°.5	50°
1	1	1	1	0.03125	0.06372	0.1219
100	1.0757	1.0728	1.0703	0.03362	0.06836	0.13047
200	1.1576	1.1515	1.1461	0.03618	0.07337	0.13971
300	1.2454	1.2356	1.2270	0.03892	0.07873	0.14957
400	1.3394	1.3254	1.3132	0.04186	0.08445	0.16009
500	1.4402	1.4214	1.4050	0.04501	0.09057	0.17127
600	1.5481	1.5240	1.5029	0.04838	0.09711	0.18320
700	1.6637	1.6336	1.6072	0.05199	0.10409	0.19592
800	1.7874	1.7506	1.7184	0.05586	0.11155	0.20947
900	1.9200	1.8755	1.8367	0.06000	0.11951	0.22389
1000	2.0618	2.0089	1.9628	0.06443	0.12801	0.23927

[1] M. Randall and B. Sosnick, J. Am. Chem. Soc. 50, p. 967, 1928.

On the other hand, in a phase (i) with many components the function $\overline{\varphi}_h^{(i)}$, as is clear from its definition (5.39), is only then accessible to direct measurement when the mol number $N_h^{(i)}$ can be changed independently from the other mol numbers. If this is impossible (owing to chemical reactions in the system), it is often still feasible to determine it in a roundabout way when this component can be isolated in another phase (j) which is in equilibrium with (i), making use of the equilibrium condition $\overline{\varphi}_h^{(i)} = \overline{\varphi}_h^{(j)}$. After being determined from observations, these data can be used for theoretical purposes, for instance to test the relations (6.49)

$$\Delta\Phi \equiv \sum_h \nu_h^{(i)} \overline{\varphi}_h^{(i)} = 0, \tag{11.08}$$

which must obtain within the phase (i).

77. Definition of activity. In some cases it is impossible or difficult to determine the absolute value of the fugacity of a component in a complex phase (for instance, in a solution), while it is feasible to measure the ratio

$$a = f/f_s \tag{11.09}$$

of the fugacities of the same component for two states of the solution, different as to pressure and concentration, but *of the same temperature.* This permits choosing f_s as the unit in which the fugacity is to be measured and regarding the state to which f_s refers as the *standard state* for the component and for the temperature in question. The ratio a was also introduced by Lewis[1] and is called *activity* or *relative fugacity.* Its relation to the partial thermodynamic potential follows from the formula (11.03), taking into account that f and f_s are measured at the same temperature so that $f_0(T)$ drops out of the ratio:

$$\overline{\varphi}_h - \overline{\varphi}_{sh} = RT \log a_h, \tag{11.10}$$

where $\overline{\varphi}_{sh}$ is the partial thermodynamic potential of the component h in the standard state. The simplest example is the case of a pure substance: in Table 31 are given the activities of liquid water. As standard states at the temperatures 25°, 37°.5, 50° C, are chosen those corresponding to the pressure $p = 1$ atm (with f_s equal to 0.03125, 0.06372, 0.1219, respectively).

It must be distinctly understood that, in systems with several components, the standard states are chosen for each component independently and arbitrarily. For the definition of $\overline{\varphi}_{sh}$, not only N_{sh},

[1] C. N. Lewis, Proc. Am. Acad. 43, p. 259, 1907; Zs. physik. Chemie 61 p. 129, 1907.

but all the mol numbers of the other components, must be given. Therefore, the $\overline{\varphi}_{sh}$ are mutually exclusive, in the sense that there does not exist any stable state of the system with these simultaneous values of the partial potentials. This implies, of course, that they do not satisfy the conditions (11.08). The expression

$$\Delta\Phi_s \equiv \sum_j \sum_h \nu_h^{(j)} \overline{\varphi}_{sh}^{(j)} = -RT \log K_s, \tag{11.11}$$

does not vanish but is a finite function of temperature and pressure. We find from (5.37)

$$\left(\frac{\partial \log K_s}{\partial p}\right)_T = -\frac{\Delta V_s}{RT}, \tag{11.12}$$

$$\left(\frac{\partial \log K_s}{\partial T}\right)_p = \frac{Q_s}{RT^2}, \tag{11.13}$$

where

$$\Delta V_s = \sum_{j,h} \nu_h^{(j)} \overline{v}_{sh}^{(j)}, \quad Q_s = \sum_{j,h} \nu_h^{(j)} \overline{\chi}_{sh}^{(j)}. \tag{11.14}$$

On the other hand, the partial potentials $\overline{\varphi}_h$ in eqs. (11.10) refer to actual states of equilibrium and satisfy the condition $\Delta\Phi = 0$. Therefore, there follows the equation

$$\sum_{j,h} \nu_h^{(j)} \log a_h^{(j)} = \log K_s, \tag{11.15}$$

which has the same analytical form as the mass law, the mol fractions being replaced by the activities.

The physical meaning of the activity becomes a little clearer from the analogy which the formulas (11.10) and (11.15) bear to those valid for dilute solutions. In section 59 we found for the partial thermodynamic potential of a dilute solute

$$\overline{\varphi}_h^{(j)} = \varphi_h^{(j)} + RT \log x_h^{(j)}. \tag{11.16}$$

Since $\log x_h$ vanishes for $x_h = 1$, it may be said that the term φ_h represents the molal thermodynamic potential of the fictitious state when the component is pure while having the same properties as in the solution. This means that the heat of solution is contained in φ_h but the entropy only partially: the second term $RT \log x_h$ represents its increase due to the entropy of mixing the solute (h) with the solvent. The interactions of the component (h) with the other solutes and the entropy of mixing it with them are negligible in dilute solutions. In the general case of non-dilute solutions, we have the analogous formula (11.10)

$$\overline{\varphi}_h^{(j)} = \overline{\varphi}_{sh}^{(j)} + RT \log a_h^{(j)}. \tag{11.17}$$

The standard state for the component h is, practically, always chosen so that, in it, it is the only solute ($x_k = 0$, $k \neq h$). The term with log a represents, therefore, the increment of the thermodynamic potential due to interactions with the other solutes, to the entropy of mixing h with them, and (in a measure depending on the definition of the standard state) also to the interactions and entropy of mixing with the solvent.

78. The activity coefficient. The simplest way of choosing the standard potentials $\overline{\varphi}_{sh}$ is identifying them with the functions φ_h of eq. (11.16) used in the theory of dilute solutions

$$\overline{\varphi}_{sh}^{(j)} = \varphi_h^{(j)}. \tag{11.18}$$

The equilibrium constant K_s becomes then identical with K in Van t'Hoff's eq. (9.13), whence (11.15) takes the form

$$\sum_{j,h} \nu_h^{(j)} \log a_h^{(j)} = \log K. \tag{11.19}$$

The activities a_h have then the meaning of *effective mol numbers* which one must substitute instead of x_h in order to conserve the form of the mass law. The ratio between the effective and the actual mol number

$$\alpha_h = a_h/x_h \tag{11.20}$$

is called the *activity coefficient*.[1]

In dilute solutions the activity coefficient is usually defined in another way: as the ratio of activity and molality m_h

$$\gamma_h = a_h/m_h. \tag{11.21}$$

The relation of the two definitions (since in the dilute state $x_h = m_h/m_0$) is

$$\gamma_h = \alpha_h/m_0, \tag{11.22}$$

where m_0 is the molality of the solvent (i.e. mol number per 1000 g weight).

It is obvious that the choice of the standard states defined by eq. (11.18) is permissible when the solution obeys (in the limit of low concentrations) the theory of dilute solutions treated in Chapter IX. The standard states are then, really, possible states of the system, and at low concentrations the activities approach the mol fractions:

$$\lim a_h = x_h, \quad \lim \alpha_h = 1. \tag{11.23}$$

[1] This term was first introduced by A. A. Noyes and W. C. Bray (Journ. Am. Chem. Soc. 33, p. 1643, 1911), but these authors defined it with respect to the molality as in eq. (11.21).

However, even if this should not be so, if the values $\overline{\varphi}_{sh} = \varphi_h$ correspond to no existing states of the system, they can still be used. They are, then, merely auxiliary mathematical quantities with respect to which the activities are defined. There is no reason why one should not use thermodynamic potentials defined with respect to fictitious states, provided there can be given an experimental way of measuring them, either separately or in combinations. Such an experimental procedure exists and will be described below.

In the first place, it is simple to measure the activity of the solvent by the method of boiling pressures or boiling (and freezing) temperatures. For the process of vaporizing $\nu_0^{(2)}$ mols of solvent, to obtain $\nu_0^{(1)}$ mols of vapor, we have from (11.19) the equation

$$\nu_0^{(1)} \log a_0^{(1)} - \nu_0^{(2)} \log a_0^{(2)} = \log K, \tag{11.24}$$

closely analogous to (9.17). We assume that the solutes in the liquid phase (2) are non-volatile so that the vapor phase (1) is pure and of sufficiently low pressure to be regarded as a perfect gas. For a perfect gas, eq. (11.16) or (9.09) is rigorous and the activity coincides with the mol fraction: $a_h^{(1)} = x_h^{(1)} = 1$. This gives for the liquid phase (dropping the superscript)

$$\nu_0 \log a_0 = - \log K. \tag{11.25}$$

In the particular case when the liquid phase also consists of the pure solvent we can apply to it the theory of section 64 and find $\log K(p,T) = 0$, where p, T are the pressure and temperature of the boiling point. When the solutes are present in a concentration that is not high, the solution boils at a lower pressure $p + \Delta p$ (provided T is the same), and we obtain from (11.25)

$$\nu_0 \log a_0 = - \log K(p + \Delta p, T) = \Delta V \cdot \Delta p \tag{11.26}$$

neglecting higher powers of Δp.

On the other hand, if the theory of section 64 were applied to this case, we would have

$$\nu_0 \log x_0 = \Delta V \cdot \Delta p_0.$$

Denoting the ratio of the actually measured pressure increase Δp to the theoretical Δp_0 (if the solutes behaved like perfect gases) by

$$\beta_0 = \Delta p / \Delta p_0, \tag{11.27}$$

we have

$$\log a_0 = \beta_0 \log x_0. \tag{11.28}$$

It is obvious, by analogy with section 64, that β_0 can also be measured as the ratio of the actual (ϑ) and the theoretical (ϑ_0) lowering of the freezing point, $\beta_0 = \vartheta/\vartheta_0$. Much of the experimental work has, in fact, been carried out by the freezing method. The above formulas imply, of course, concentrations sufficiently low for higher powers of Δp being neglected in the expansion (11.26). A more accurate formula for the activity of water as a solvent, taking in second and third powers of the lowering ϑ of the freezing point, is[1]

$$\log_{10} a_0 = -\,(421.0\vartheta + 0.164\vartheta^2 - 0.0037\vartheta^3) \times 10^{-5}. \qquad (11.29)$$

79. The activity function of electrolytes. Equations (11.28), (11.29) give a convenient way of determining the activity of the solvent. As to *the solutes*, their activities can be measured directly if they are volatile. This is, however, a comparatively rare case. A very important field of investigation are the electrolytes whose ions are mostly non-volatile. It was shown by Lewis that valuable knowledge about their activities can be obtained from eq. (11.28) by means of Duhem's relation (6.16). Let us consider the case that every molecule of an electrolytic solute is completely dissociated into ions according to the formula $\nu_1 G_1 + \ldots + \nu_\tau G_\tau - G_n = 0$. If the mol number of the neutral electrolyte dissolved was N_n, those of the ions are $N_h = \nu_h N_n$, the sum being $\nu_e N_n$, ($\nu_e = \nu_1 + \ldots + \nu_\tau$). Denoting

$$x = \frac{\nu_e N_n}{N_0 + \nu_e N_n} = 1 - x_0, \qquad (11.30)$$

(where N_0 and x_0 refer to the solvent), the mol fractions become

$$x_h = \nu_h\, x/\nu_e, \quad (h = 1, 2 \ldots \tau). \qquad (11.31)$$

In Duhem's equation (6.16) the partial thermodynamic potentials $\overline{\varphi}_h$ can be replaced by $\log a_h$ because, in eq. (11.10) defining the activity, the function $\overline{\varphi}_s$ is independent of the mol fractions x_h. As the variable of differentiation we take x

$$\sum_{h=0}^{\tau} x_h \frac{\partial \log a_h}{\partial x} = 0.$$

Now, from (11.20) and (11.31): $\log a_h = \log \alpha_h + \log x + \text{const.}$ Substituting this for the activities of the ions,

$$(1 - x)\frac{\partial \log a_0}{\partial x} + 1 + \frac{x}{\nu_e}\sum_{h=1}^{\tau} \nu_h \frac{\partial \log \alpha_h}{\partial x} = 0.$$

[1] Abel, Redlich, and Lengyel, Zs. phys. Chem. **132**, p. 201, 1928.

The expression

$$\log \gamma = \frac{1}{\nu_e} \sum_{h=1}^{r} \nu_h \log \alpha_h \tag{11.32}$$

defines the quantity γ called the *activity function* of the electrolyte (sometimes also referred to as *activity coefficient* or *activation function*).

$$(1 - x) \frac{\partial \log a_0}{\partial x} + 1 + x \frac{\partial \log \gamma}{\partial x} = 0. \tag{11.33}$$

In the limit of zero concentration ($x = 0$) the solution is reduced to the pure solvent ($\beta_0 = 1$) and it is experimentally ascertained that $\lim \log \alpha_h = \lim \log \gamma = 0$. The integration of (11.33) gives, therefore,

$$\log \gamma = -\int_0^x \left[\frac{1}{x} + \frac{1 - x}{x} \frac{\partial \log a_0}{\partial x}\right] dx.$$

In the particular case of considerable dilution, the expression (11.28) may be used for $\log a_0$, and, moreover, it is then permissible to neglect terms of second order in the small quantities x and β_0. Hence *the limiting law for low concentrations*

$$\log \gamma = -\int_0^x \left(\frac{1 - \beta_0}{x} - \frac{\partial \beta_0}{dx}\right) dx.$$

Since in *dilute* solutions $x \propto m$ (molality) this can be also written

$$\log \gamma = -\int_0^m \left(\frac{1 - \beta_0}{m} - \frac{\partial \beta_0}{\partial m}\right) dm. \tag{11.34}$$

The pioneer work of collecting data about activities of electrolytes by the freezing method was largely carried out by American chemists under the leadership of G. N. Lewis and A. A. Noyes. This material confirmed the division of these substances in two groups discovered earlier by other lines of study.[1]

(A) *Weak electrolytes* (mostly organic acids and their salts) are those which form aqueous solutions obeying, in their dilute state, the theory of Chapter IX. This implies $\beta_0 = 1$, $\gamma = 1$ for all low concentrations, so that eq. (11.34) is identically satisfied ($0 = 0$).

(B) *Strong electrolytes* (the common strong acids and their salts) which exhibit the electrolytic properties in their most typical form

[1] There are two other methods of measuring the activities of electrolytes. (1) Electrical measurements (conductivity or electromotive force), as described in section 114. (2) Influence of other solutes on the solubility. This method is limited to electrolytes of low solubility.

do not obey the laws of dilute solutions. While β_0 tends towards 1 in the limit of infinite dilution ($m = 0$), it appreciably deviates from unity even for very low molalities. In fact, the curve representing $\beta_0 = \beta_0(m)$ has a vertical tangent at $m = 0$, i.e. $\partial\beta_0/\partial m = \infty$. Several empirical formulas have been proposed for this function, among them

$$\beta_0 = 1 - \tfrac{1}{3}km^{1/2}, \tag{11.35}$$

which is supported theoretically (section 115) and represents the experimental material as well as any of the others. This formula permits one to carry out the integration of (11.34) and to find the *limiting law for the activity function*

$$\log \gamma = - km^{1/2}. \tag{11.36}$$

It will be better to postpone the discussion about the structure of the factor k and about the agreement of this formula with the experimental data until section 115.

80. Activities in binary gas mixtures. The deviations from the laws of perfect gases in electrolytes (preceding section) are due, primarily, to electric forces. It will be instructive to mention, as another example, the deviations in gas mixtures which are caused by molecular cohesion. The activities of a number of gases in mixtures have been determined by several investigators from their chemical equilibrium with liquid or solid substances, and a summary of their results is contained in a paper by Randall and Sosnick.[1] The activity coefficient of a component is defined as $\alpha_h = f_h/f_h^{(0)}x_h$ where f_h is the fugacity of the gas h in the mixture, $f_h^{(0)}$ its fugacity in the pure state, at the same pressure.

Randall and Sosnick confirm for binary gas mixtures an equation which was found by Hildebrand[2] to hold for liquid solutions, namely,

$$\log (f_1/f_1^{(0)}x_1) = (Bx_2^2 + Cx_2^3 + Dx_2^4 + \ldots)/RT. \tag{11.37}$$

The character of this function appears from the curves of Fig. 39[3] relating to mixtures of ethylene and argon at 25° C.

The only theoretical equation of state for gas mixtures is Lorentz' extension of the Van der Waals formula given in section 5. Although its validity is uncertain and, presumably, restricted to a narrow range, it is interesting to note that it leads to an expression similar to (11.37). Lorentz' equation is formally identical with the ordinary Van der

[1] M. Randall and B. Sosnick, J. Am. Chem. Soc. **50**, p. 967, 1928.
[2] Hildebrand, Proc. Nat. Acad. Sci. **13**, p. 267, 1927.
[3] Randall and Sosnick, *loc. cit.*

Waals formula (1.21); only, the "molal volume" v has here a different meaning, namely, $v = V/N$ (where $N = N_1 + N_2$), while the constants depend on the mol fractions as follows:

$$\left.\begin{aligned} a &= a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2, \\ b &= b_{11}x_1^2 + 2b_{12}x_1x_2 + b_{22}x_2^2. \end{aligned}\right\} \tag{11.38}$$

The thermodynamic potential is obtained by an obvious generalization of (5.44)

$$\Phi = N_1\,\omega_1(T) + N_2\,\omega_2(T) + NRT\left[\log\left(p + \frac{a}{v^2}\right) - \frac{2a}{RTv} + \frac{b}{v-b}\right] + T\,S_0(N_1,N_2),$$

$$\omega_1(T) = \int c_{p1}dT - T\int \frac{c_{p1}}{T}\,dT + u_{01} - T\,s'_{01}.$$

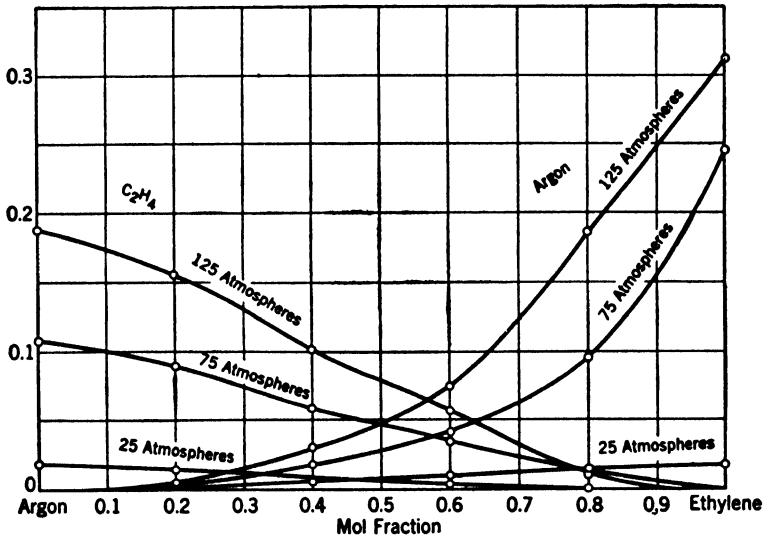

FIG. 39.—Logarithms of activity coefficients ($\log \alpha_h$)

The entropy of the mixture must contain a term depending on the mol numbers of both components which represents the entropy of mixing the two gases. It can be evaluated by noticing that, in the limit of very large v, the components become perfect. For a binary mixture of perfect gases the thermodynamic potential is known to be (section 50)

$$\Phi_i = N_1\omega_1(T) + N_2\omega_2(T) + NRT\log p + RT(N_1\log x_1 + N_2\log x_2),$$

where the subscript i stands for " ideal." Comparing the two expressions, we conclude that

$$S_0(N_1, N_2) = R(N_1 \log x_1 + N_2 \log x_2). \tag{11.39}$$

Hence

$$\frac{\Phi - \Phi_i}{RT} = N\left[\log\left(1 + \frac{a}{pv^2}\right) - \frac{2a}{RTv} + \frac{b}{v-b}\right]. \tag{11.40}$$

It is our purpose to calculate the expression (11.37) to terms of second order in the coefficients a, b. Expanding and making use of the equation of state (1.21), we find

$$\Phi - \Phi_i = N\left[p\left(b - \frac{a}{RT}\right) + \left(\frac{p}{RT}\right)^2 a\left(b - \frac{a}{RT}\right)\right].$$

According to (11.04), the fugacity of a perfect gas is equal to its (partial) pressure, $f_{i1} = p_1 = px_1$. Consequently (11.06) leads to

$$\log (f_1/px_1) = \frac{1}{RT}\frac{\partial(\Phi - \Phi_i)}{\partial N_1}.$$

This relation holds for all values of the mol fractions, including $x_2 = 0$, $x_1 = 1$, when the left side is identical with $\log (f_1^{(0)}/p)$. Taking the difference of the two expressions, we obtain, in fact, an equation of the type (11.37) with the following values of the coefficients.

$$\begin{aligned}
B &= p[(a_{11} - 2a_{12} + a_{22})/RT - (b_{11} - 2b_{12} + b_{22})] \\
&\quad + \left(\frac{p}{RT}\right)^2 \cdot [(6a_{11} + 6a_{12} + a_{22})(a_{11}/2RT - b_{11}) \\
&\quad - (6a_{11} - 4a_{12})(a_{12}/2RT - b_{12}) + a_{11}(a_{22}/2RT - b_{22}),] \\
C &= 4\left(\frac{p}{RT}\right)^2 [-(2a_{11} - 3a_{12} + a_{22})(a_{11}/2RT - b_{11}) \\
&\quad + (3a_{11} - 4a_{12} + a_{22})(a_{12}/2RT - b_{12}) \\
&\quad - (a_{11} - a_{12})(a_{22}/2RT - b_{22})], \\
D &= 3\left(\frac{p}{RT}\right)^2 \cdot (a_{11} - 2a_{12} + a_{22}) \cdot [(a_{11} - 2a_{12} + a_{22})/2RT \\
&\quad - (b_{11} - 2b_{12} + b_{22})] \cdot
\end{aligned}$$

In the case of ethylene (1) and argon (2) at 25° C, the table values are $a_{11}/RT = 135$, $b_{11} = 42$, $a_{22}/RT = 53$, $b_{22} = 30$. The order of magnitude of the data in Fig. 39 is consistent with this if a_{12} and b_{12}

have commensurate values. At pressures of 25 atm the terms with p^2 are still unimportant and, neglecting them, our formula is symmetrical in the subscripts (1) and (2). This is borne out by the symmetrical character of the curves for argon and ethylene at this pressure. The constants can be adjusted so as to describe also the general character of the curves at the higher pressures of 50 and 75 atm, but it remains to be seen whether the expressions are fit for a quantitative description of the phenomena.

CHAPTER XII

THE CAPILLARY LAYER [1]

81. Surface layer and surface tension. The equilibrium of two adjacent phases was treated in Chapter VI as if each of them were uniform in its properties up to the very surface of discontinuity separating them from each other. This, however, is not strictly true: the state of a substance at any point within it is influenced, not only by the molecules nearest to this point, but also by all the others in a small radius around it called the *radius of molecular action.* The surface layer of the thickness of this radius, between the phases or at the boundary, is, therefore, in a condition different from interior points, as it stands under the action of molecules of both media. It is called the *capillary layer* and exhibits peculiar properties depending on the nature of the two phases. When the phases are of large size, the energy and entropy of the capillary layer become negligible, and the conditions are those discussed in Chapter VI. But when the size of the phases is small, in one or several dimensions, the influence of the capillary layer is important.

A general characteristic of the capillary layer is that it *tends to contract.* From the point of view of mechanics, it acts like a membrane in a state of uniform tension. By this we mean a condition of the membrane (Fig. 40) in which every line element dl of its boundary AB experiences a normal force $F_n = \sigma\, dl$ to the inward, σ being the constant tension. If we draw an imaginary line CD in the interior of the membrane it is also under the action of two oppositely equal normal forces of the magnitude σ per unit length of the line. When the membrane has a chance to contract, it performs work in doing so. Suppose that the boundary line is displaced from the position AB to $A'B'$, and the element dl to dl', through the distance ΔL, as a result of the contraction. The work done against the element dl is, according to (2.01), $F_n \Delta L \cos(n,L) = \sigma\, dl \Delta L \cos(n,L)$, or it is equal to σ multiplied by the area which is swept over by dl in its displacement. Consequently, the total work is equal to σ multiplied by the area swept over

[1] This chapter can be skipped without loss of continuity.

by the whole boundary (which, in turn, equals the decrease of the area Σ of the membrane):

$$DW = -\sigma\, d\Sigma, \tag{12.01}$$

counting $d\Sigma$ positive when it is an increase. It does not matter whether the membrane is plane or curved.

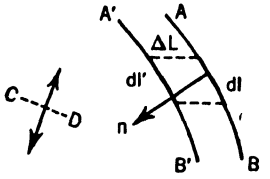

FIG. 40.—Work done by surface tension.

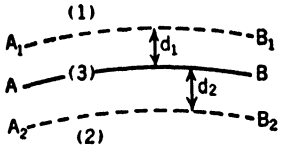

FIG. 41.—Capillary layer.

The tension σ of the capillary layer is called the *surface tension.* Its numerical values for the more important substances are contained in Table 32. A few additional data for solutions and for solids will be found in sections 86 and 87.

The thickness of the capillary transition layer is not well defined as it represents a continuous change of properties from one phase to the other. In the interest of the next section we shall, therefore, proceed as follows. We envisage a point in this layer and lay an imaginary geometrical surface AB through it and through all the other points which are similarly situated in relation to the two adjacent phases (Fig. 41). We lay a second imaginary surface, A_1B_1, parallel to it, in the upper phase (1), at a distance d_1 where that phase is already uniform, and a third parallel surface, A_2B_2, in the lower medium (2) where this medium is uniform. In all the variations which we shall let the phases undergo, the distances d_1, d_2 from AB to A_1B_1 and A_2B_2 shall be considered as constant and not subject to variation. We shall restrict ourselves to the case when the distances d are small compared with the radius of curvature of the layer. Imagine now a wide [1] rigid and adiabatic envelope which contains parts of both phases and cuts through the capillary layer. By our device the space within it is divided into three regions, as labeled in Fig. 41, and the total internal energy and entropy can be divided into three parts pertaining to these three regions

$$U = U^{(1)} + U^{(2)} + U^{(3)}, \quad S = S^{(1)} + S^{(2)} + S^{(3)}. \tag{12.02}$$

[1] Near the envelope the capillary layer is distorted because the walls add their own surface effects; but when the envelope is sufficiently wide, the distorted parts are negligible compared with the undistorted remainder.

TABLE 32

SURFACE TENSIONS OF LIQUIDS IN CONTACT WITH GASES OR OTHER LIQUIDS

Substance	Adjacent medium	Temp	σ (dyne/cm)
Water	Air	0° C	75.49
		20°	72.35
		30°	71.03
		80°	62.3
Water	Water vapor	0°	73.21
		20°	70.60
Water	Benzene	20°	33
Water	Chloroform	20°	27.7
Water	Ethyl ether	20°	9.7
Mercury	Air	20°	471.6
		100°	456.2
		360°	376.4
Mercury	Vapor	20°	480.3
Mercury	Ethyl ether	20°	398.3
Mercury	Ethyl alcohol	20°	364.3
Mercury	Chloroform	20°	356.6
Oxygen	Vapor	70° K	18.3
		90°	13.2
Nitrogen	Vapor	70°	10.53
		90°	6.16
Hydrogen	Vapor	15°	2.83
		20°	1.97
Argon	Vapor	85°	13.2
Carbon monoxide	Vapor	70°	12.11
Carbon dioxide	Vapor	0° C	9.13
		20°	1.16
		30°	0.06
Ethyl ether	Vapor	20°	16.49
		100°	7.63
Benzene	Vapor	80°	20.28
		100°	18.02
Methyl alcohol	Vapor	20°	23.02
		100°	14.80
Acetic acid	Vapor	20°	23.46
Carbon tetrachloride	Vapor	20°	25.68
		100°	16.48
Ethyl alcohol	Vapor	20°	23.03
		100°	14.67

The energy differentials in the first and second region (first phase and second phase) have the usual expressions

$$dU^{(1)} = T^{(1)}dS^{(1)} - p_1 dV^{(1)}, \quad dU^{(2)} = T^{(2)}dS^{(2)} - p_2 dV^{(2)}, \quad (12.03)$$

while that of the inhomogeneous intermediate layer is

$$dU^{(3)} = T^{(3)}dS^{(3)} - DW^{(3)} = T^{(3)}dS^{(3)} + \sigma\, d\Sigma - p_3 dV^{(3)}, \quad (12.04)$$

where $T^{(3)}$ and p_3 are the mean temperature and mean pressure in it.

82. Conditions of equilibrium as modified by the surface layer. The fundamental conditions (5.03), in view of the relations (12.04), take the form

$$\delta U^{(1)} + \delta U^{(2)} + \delta U^{(3)} = 0, \quad \delta S^{(1)} + \delta S^{(2)} + \delta S^{(3)} = 0. \quad (12.05)$$

When treating equilibrium with neglect of the capillary layer (section 40) we found it convenient to divide the problem into two parts by suitable restrictions of the virtual variations (auxiliary constraints). We shall now go a step farther and break up the present treatment into *three* partial problems.

(1) We do not admit any changes in the composition and mass or in the volume and geometrical shape of the phases. The only permissible variations are those of transfer of heat from one phase to another. Under these conditions

$$\delta U^{(j)} = T^{(j)}\delta S^{(j)}, \quad (j = 1, 2, 3).$$

We substitute this into the first eq. (12.05) and add the second, multiplied by the Lagrangean factor λ

$$(T^{(1)} + \lambda)\delta S^{(1)} + (T^{(2)} + \lambda)\delta S^{(2)} + (T^{(3)} + \lambda)\delta S^{(3)} = 0,$$

whence

$$T^{(1)} = T^{(2)} = T^{(3)} = T = -\lambda. \quad (12.06)$$

In equilibrium *the temperature is uniform throughout the system.*

(2) We consider only variations at constant temperatures and constant total volume. As was shown in section 36, the equilibrium is then determined by the minimum of the sum of the work functions

$$\Psi = \Psi^{(1)} + \Psi^{(2)} + \Psi^{(3)},$$

whose differentials are (5.24)

$$d\Psi^{(j)} = -S^{(j)}dT - DW^{(j)}.$$

Moreover, we disallow any changes of composition or mass in the phases and permit only changes in volume and shape of the three regions at the expense of one another. Since $\delta T = 0$, the variation $\delta\Psi$ becomes, according to (12.03), (12.04)

$$p_1\delta V^{(1)} + p_2\delta V^{(2)} + p_3\delta V^{(3)} - \sigma\,\delta\Sigma = 0.$$

The variations of volume are subject to certain subsidiary conditions. In the first place the total volume is constant since we suppose it enclosed in a rigid envelope

$$\delta V^{(3)} = -(\delta V^{(1)} + \delta V^{(2)})$$

or

$$(p_1 - p_3)\delta V^{(1)} + (p_2 - p_3)\delta V^{(2)} - \sigma\,\delta\Sigma = 0. \qquad (12.07)$$

As a further restriction, we specialize the geometrical shape of the phases in the following manner: let the capillary layer have the constant curvature

$$\pm C = \frac{1}{r} + \frac{1}{r'}, \qquad (12.08)$$

r and r' being its main radii, and let the walls of the vessel be normal to the layer. We consider a transfer in which mass is added to the lower phase (1) and taken from the upper phase (2), so that all three surfaces defining the layer are displaced upward through the distance δl. If we denote the respective areas of the surfaces AB, A_1B_1, A_2B_2 by Σ, Σ_1, Σ_2 (Fig. 42)

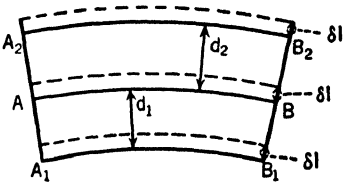

FIG. 42.—Virtual displacement of capillary layer.

$$\delta V^{(1)} = \Sigma_1\,\delta l, \quad \delta V^{(2)} = -\Sigma_2\,\delta l.$$

On the other hand, we have from geometry

$$\Sigma/rr' = \Sigma_1/(r - d_1)(r' - d_1), \text{ etc.},$$

or neglecting squares of d/r, d/r',

$$\Sigma_1 = (1 - Cd_1)\cdot\Sigma, \quad \Sigma_2 = (1 + Cd_2)\cdot\Sigma.$$

In the same way the increase of the area Σ due to the displacement is

$$\delta\Sigma = C\Sigma\cdot\delta l.$$

Substituting all this into (12.07), we find

$$p_1 - p_2 = [\sigma - (p_3 - p_1)d_1 - (p_3 - p_2)d_2]C. \qquad (12.09)$$

The terms $(p_3 - p_1)d_1$ and $(p_3 - p_2)d_2$ represent the difference between the actual force of pressure on the unit length of the cross-section through the region (3), and the force which would act if the phases (1) and (2) extended to the surface AB and changed discontinuously at it. Because of this subtraction, any indeterminateness,

due to the arbitrary choice of the thickness d_1 and d_2, cancels out. The difference itself is an intrinsic property of the capillary layer of the same nature as the surface tension. In fact, there is no experiment which would permit its measurement separately from it. It is, therefore, appropriate to throw it together with the surface tension and to denote by the symbol σ the whole bracket expression of (12.09). In this sense, we write

$$p_1 - p_2 = C\sigma = \pm\,\sigma\left(\frac{1}{r} + \frac{1}{r'}\right). \tag{12.10}$$

It should be noted that in Fig. 42 the region (1) lies on the concave side of the surface AB. We therefore make the rule that *C is to be counted as positive when (1) is on the concave side* and as negative when it is on the convex. Since σ is essentially positive, *the pressure is always higher on the concave side of the capillary layer.* The relation (12.10) is known as *Lord Kelvin's formula* because it was deduced by that physicist from mechanical considerations (next section).

(3) We maintain constant the temperature T and the local pressures p_1, p_2, p_3 in all the three regions. As we know from section 36, the equilibrium is then determined by the minimum of the thermodynamic potential: $\delta\Phi = 0$. The only permissible variations are now those of transfer of mass from one phase into another. Besides, we restrict these variations still further by prohibiting any changes of mass or composition in the region (3) and we consider only the transfers of mass of any component h (through the capillary layer) from phase (1) into phase (2), or vice versa. These variations are precisely the same as those considered in section 40, and the presence of the capillary layer in no way influences the form of the conditions of equilibrium. We may, therefore, refer to that section and to 42 and take over the equations (6.43) and (6.45)

$$\nu_h^{(1)}\overline{\varphi}_h^{(1)} + \nu_h^{(2)}\overline{\varphi}_h^{(2)} = 0, \tag{12.11}$$

or

$$\overline{\varphi}_{Mh}^{(1)} = \overline{\varphi}_{Mh}^{(2)}. \tag{12.12}$$

In the second of these equations the partial thermodynamic potential is referred to 1 g of the component h (and not to 1 mol).

We may summarize the results of this section in the following way. We derived the conditions of equilibrium for two phases separated by a capillary layer. Comparing them with those obtained neglecting the surface layer, we find all the conditions the same, except that relating to the pressures of the phases. Instead of equality of pres-

sure, we find a pressure difference (12.10) depending on the curvature of the capillary layer. When the layer is plane, $C = 0$, its influence on the equilibrium vanishes.

83. Direct observation of the capillary pressure difference. It was known for a long time that the level of water is higher in narrow tubes (capillaries) than in large vessels (Fig. 43). The theoretical explanation of this phenomenon was given by Laplace, who showed that the column of liquid in the capillary tube is supported by the surface layer of the meniscus. In this way the names " capillary layer " and " capillarity " originated. A particularly simple way of calculating the difference l of levels in the tube and in the wide vessel (" capillary rise ") was given by Lord Kelvin. Let us consider the case that a liquid rises in a tube of circular cross-section (with the radius R) and that the meniscus includes the angle ϑ with the walls. The vertical component of the force of tension which acts on the rim of the capillary layer is then $F = 2\pi R\sigma \cos \vartheta$. This force supports the liquid column of height l and must be equal to its weight in the surrounding gaseous atmosphere. Denoting the densities of the liquid and gas by ρ_2 and ρ_1, respectively, and by g the acceleration of gravity, $F = \pi R^2 l\, g(\rho_2 - \rho_1)$, whence $2\sigma \cos \vartheta = Rlg(\rho_2 - \rho_1)$. For simplicity, let us assume the curvature of the meniscus as constant over its whole surface. The radius of curvature is then $r = R/\cos \vartheta$, and we find

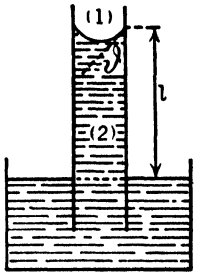

FIG. 43.—Capillary rise.

$$l = \frac{2\sigma}{r} \cdot \frac{1}{g(\rho_2 - \rho_1)}. \tag{12.13}$$

For water and other wetting liquids $\vartheta = 0$ and, roughly, $R = r$. On the other hand, for completely non-wetting liquids, like mercury, $\vartheta = \pi$: i.e. r and l are negative. This means that the liquid is on the concave side of the meniscus and its level is lower in the capillary. The formula (12.13) offers one of the most accurate methods of measuring surface tensions.

If p is the pressure at the plane surface in the vessel, the pressure in the gas at the meniscus is smaller by the pressure of the layer of gas of the thickness l, viz. $\rho_1 gl$:

$$p_1 - p = \frac{2\sigma}{r} \frac{\rho_1}{\rho_1 - \rho_2}. \tag{12.14}$$

Similarly the pressure p_2 in the liquid at the meniscus is decreased by $\rho_2 gl$:

$$p_2 - p = \frac{2\sigma}{r} \frac{\rho_2}{\rho_1 - \rho_2}.$$

Consequently

$$p_1 - p_2 = \frac{2\sigma}{r}. \tag{12.15}$$

This is identical with the thermodynamical formula (12.10), in the special case $r = r'$.

84. Influence of curvature on the pressure and temperature of transformations. Let the pressure and temperature of equilibrium between two phases be p and T when the capillary layer is flat (wide vessel). We first consider the case of a pure substance (or of a system with one independent component), $\overline{\varphi} = \varphi$, and use the equation of equilibrium in the form (12.12), since we are not interested in the effects of association. p and T must then satisfy the relation

$$\varphi_M^{(1)}(p,T) = \varphi_M^{(2)}(p,T). \tag{12.16}$$

When the capillary layer is curved, the conditions are slightly different. We denote the temperature $T + \Delta T$ and we have two pressures $p_1 = p + \Delta p$ and $p_2 = p + \Delta p - \sigma C$, according to (12.10). The relation of equilibrium still has the same form

$$\varphi_M^{(2)}(p + \Delta p - \sigma C,\ T + \Delta T) - \varphi_M^{(1)}(p + \Delta p,\ T + \Delta T) = 0.$$

Restricting ourselves to quantities of the first order in the small increments, we expand into a Taylor series and subtract (12.16)

$$\left[\left(\frac{\partial \varphi_M^{(1)}}{\partial p}\right)_T - \left(\frac{\partial \varphi_M^{(2)}}{\partial p}\right)_T\right]\Delta p + \left(\frac{\partial \varphi_M^{(2)}}{\partial p}\right)_T \sigma C + \left[\left(\frac{\partial \varphi_M^{(1)}}{\partial T}\right)_p - \left(\frac{\partial \varphi_M^{(2)}}{\partial T}\right)_p\right]\Delta T = 0.$$

This formula can be specialized in two ways:

(1) *Transformation pressure at given temperature.* Suppose that the flat and the curved boundaries are at the same temperature: $\Delta T = 0$, so that the third term of the equation vanishes. According to section 35, $(\partial \varphi_M / \partial p)_T = v_M$, the specific volume referred to 1g, which is the reciprocal of the density, $v_M = 1/\rho$. Hence

$$\Delta p = \frac{\rho_1}{\rho_1 - \rho_2} \sigma C. \tag{12.17}$$

In the special case of equilibrium between a liquid and its vapor this is identical with the relation (12.14) which was obtained by Lord

Kelvin's method. In fact, the liquid boils at the meniscus in the tube at a slightly different pressure from that at the plane surface of the vessel, corresponding to the difference of altitudes.

(2) *Transformation temperature at given pressure.* Suppose the pressure of the phase (1) is the same at its plane and at its curved boundaries: $p_1 = p$ or $\Delta p = 0$. We know from section 42 that

$$\left(\frac{\partial \varphi_M^{(1)}}{\partial T}\right)_p - \left(\frac{\partial \varphi_M^{(2)}}{\partial T}\right)_p = -\frac{l_M}{T}, \tag{12.18}$$

where l_M is the latent heat of transformation *at the plane surface*, i.e. the heat necessary to transform 1g of the substance from the phase (2) into the phase (1),

$$\Delta T = \frac{\sigma C T}{\rho_2 l_M}. \tag{12.19}$$

In addition to the case of a pure substance, we shall be interested in another which is but slightly more general. We assume that one of the phases, say (2), is condensed and pure, containing only the component h, while the other phase (1) is either a gas mixture or a dilute solution. We consider first the case of the gas mixture and apply to it eq. (9.24), since it can be considered an immediate consequence of (6.43) or (12.11),

$$RT \log p_h^{(1)} = [\varphi_h^{(2)}(p,T)/g_h - \omega_h(T)], \tag{12.20}$$

where $g_h = \nu_h^{(1)}/\nu_h^{(2)}$. At a flat surface of discontinuity, p means the pressure in phase (2) identical with that in phase (1) where it is composed of the partial pressure $p_h^{(1)}$ of the component (h) and of the pressures of all the other components whose sum we shall denote by p_0, viz. $p = p_h^{(1)} + p_0$. The curvature of the surface of discontinuity cannot influence the pressure p_0 of those components which are absent in the pure condensed phase. It remains the same, and only the partial pressure of the component h changes into $p_h^{(1)} + \Delta p_h^{(1)}$. Consequently $p_1 = p + \Delta p_h^{(1)}$ and $p_2 = p + \Delta p_h^{(1)} - \sigma C$, according to (12.10). At the temperature T, we have, therefore, from (12.20)

$$RT \log (p_h^{(1)} + \Delta p_h^{(1)}) = [\varphi_h^{(2)}(p + \Delta p_h^{(1)} - \sigma C, T)/g_h - \omega_h(T)]$$

or, as above,

$$\Delta \log p_h^{(1)} = \frac{\Delta p_h^{(1)}}{p_h^{(1)}} = \frac{v_h^{(2)}(\Delta p_h^{(1)} - \sigma C)}{g_h RT}.$$

When the first phase is a gas mixture ($p_h^{(1)} = RT/v_h^{(1)}$), this is identical with eq. (12.14) since obviously $(g_h v_h^{(1)} - v_h^{(2)})/v_h^{(2)} = (\rho_2 - \rho_1)/\rho_1$.

In the case of a dilute solution, (1) labels the liquid phase and (2) the solid precipitate. $p_h^{(1)}$ must be interpreted as the osmotic pressure of the component h which is proportional to the solubility $x_{sh}^{(1)}$, according to the relation (9.50). Neglecting Δp_h in the parentheses beside σC, (where C is negative, since the solid particles are convex)

$$\Delta \log x_{sh}^{(1)} = \frac{\Delta x_{sh}^{(1)}}{x_{sh}^{(1)}} = -\frac{v_h^{(2)} \sigma C}{g_h RT}, \tag{12.21}$$

which expresses the influence of the curvature upon the solubility and is called the *Ostwald-Freundlich formula.* It is to be remembered that $v_h^{(2)}$ is the *molal* volume in the condensed phase. If the substance is dissolved without change of molecule ($g_h = 1$), the solubilities for the two negative curvatures C_1 and C_2 are related by the formula

$$\log x_{sh1}^{(1)} - \log x_{sh2}^{(1)} = -v_h^{(2)} \sigma (C_1 - C_2)/RT. \tag{12.22}$$

85. Applications. The effects listed in the preceding section have an appreciable magnitude only in the case of very large curvatures. Let us take as an example drops of water at room temperature. The constants for water at 20° C are $v_M^{(2)} = 1$, $v_M^{(1)} = 5.0 \times 10^4 \text{cm}^3/\text{g}$, $l_M = 2.45 \times 10^{10}$ erg/g, $\sigma = 72.3$ dyne/cm. Thence and from (12.19), with $C = -2/r$,

$$\Delta T = -\frac{1.74 \times 10^{-6}}{r}. \tag{12.23}$$

Even for tiny droplets of the radius $r = 10^{-5}$ cm the boiling point is only 0.174 degree below that at a plane surface. However, the surface layer is only two or three molecular layers thick, so that our formula is quantitative down to about $r = 5 \times 10^{-7}$ cm.

Why then pay much attention to this apparently insignificant phenomenon? Because it plays a large role in the processes of transformation of state, as they actually occur in nature. Let us consider, for instance, the condensation of water vapor when its temperature falls slightly below the point of saturation. Granting that the boundary layers of the vapor can and do condense on the surface of the container, its main mass is spread through the volume. Here the condensation must first form a liquid nucleus before it can proceed further, a tiny droplet which has a low boiling point, according to eq. (12.23), and is, therefore, unstable. Instead of growing it is more likely to dissolve by vaporization. This is the reason why condensation does not take place through the volume of a completely pure vapor. Only when dust particles are present, do they offer to the vapor a surface of reasonably low curvature and act as nuclei of con-

densation. Very effective in this respect are electrically charged particles: their field produces an electrostatic tension at the surface of the condensed droplet which is inversely proportional to the fourth power of its radius[1]. When the radius is very small, it may overcompensate the effect of the curvature and make the condensation easier than at the plane surface.

Quite similar conditions obtain in the case of vaporization. When water boils at 100° C, the outer pressure does not prevent small vapor bubbles arising in it. However, from the point of view of the water, the surface of the bubbles has a negative curvature, so that the boiling point in them is above 100° and they are unstable. Only when bubbles of gases already exist in the water from the start, does the boiling take place through its volume.

In the same way, surface tension has an effect on transformations in condensed phases. It is well known that crystallization does not begin without suitable nuclei, and the explanation is the same as for the condensation of gases. The case of fusion is also interesting, since most solids consist of very small microcrystals. The phenomena in crystals are somewhat complicated by the fact that the different crystallographic planes have different surface tensions, but, qualitatively, they are similar to those treated above. We should, therefore, expect that, with the rise of temperature, the smallest units and the sharp corners and edges of the larger ones would melt first (because these parts have the lowest point of fusion) while the larger crystals swim loosely in this melt. This influence of microcrystalline structure upon the process of fusion has not yet been sufficiently appreciated. However, it seems to have a bearing on the observation of Errera that glacial acetic acid and a few other organic solids show an abnormally high dielectric constant two or three degrees below their melting points.[2]

[1] The electrostatic tension or additional difference in pressure between the atmosphere and the interior of the droplet, due to the charge e on it, is equal to $e^2/8\pi a^4$. This term must be added to σC in eq. (12.17).

[2] J. Errera (Trans. Far. Soc. **24**, p. 162, 1928) determined the dispersion curve of the dielectric constant in the vicinity of the melting point and found that the effect in acetic acid has its maximum at 3° below T_F and for a critical frequency of electromagnetic waves $\nu = 10^3$. Assuming that the phenomenon is due to free solid particles capable of rotating in the liquid melt, my colleague Prof. G. W. Potapenko calculated from the critical frequency the mean radius of the particles and obtained $r = 3 \times 10^{-6}$ cm. This result agrees well with the formula (12.19) which gives for the surface tension $\sigma = -\frac{1}{2} r \rho_2 l_M \Delta T/T$. Substituting $\Delta T = -3°$ (as found by Errera), $l_M = 1.9 \times 10^9$ erg/g, $\rho_2 = 1.266$ we obtain (at $T = 298°$) $\sigma = 40$ dyne/cm as the surface tension of solid acetic acid. This value lies in the range found experimentally and theoretically for other solids (section 86).

Attempts to use eq. (12.22) as a means for determining the surface tension of solid salts against their saturated solutions were not very successful. The solubility of barium sulfate and calcium sulfate, in several states of dispersion, was measured by determining the electric conductivity of the solutions [1] which increased with the dispersion. But the very high surface tensions calculated from these data [2] have been questioned since there are possible sources of error which would produce a similar rise of the conductivity.[3]

86. Formulas for surface tension. Only when the molecular forces holding a substance together are completely known, is the theoretical calculation of its surface tension possible. So far, this knowledge is available only in the case of crystalline solids and, even here, it is restricted to a few simple space lattices. For heteropolar halogen compounds of the type of NaCl (rock salt), KCl (sylvine), etc. Born and Stern[4] calculated the following expression

$$\sigma = 4.022 \times 10^3 \frac{\rho}{A_1 + A_2}, \tag{12.24}$$

where ρ is the density of the crystal and A_1, A_2 the atomic weights. This gives:

TABLE 33

Substance.....	LiCl	NaCl	KCl	NaBr	KI
σ (dyne/cm)...	320	149	108	125	76

Although the Born-Stern formula is only an approximation, the values derived from it are, presumably, as accurate as the results of the very difficult experiments with surface tensions of plastic solids. Experiments of this kind gave for *pitch*, at 20° C, about 50 dyne/cm (Ignatiew), and for *lead glass*, at 500° C, 70 dyne/cm (Berggren).

Eötvos [5] proposed a formula for the tension of liquids against their own vapor which he obtained by a partially theoretical reasoning. He starts from the assumption that the extended law of corresponding states of section 27 applies also to the surface energy $\sigma \Sigma$ which must be treated on the same footing as the volume energy pV or the internal energy U. In other words, for substances which obey the law of cor-

[1] Hulett, Zs. phys. Chem. **37**, p. 385, 1901; Dunadon and Mack, J. Am. Chem. Soc. **45**, p. 2479, 1923.

[2] W. J. Jones, Zs. phys. Chem. **82**, p. 448, 1913.

[3] Balarew, Zs. anorgan. Chem. **154**, p. 170, 1926.

[4] M. Born, Verh. Deutsch. phys. Ges. **21**, pp. 13, 533, 1919.

[5] R. Eötvos, Ann. Phys. **27**, p. 448, 1886.

responding states, the ratio $\sigma \Sigma/T$ must be a universal function of the reduced variables π, τ. If we imagine 1 mol of the liquid substance expanding with the temperature in such a way as to retain its geometrical similitude, its free surface Σ will change proportionally to $v^{2/3}$. Therefore, the extended law of corresponding states leads to

$$\frac{\sigma v^{2/3}}{T} = f(\pi, \tau).$$

When the function f is found for one substance, it is the same for all others obeying the law of correspondence. From experiments with ethyl ether between 0° and 190° C, Eötvos inferred that the function is $f(\pi, \tau) = 2.22(1/\tau - 1) = 2.22(T_c/T - 1)$. Hence

$$\sigma v^{2/3} = 2.22(T_c - T) \tag{12.25}$$

must be a universal relation between surface energy and temperature. In fact, this formula, due to Eötvos, holds with a fair approximation for numerous substances.

Ramsey and Shields [1] secured a better fit with experiments by writing

$$\sigma v^{2/3} = k(T_c - T - d), \tag{12.26}$$

where k is slightly variable (but not greatly different from Eötvos' value) and d is a new constant (Table 34). The formula loses, of course, its theoretical significance and becomes empirical.

TABLE 34

Substance	t_c°C	k	d	Range in °C
Ethyl ether	194.5	2.1716	8.5	20–160
Methyl formate	214	2.0419	5.9	20–190
Ethyl acetate	251	2.2256	6.7	20–200
Carbon tetrachloride	283	2.1052	6.0	80–250
Benzene	288.5	2.1043	6.5	80–250
Chlorobenzene	360	2.077	6.3	150–300

A purely empirical formula, giving the surface tension as a function of temperature, is due to Van der Waals [2]

$$\sigma = A(1 - T/T_c)^B. \tag{12.27}$$

[1] W. Ramsey and J. Shields, Zs. phys. Chem. **12**, p. 433, 1893.
[2] J. D. Van der Waals, Proc. Amsterdam, 1893.

It has been extensively tested by Verschaffelt [1] and represents the data for a number of substances fairly well.

TABLE 35

Ether	$\log_{10} A$	= 1.761,	B = 1.270
Benzene		1.839,	1.230
Chlorobenzene		1.810,	1.214
Carbon tetrachloride		1.445,	1.185

87. Influence of temperature and of impurities. The experimental data on surface tensions in solutions can be summarized as follows. All the solutes can be divided into two classes:

(*A*) *Inactive solutes* produce a *slight increase* of σ, proportional to their molality m_h (provided the concentration is not high)

$$\sigma = \sigma_0(1 + km_h), \tag{12.28}$$

where σ_0 is the surface tension of the pure solvent. Alkali salts are inactive in aqueous solutions and the coefficient k is of the same order of magnitude for all of them, namely, between 0.0174 and 0.0357. Similar conditions obtain for solutions of aromatic substances, like camphor, aniline, benzoic acid in organic solvents.

(*B*) *Active solutes* have the opposite property of *strongly lowering* the surface tension. Such are many organic substances in aqueous solutions, for instance, alcohols, aldehydes, ethers, fatty acids, terpenes, etc. Soaps are particularly effective: a solution of sodium oleate of the molality $m_h = 0.002$ has a surface tension $\sigma = 25$ dyne/cm, while that of pure water is $\sigma_0 = 73$. The cleaning properties of soap solutions rest on the low values of their surface tensions.

In a qualitative way these facts were explained already by Gibbs. Let us write down the expression for the differential of *internal energy of the surface layer*. We consider the case that the mass of the system is variable and write dU in a form analogous to (5.06), taking into account (12.01) and (5.40)

$$dU^{(3)} = TdS^{(3)} + \sigma\, d\Sigma + \sum_h \overline{\varphi}_h dN_h^{(3)}. \tag{12.29}$$

The term pdV does not appear in this expression because it is included in $\sigma\, d\Sigma$ (as far as the surface layer is concerned), as was explained in discussing the formula (12.09). Similarly, $N_h^{(3)}$ represents here the *difference* between the actual value which the mol number of the components h has in the whole system and that which it would

[1] J. E. Verschaffelt, Mitteil. Naturk. Labor. Gent No. 2, pp. 16, 19, 1925.

have if the surface layer were replaced by a sharp discontinuity. In other words, $N_h^{(3)}$ *is the quantity* of the component h (in mols) *adsorbed by the surface layer.* Although not expressly stated in section 82, it follows from it that $\overline{\varphi}_h$ in a surface layer of negligible curvature is the same as in the two adjacent volumes. For the further discussion it is convenient to introduce the generalized work function

$$\Psi^{(3)} = U^{(3)} - TS^{(3)} - \sum_h \overline{\varphi}_h N_h^{(3)} \quad , \tag{12.30}$$

whose differential is

$$d\Psi^{(3)} = -S^{(3)}dT - \sum_h N_h^{(3)}\, d\overline{\varphi}_h + \sigma\, d\Sigma. \tag{12.31}$$

We now make the assumption (borne out by all observations) that the work function has the analytical form $\Psi^{(3)} = \psi_\Sigma \Sigma$, where ψ_Σ, *the work function per unit area*, is a specific thermodynamical characteristic of the surface layer independent of its area Σ. Substituting into (12.31), we obtain

$$\sigma = \psi_\Sigma. \tag{12.32}$$

The surface tension is identical with the specific work function per unit area of the capillary layer. Moreover, we find

$$\frac{\partial \sigma}{\partial T} = -\frac{S^{(3)}}{\Sigma} = -s_\Sigma, \quad \frac{\partial \sigma}{\partial \overline{\varphi}_h} = -\frac{N_h^{(3)}}{\Sigma} = -n_{\Sigma h}. \tag{12.33}$$

We apply the last formula to the special case when one of the phases, adjacent to the surface layer and containing the component (h), is either a perfect gas or a dilute solution in the sense of Chapter IX. According to (9.09) and (9.10), $\overline{\varphi}_h = \varphi_h + RT \log x_h$, where φ_h is a function of p and T only. The partial with respect to $\overline{\varphi}_h$ in (12.33) is taken in the sense that all the other variables (including T and p) are to be kept constant: $\partial \overline{\varphi}_h = RT \partial \log x_h$. In dilute solutions x_h can be replaced by m_h/m_0, so that

$$\frac{m_h}{RT}\,\frac{\partial \sigma}{\partial m_h} = -n_{\Sigma h}. \tag{12.34}$$

This formula is the key to the behavior of solutes. (A) In the case of *inactive solutes*: $\partial\sigma/\partial m_h > 0$, whence $n_{\Sigma h} < 0$, i.e. the adsorption (per unit area) of the capillary layer is negative. This means that the concentration of the component (h) is less in the capillary layer than in the bulk of the solution. As we deal here with dilute solutions, the solute can exercise but a small effect upon the surface tension, in agreement with the observed facts. (B) In the case of

active solutes there follows $n_{\Sigma h} > 0$, the adsorption is positive. The surface layer is very much smaller in volume than the adjacent phases and may build up to a high concentration in the solute (h), by adsorbing it even from a very dilute solution. This is the explanation why the *increase* of the surface tension by a small amount of solute is always slight, while the *decrease* may be considerable.

It will be well to say here a few words about the *temperature dependence of the surface tension.* As the data of Table 32 indicate, σ decreases with rising T. Moreover, it may be concluded from the good fit of the formulas (12.25) and (12.26) that this *drop is linear* over wide ranges of temperature. In fact, the molal heat v appearing in these expressions changes but little with T and can be regarded as constant in the first approximation. The underlying cause of the linear drop can be inferred from the following considerations. Let us apply eq. (12.30) to a pure substance: the question of adsorption has, then, no interest and we may leave out the last term, writing it in the form (dividing by Σ) $\psi_\Sigma = u_\Sigma - Ts_\Sigma$ or from (12.32), (12.33)

$$u_\Sigma = \sigma - T\frac{\partial \sigma}{\partial T}.$$

Within the range where σ can be represented as a linear function ($\sigma = \sigma_1 - \alpha T$) this gives

$$u_\Sigma = \sigma_1 = \text{const.}$$

The internal energy (per unit area) *of the capillary layer is constant and independent of temperature.* This ceases to be true in the vicinity of the critical temperature T_c where the linear laws (12.25) and (12.26) are no longer valid.

The understanding of the physical nature of certain surface films (oil films) has been considerably advanced by investigations of Harkins (and collaborators), Langmuir, and Adam,[1] but this subject lies outside the scope of the present book.

[1] W. D. Harkins, F. H. Brown, and E. C. H. Davies, J. Am. Chem. Soc. **39**, p. 354, 1917; I. Langmuir, *ibidem* **39**, p. 1848, 1917; N. K. Adam, Proc. Roy. Soc. (A) **99**, p. 336, 1921; **101**, pp. 452, 516, 1922; **103**, pp. 676, 687, 1923.

CHAPTER XIII

NERNST'S HEAT POSTULATE OR THE THIRD LAW OF THERMODYNAMICS

88. The principle of Thomsen and Berthelot. It was emphasized in Chapter IV that the fundamental eq. (4.07) by means of which the concept of the entropy is derived from the second law is *a differential equation.* Because of this, the definition (4.09) of S *contains an additive constant of integration* so that the absolute value of the entropy cannot be determined from the first and second law. The indeterminateness of the entropy constant has serious implications for the general character of the thermodynamical laws, in that they contain coefficients of indeterminate numerical value. As an example, we can point to the law (8.17), (8.16) of chemical equilibrium of perfect gases: The expression of the equilibrium constant K contains a factor I, which depends, according to the formula (8.14), upon the entropy constants of the gases taking part in the reaction. It is clear from this that the knowledge of the absolute entropy would be of inestimable value, as it would greatly enhance the usefulness of many thermodynamical formulas. To obtain this knowledge one must have recourse either to experiment, or to new theoretical principles not contained in the first and second law. Of course, it is quite sufficient to determine the entropy of a substance in one special case, in order to deduce the entropy constant, and it was pointed out by Nernst (1906) that experimental data were available to make a general conclusion about the behavior of the entropy of condensed systems in the vicinity of the absolute zero point of temperature.

Let us start our considerations from the Gibbs-Helmholtz equation (5.48) relating to an isothermal process

$$\Delta\Phi - \Delta\mathbf{X} = T\left(\frac{\partial\Delta\Phi}{\partial T}\right)_p. \tag{13.01}$$

We have seen in section 36 that, under ordinary conditions, the process (reaction) takes place spontaneously when $\Delta\Phi>0$. The difference of thermodynamic potentials $\Delta\Phi \equiv \Phi_2 - \Phi_1$ can be regarded, therefore, as a measure of the chemical affinity. Suppose now that

the partial $(\partial\Delta\Phi/\partial T)_p$ *does not become infinite*, when T goes to zero. In this case we find, putting $T = 0$,

$$\lim_{T=0}(\Delta\Phi - \Delta\mathbf{X}) = 0, \tag{13.02}$$

or $\lim_{T=0}(\Delta\Phi - Q_p) = 0$, if the process is conducted also at constant pressure.

In the vicinity of the absolute zero point the heat of reaction becomes identical with $\Delta\Phi$ and the criterion of the reaction taking place can be replaced by $\Delta\mathbf{X} > 0$ or $Q_p > 0$. For a long time it was thought that this form of the criterion holds good at any temperature. In fact, Thomsen and, independently, Berthelot stated the principle that *out of a number of possible reactions the one will take place which evolves the largest amount of heat.* According to our present knowledge, this would be true if the right side of eq. (13.01) were always negligible so that we could write at all temperatures

$$\Delta\Phi - \Delta\mathbf{X} = 0. \tag{13.03}$$

As we have already mentioned in section 37, this equation is erroneous. Modern investigations have shown that the term $T(\partial\Delta\Phi/\partial T)_p$ must be taken into consideration. Nevertheless, the approximation given by the principle of Thomsen-Berthelot, and by eq. (13.03), is surprisingly good even at room temperature, provided the system is condensed and the affinity of the reaction not very small. A comprehensive set of measurements of $\Delta\Phi = \Phi_2 - \Phi_1$ for reactions in condensed systems was carried out by T. W. Richards [1] with the result that the difference $\Delta\Phi - \Delta\mathbf{X}$ was very small, indeed.

Exercise 99. Check that at room temperatures $T(\partial\Delta\Phi/\partial T)_p$ is small compared with $\Delta\Phi$ for the reactions in galvanic cells given in formula (5.52) and in exercises 56, 57.

89. Nernst's own formulation of his postulate. This last fact led Nernst to assume that in condensed systems the right side of eq. (13.01) decreases more rapidly, when the temperature goes to zero, than is accounted for by the factor T. According to him, the remaining factor also decreases to naught in the limit $T = 0$: for any isothermal process

$$\lim_{T=0}\left[\frac{\partial(\Phi_2 - \Phi_1)}{\partial T}\right]_p = 0. \tag{13.04}$$

The assumption expressed in this formula is known as *Nernst's postulate or the third law of thermodynamics.* That it is natural and

[1] T. W. Richards, Zs. phys. Chemie 38, p. 293, 1902.

convincing is best brought out by the following considerations. Equation (13.01) can be written in the following form

$$\left(\frac{\partial \Delta\Phi}{\partial T}\right)_p = \frac{\Delta\Phi - \Delta\mathbf{X}}{T}. \tag{13.05}$$

If the partial on the left side does not become infinite, there follows from (13.01) that both $\Delta\Phi - \Delta\mathbf{X}$ and T become zero in the limit $T = 0$. It must be well understood what a partial with respect to T *at constant pressure* means in this case. The pressure in the two terms of $\Delta\Phi = \Phi_2 - \Phi_1$ and $\Delta\mathbf{X} = \mathbf{X}_2 - \mathbf{X}_1$ is not necessarily the same: $\Delta\Phi = \Phi_2(T,p_2) - \Phi_1(T,p_1)$, etc. But the partial is taken so that it remains equal to p_2 in the first term and to p_1 in the second. Let us now take the limiting values of both sides of eq. (13.05) for $T \to 0$, keeping the pressure constant (i.e. equal to p_2 in Φ_2 and $\mathbf{X}_2$ and to p_1 in Φ_1 and $\mathbf{X}_1$). The right side is indeterminate, being equal to 0/0, but the indeterminacy can be readily resolved by means of the well-known mathematical rule: instead of the numerator and the denominator, one has to substitute, respectively, their partials with respect to T.

$$\lim_{T=0}\left(\frac{\partial \Delta\Phi}{\partial T}\right)_p = \lim_{T=0}\left(\frac{\partial \Delta\Phi}{\partial T}\right)_p - \lim_{T=0}\left(\frac{\partial \Delta\mathbf{X}}{\partial T}\right)_p,$$

whence

$$\lim_{T=0}\left(\frac{\partial \Delta\mathbf{X}}{\partial T}\right)_p = 0. \tag{13.06}$$

If we plot the change of the heat function $\Delta\mathbf{X}$ in any isothermal, chemical or physical, process against the temperature T at which it is conducted, the curve has a horizontal tangent at the limit $T = 0$ (Fig. 44). We repeat that *this conclusion is independent of Nernst's postulate*: the only assumption on which it rests is that $(\partial\Delta\Phi/\partial T)_p$ does not become infinite for $T = 0$.

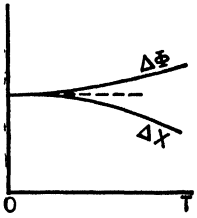

FIG. 44.—Nernst's postulate.

The difference $\Delta\Phi$ is equal to $\Delta\mathbf{X}$ in the limit $T = 0$, and is very little different from $\Delta\mathbf{X}$ over a considerable range of temperatures, according to the experimental data mentioned in the preceding section. Nernst's heat postulate (13.04) has the purpose of insuring such behavior. The curves for $\Delta\Phi$ and for $\Delta\mathbf{X}$ have, if it is accepted, a common horizontal tangent, at $T = 0$, and remain for some distance close to each other.

Owing to eq. (5.37), $(\partial\Phi/\partial T)_p = -S$, an alternative form of Nernst's postulate (13.04) is

$$\lim_{T=0}(S_2 - S_1) = 0. \tag{13.07}$$

The entropy remains unchanged in any isothermal process taking place in a condensed system in the vicinity of the absolute zero.

Although Nernst enunciated his postulate only for condensed systems, this restriction may now be dropped for the following reasons: (1) In sufficient proximity to the zero point of temperature every known system of nature is condensed, if the pressure is finite. (2) We shall see in Chapter XVI that even the ideal equation of perfect gases has been changed by the modern theory of statistics so as to satisfy Nernst's law.

Exercise 100. Starting from eq. (5.58) prove:
(*a*) If $\lim_{T=0} (\partial\Delta\Psi/\partial T)_V \neq \infty$, then $\lim_{T=0} (\partial\Delta U/\partial T)_V = 0$.
Use the same argument as that used in the text for proving (13.06).
(*b*) From (*a*) and from (13.06) there follows

$$\lim_{T=0} (C_{V2} - C_{V1}) = 0, \quad \lim_{T=0} (C_{p2} - C_{p1}) = 0.$$

These results are independent of Nernst's postulate.
(*c*) Equation (13.07) requires

$$\lim_{T=0} (\partial\Delta\Psi/\partial T)_V = 0.$$

90. Thermal expansion in the vicinity of the absolute zero. There can be deduced from the formula (13.07) some immediate consequences about the properties which all substances have in their condensed state at temperatures close to $T = 0$. Let the process to which we apply this equation consist, merely, in an infinitesimal increase of pressure (from $p_1 = p$ to $p_2 = p + dp$) at constant temperature. The entropy of the system is changed, accordingly, from $S_1 = S$ to $S_2 = S + (\partial S/\partial p)_T dp$, and Nernst's postulate (13.07) takes the form

$$\lim_{T=0} (\partial S/\partial p)_T = 0. \tag{13.08}$$

Because of the relation (4.46) of section 28 this is identical with

$$\lim_{T=0} \left(\frac{\partial V}{\partial T}\right)_p = 0. \tag{13.09}$$

The coefficient of thermal expansion vanishes in the vicinity of $T = 0$. This fact is important in itself and leads to some interesting inferences. If the pressure is kept constant, the volume is sure to remain constant automatically: in the limit $T = 0$, a partial with respect to T at constant p is, at the same time, a partial at constant v. In the formulas of the last sections we could replace the subscript p by v or drop it altogether. According to the definition (3.08) of the specific heat this applies also to the quantities c_p, c_v,

$$\lim_{T=0} c_p = \lim_{T=0} c_v = \lim_{T=0} c. \tag{13.10}$$

We can readily obtain the generalization of the formula (13.08) for the case when the system is not simple but is described by the variables $X_1, X_2, \ldots X_n$ and the generalized forces $y_1, y_2, \ldots y_n$, in addition to T (compare section 7). In fact, let us consider processes which consist in changing only one parameter, while the rest of them remain constant: for instance, X_h changes to $X_h + dX_h$, while all the other X_j $(j \neq h)$ and all the y_j (including y_h) stay constant; or else, y_h changes to $y_h + dy_h$ and y_j $(j \neq h)$ and all the X_j are constant. We find as above, respectively,

$$\lim_{T=0} \frac{\partial S}{\partial X_h} = 0, \qquad \lim_{T=0} \frac{\partial S}{\partial y_h} = 0. \tag{13.11}$$

Because of (5.30) and (5.45) this is equivalent to

$$\lim_{T=0} \frac{\partial y_h}{\partial T} = 0, \qquad \lim_{T=0} \frac{\partial X_h}{\partial T} = 0. \tag{13.12}$$

The temperature gradients of all the parameters X_h, y_h describing the system vanish in the vicinity of $T = 0$. In particular, we conclude that

$$\lim_{T=0} \left(\frac{\partial S}{\partial V}\right)_T = 0, \qquad \lim_{T=0} \left(\frac{\partial p}{\partial T}\right)_V = 0. \tag{13.13}$$

91. Specific heat in the vicinity of the absolute zero. Nernst's postulate implies that the entropy is finite at all (finite) temperatures, including the limiting case $T = 0$. We can choose, therefore, $T = 0$ as the lower limit of the integrals (4.33), (4.34) representing the entropy of a simple system

$$\left.\begin{aligned} s(T,v) &= \int_0^T \frac{c_v dT}{T} + f_1(v), \\ s(T,p) &= \int_0^T \frac{c_p dT}{T} + f_2(p). \end{aligned}\right\} \tag{13.14}$$

These integrals must be convergent, a requirement which could not be satisfied, if c_p and c_v had a finite value for $T = 0$ (because this would make the integrals logarithmically infinite). We must conclude, therefore, that the limiting values of c_p, c_v vanish

$$\lim_{T=0} c_p = \lim_{T=0} c_v = 0. \tag{13.15}$$

The specific heat vanishes in the vicinity of $T = 0$: It should be noted that Nernst's postulate is not needed for this conclusion in its

entirety: it is derived merely from the assumption that the entropy is not infinite in the limit $T = 0$ ($\lim_{T=0} S \neq \infty$).

As far as the second law is concerned, the terms $f_1(v)$, $f_2(p)$ in (13.14) may be any functions of volume and pressure (section 26). However, if we apply to them the conditions (13.08) and (13.13) flowing from Nernst's postulate we find $\partial f_1/\partial v = \partial f_2/\partial p = 0$. These terms turn out to be independent of v and p and are, therefore, constant

$$s(v,T) = \int_0^T \frac{c_v}{T} dT + s_0, \qquad s(p,T) = \int_0^T \frac{c_p}{T} dT + s_0. \quad (13.16)$$

s_0, the limiting value of the entropy at the absolute zero point, is a constant independent of the process by which this point is reached, as may be inferred from the requirement (13.07). From these expressions can be obtained the molal thermodynamic potential, for a condensed simple system,

$$\varphi = u + pv - T\int_0^T c_p \, d\log T - Ts_0. \quad (13.17)$$

Exercise 101. Prove eq. (13.15) in a different way. The condition $\lim_{T=0} S \neq \infty$ can also be written in the forms $\lim_{T=0} (\nabla\Psi/\partial T)_V \neq \infty$ and $\lim_{T=0} (\partial\Phi/\partial T)_p \neq \infty$. Derive from the eqs. (5.56) and (5.54) by the method used in obtaining (13.06)

$$\left.\begin{aligned} &\lim_{T=0} \left(\frac{\partial U}{\partial T}\right)_V = \lim_{T=0} \left(\frac{\partial \mathbf{X}}{\partial T}\right)_p = 0 \\ \text{or} \qquad &\lim_{T=0} C_V = \lim_{T=0} C_p = 0. \end{aligned}\right\} \quad (13.18)$$

92. Planck's formulation of Nernst's postulate. It is obvious that the last result can be generalized for the case of systems which are not simple but depend on any number of variables. Let us suppose, in fact, that the zero point of temperature is attained at definite values of all the other variables and that the entropy is found to be equal to S_0. According to the postulate (13.07) or to eqs. (13.11), further changes in the variables (leaving the temperature constant) will fail to have any effect upon S_0. The state $T = 0$ is, therefore, a state of constant entropy.

Planck goes beyond Nernst in that he makes an additional assumption about this limiting value of the entropy: he postulates that *the entropy in the state $T = 0$ is equal to zero, in every system occurring in nature:*

$$\lim_{T=0} S = 0. \quad (13.19)$$

In the special case of simple systems, the entropy expressions (13.14) are reduced to

$$s(T,v) = \int_0^T \frac{c_v}{T} dT, \qquad s(T,p) = \int_0^T \frac{c_p}{T} dT. \tag{13.20}$$

The modern statistical theory has borne out Planck's contention. When we refer to Nernst's postulate in the following chapters, we shall always mean Planck's formulation of it, unless expressly stated otherwise.

Equation (13.19) helps to determine the constants or arbitrary functions of integration in many thermodynamical relations. Thus, the presence of the functions $f(p)$, $f_1(v)$ in eqs. (5.55) and (5.57) is but a consequence of the indeterminacy of the entropy inherent in the second law. This is brought out, for instance, by partial integration (taking into account the formulas 3.12 and 3.26)

$$\Psi = U - T\left(\int \frac{c_v}{T} dT - f_1(v)\right); \quad \Phi = \mathbf{X} - T\left(\int \frac{c_p}{T} dT - f(p)\right).$$

The parentheses are equivalent to the entropy expressions (13.14). Replacing them by (13.20) we obtain

$$\Psi = T\int_0^T U_V \, d(1/T), \quad \Phi = T\int_0^T \mathbf{X}_p \, d(1/T). \tag{13.21}$$

Since $(\partial\Psi/\partial V)_T = p$, the first of these equations gives

$$p = -\int_0^T \left(\frac{\partial U}{\partial V}\right)_T \frac{dT}{T^2}. \tag{13.22}$$

Knowing the internal energy as a function of T and V, down to $T = 0$, we can deduce the equation of state.

Exercise 102. The molal heats c_p (in cal mol^{-1}, at 1 atm) of diamond, graphite, and copper are given in the following table:

T.....	20° K	30	40	50	60	70	80	90	100	150	200	250	300
Diamond	....	....	....	....	....	....	....	0.01	0.06	0.33	0.60	1.00	1.50
Graphite	0.02	0.06	0.10	0.14	0.18	0.24	0.30	0.33	0.38	0.77	1.2	1.4	2.05
Copper..	0.1	0.4	0.8	1.4	1.94	2.5	3.0	3.5	3.9	5.0	5.4	5.7	5.9

Calculate in a rough, graphical way the absolute entropies of these substances at 300° K.

93. Einstein's formula for the specific heat of solid bodies. In order to establish his postulate it became necessary for Nernst to test whether its consequences are borne out by experiment. In particular

he carried out with his pupils [1] an extensive program of measurements on specific heats of solid bodies at low temperatures. In all cases the law expressed in formula (13.15) was confirmed: as the substances were cooled, their specific heat decreased, and, at the lowest point attained (temperature of liquid air, later liquid hydrogen and helium), it amounted to only a small fraction of its value at room temperature.

The previous knowledge of this question had been as follows. In 1819 Dulong and Petit deduced from their measurements the law that elementary substances in the solid state have all the same molal (or atomic) heat of approximately $c = 6$ cal/deg (section 16). However, it was realized for a long time prior to Nernst's work that the law of Dulong and Petit is not accurate and that c varies with the temperature. A well-known example of this was the diamond, which exhibited, in a striking way, the type of behavior later found to be general by Nernst and his pupils. The specific heat of diamond has a value approaching the 6 cal/deg of Dulong and Petit only at temperatures which are comparatively high. It decreases rapidly upon cooling and is already pretty small (1.5 cal/deg) at room temperature, a fact which was the source of much embarrassment for the kinetic theory of matter.

Boltzmann had given the following simple approach to the problems of the internal energy of elementary solid bodies: In such a body every atom has a position of rest about which it carries out thermokinetic oscillations. As a first approximation, one can regard the forces with which the atom is attached to its normal position as proportional to the distance from it. It is well known that forces of this kind (called " elastic forces ") cause the atoms to oscillate harmonically, with a constant frequency ν. Since all atoms of an elementary body are equivalent, each of them is attached by the same force and has the same frequency ν. What is the energy of such a model of the solid body, according to statistical mechanics? According to (4.71), the classical statistics of Boltzmann-Gibbs leads to the so-called principle of *equipartition of energy*. The mean kinetic energy of every particle subject to heat motion is $kT/2$ per each degree of freedom (where k denotes Boltzmann's constant of section 4). It was also stated in section 30 that, in the case of elastic forces, the mean potential energy

[1] Monographs on Nernst's postulate: W. Nernst, Thermodynamics and Chemistry. New York 1907; W. Nernst, Die theoretischen und praktischen Grundlagen des neuen Wärmesatzes. Halle 1918; F. Politzer, Berechnung der chemischen Gleichgewichte. Stuttgart 1912. A very useful critical study of the subject is due to W. H. Van de Sande Bakhuyzen, Het Warmte-Theorema van Nernst, Thesis. Leiden 1921.

is equal to the mean kinetic and the total energy becomes kT per degree of freedom. An atom is supposed to have only three degrees of freedom and, therefore, the mean energy 3 kT. Correspondingly, the internal energy of one mol is

$$u = 3n_A kT + u_0 = 3RT + u_0,$$

since $n_A k = R$, according to eq. (1.14), and the specific heat

$$c = du/dT = 3R. \tag{13.23}$$

Substituting $R = 1.986$ cal/deg, we obtain from this theory the numerical value $c = 5.95$, in good agreement with the law of Dulong and Petit. However, it does not offer any explanation for the deviations at low temperatures.

This difficulty was resolved by Einstein [1] in one of his most important papers. He pointed out that the quantum theory provides a modification of statistics sufficient to account for these phenomena. In fact, Planck had found that, in the case of the harmonic oscillations of an electron of frequency ν, the mean energy is not the equipartition value kT but $kTx/(e^x - 1)$, where x is an abbreviation for $x = h\nu/kT$, and h denotes Planck's quantum of action ($h = 6.55 \times 10^{-27}$ erg sec). Einstein made the assumption that what is true for an oscillating electron must also apply to an oscillating atom. It was the first application of the quantum theory to atoms and molecules, and led directly to the result

$$u = 3RT\frac{x}{e^x - 1} + u_0, \tag{13.24}$$

$$c = \frac{du}{dT} = 3R\frac{x^2 e^x}{(e^x - 1)^2}. \tag{13.25}$$

The entropy follows from the expression (13.20) of Nernst's theorem in Planck s formulation

$$s = \int_0^T \frac{c\,dT}{T} = 3R\left[\frac{x}{e^x - 1} - \log\,(1 - e^{-x})\right]. \tag{13.26}$$

When the temperature T is high compared with $\Theta = h\nu/k$ (i.e. $x \ll 1$), we find, neglecting terms of the order x

$$\left.\begin{aligned} u &= 3RT + u_0, \quad c = 3R, \\ s &= 3R(1 - \log x). \end{aligned}\right\} \tag{13.27}$$

[1] A. Einstein, Ann. Physik 22, pp. 180, 800, 1907.

The limiting values, for high temperatures, are the same as in classical statistics and in agreement with the law of Dulong and Petit. On the other hand, in the vicinity of the absolute zero point ($T \to 0$, $x \to \infty$) the formulas (13.24), (13.25) reduce to $u = u_0$, $c = 0$, satisfying the requirements of Nernst's postulate.

Einstein's formula agrees with the general trend shown by the experimental values of the specific heats but the numerical agreement is not very close. Later work on the subject, which resulted in more accurate formulas, will be treated in section 123. For theoretical uses, however (when a fictitious solid body is as good as real one), Einstein's model is very convenient because of its simplicity.

Exercise 103. Find the work function ($\psi = u - Ts$) of the Einstein model and calculate its approximate expressions for very high and for very low temperatures ($x << 1$ and $x >> 1$).

CHAPTER XIV

BEARING OF NERNST'S POSTULATE ON THE ABSOLUTE ENTROPY OF GASES

94. Chemical equilibrium and Nernst's postulate. The bearing of the first and second laws of thermodynamics upon the problem of the chemical equilibrium of perfect gases was discussed in Chapter VIII. It was stated in section 51 that the first step in solving this problem was the *mass law* of Guldberg and Waage (1867)

$$\sum_{h=1}^{\sigma} \nu_h \log p_h = \log K_p, \tag{14.01}$$

which gives a relation between the partial pressures $p_1, \ldots p\sigma$ of the gases taking part in a reaction

$$\sum_h \nu_h G_h = 0, \tag{14.02}$$

conducted at a given temperature.

The next big advance was due to Gibbs (1871) who determined the dependence (8.16) of the mass constant K_p on temperature. Within the range where the molal heats can be regarded as constant

$$\log K_p = \frac{\Delta C}{R} \log T - \frac{Q_p}{RT} + \log I. \tag{14.03}$$

Provided the heat of the reaction Q_p and the change of the heat capacity ΔC in it are known, the constant of integration I can be determined from the measurement of K_p at one single temperature. The formula (14.03) serves, then, to calculate the mass constant for any other temperature. We have seen that the constant I depends upon the entropy constant of the gases in a way expressed by eq. (8.14)

$$R \log I = \sum_{h=1}^{\sigma} \nu_h s_{0h}. \tag{14.04}$$

This shows that a theoretical calculation of the constant I is beyond the scope of the first and second law of thermodynamics, which provide

no way of determining the absolute value of the entropy. The formula (14.03) with an empirical constant I represents, therefore, all the information which can be obtained from the older thermodynamics, with respect to the chemical equilibrium of gases. It was pointed out in section 59 how Van t'Hoff (1878) succeeded in generalizing this formula (still with the empirical constant I) for the case of the chemical equilibrium of solutes in a dilute solution.

The problem remained in this state until 1907 when Nernst brought his postulate to bear on it. It is possible to establish a relation between the entropy constants of a substance (h) in its gaseous state s_{0h} and its condensed state $s_{0h}^{(c)}$. In fact, let us consider the equilibrium between the vapor and the solid phase. According to eq. (7.02), the condition of equilibrium is $\overline{\varphi}_h = g_h \varphi_h^{(c)}$, where $\overline{\varphi}_h$ without upper index represents the molal thermodynamic potential of the gas and $\varphi_h^{(c)}$ that of the condensed phase while $g_h = \mu_h/\mu_h^{(c)} = \nu_h^{(c)}/\nu_h$ is the ratio of the molecular weights in the two phases. We suppose that the temperature and pressure are such that the vapor can be considered as a perfect gas. In this case we can substitute for $\overline{\varphi}_h$ the expression (8.08), (8.10) where we consider c_{ph} as constant, and for $\varphi_h^{(c)}$ the eq. (13.17) and obtain a relation which may be written in the form

$$\log p_h = -\frac{l_h}{RT} + \frac{c_{ph}}{R}\log T - \frac{g_h}{R}\int_0^T \frac{c_{ph}^{(c)}}{T}\,dT + \log i_h, \quad (14.05)$$

where

$$l_h = u_h - g_h u_h^{(c)} + p(v_h - g_h v_h^{(c)}), \quad (14.06)$$

denotes the latent heat of vaporization per 1 mol of the vapor, and

$$i_h = (s_{0h} - g_h s_{0h}^{(c)})/R \quad (14.07)$$

is a constant called by Nernst the *chemical constant of the gas.*

Equation (14.05) is, of course, only the integrated form of eq. (7.05) of section 44. It is, however, important for us to know that the constant of integration i_h is connected with the entropy constant by the relation (14.07) which permits us to express s_{0h} in the form

$$s_{0h} = Ri_h + g_h s_{0h}^{(c)}. \quad (14.08)$$

Substituting this into (14.04) we find

$$R\log I = R\sum_h \nu_h i_h - \sum_h \nu_h^{(c)} s_{0h}^{(c)} \quad (14.09)$$

The second sum on the right side is of a structure familiar to us: It represents the limiting value (for $T = 0$) of the entropy change ΔS in the reaction $\sum \nu_h^{(c)} G_h^{(c)} = 0$; in other words, it is the entropy

change which would result if all the components taking part in the gas reaction (14.02) were condensed and the reaction conducted in the condensed state in the vicinity of $T = 0$. We know from Nernst's postulate in the form (13.07) that

$$\sum_h \nu_h^{(c)} s_{0h}^{(c)} = \lim_{T=0} \Delta S = 0.$$

Therefore the relation (14.09) is reduced to

$$\log I = \sum_h \nu_h i_h. \tag{14.10}$$

This formula represents the third important advance in the problem of the chemical equilibrium of gases and is due to Nernst. While before 1907 the constant I had to be determined experimentally for every separate gas reaction, eq. (14.10) made it possible to compute it from the chemical constants i_h of the components if they were known. It was sufficient to determine by measurement the constants i_h of the individual gases by investigating their equilibrium with the condensed phases in order to know the constants I for all possible reactions between them.

We have derived the relation (14.10) using the more restricted form (13.07) of Nernst's postulate. If we accept Planck's formulation of it (13.19), we have to put $s_{0h}^{(c)} = 0$, and this reduces eq. (14.07) to

$$i_h = s_{0h}/R. \tag{14.11}$$

From this point of view the chemical constant of a perfect gas is, simply, proportional to its entropy constant. Nernst's relation (14.10) is then an immediate consequence of the definition of the constant I given by eq. (14.04).

95. The Sackur–Tetrode formula for the chemical constant. The experimental determination of the chemical constant i involves very difficult measurements. It was, therefore, fortunate that in 1912 Sackur [1] and Tetrode [2] succeeded in making an important step beyond Nernst. Working independently they gave theoretical expressions for the chemical constant of monatomic gases which differed but slightly. Tetrode's formula proved to be the correct one

$$j = i - \frac{5}{2} = \log \frac{(2\pi\mu)^{3/2} R^{5/2}}{n_A^4 \, h^3}. \tag{14.12}$$

[1] O. Sackur, Nernst–Festschrift, p. 405, 1912; Ann. Physik **40**, p. 67, 1913.
[2] H. Tetrode, Ann. Physik **38**, p. 434; **39**, p. 255, 1912.

Of course, this result could not have been obtained by thermodynamical reasoning: the resources of thermodynamics, including Nernst's theorem, are exhausted with the formula (14.10). Sackur and Tetrode used statistical methods about which we shall say more in the next section.

The argument of the logarithm in eq. (14.12) is not a pure number, so that the numerical value of i depends on the system of units used for the description of the gas. The reason of this lies in the structure of eq. (14.05), where in addition to two terms of dimension zero, we have two logarithmic terms. Taking into consideration that, for a monatomic gas $c_p/R = \frac{5}{2}$, the combination of the two logarithmic terms is $\log (p/T^{5/2})$. This term depends on the units in which the pressure and the temperature of the gas are measured and, therefore, the same is true with respect to the chemical constant i. If we substitute into (14.12) the numerical values in the G.C.S. system $R = 8.315 \times 10^7$ erg/deg, $n_A = 6.061 \times 10^{23}$ mol^{-1}, $h = 6.554 \times 10^{-27}$ erg sec, we obtain

$$j = i - \tfrac{5}{2} = 10.171 + \tfrac{3}{2} \log \mu, \tag{14.13}$$

an expression which corresponds to pressures measured in dyne/cm. For use with decimal logarithms, this expression must be divided by $\log 10 = 1/0.4343$

$$j_{10} = i_{10} - 1.086 = 4.417 + \tfrac{3}{2} \log_{10} \mu. \tag{14.14}$$

If we wish to measure the pressure in atmospheres instead of dyne/cm and to use decimal logarithms, we have to subtract $\log_{10} 1\ 013\ 249 = 6.0057$, obtaining the constant

$$j_{10,\,\mathrm{atm}} = i_{10,\,\mathrm{atm}} - 1.086 = -1.589 + \tfrac{3}{2} \log_{10} \mu. \tag{14.15}$$

It was later found that the Sackur-Tetrode expression gives the main part of the chemical constant but is incomplete: there are *additional terms depending on the electronic and nuclear spins.* The agreement of the theoretical values with the experimental is, on the whole, very good but it will be better to postpone the comparison until section 120 where we shall derive the missing terms.

When accuracy is not required and the question is only as to the order of magnitude, it is permissible to neglect the refinements and to use the above expressions without correction. Therefore, it will be useful to write out here the explicit form which the equation (8.16),

(8.17) of equilibrium of perfect gases assumes when the numerical values of the constants are substituted in the form (14.15)

$$\log_{10} K_p = \sum_h \nu_h \log_{10} p_h = -0.503\nu - \tfrac{3}{2}\sum_h \nu_h \log_{10} \mu_h + \log_{10} T \cdot \sum_h \nu_h (c_{ph}/R) - \frac{0.2186 Q_p}{T}. \qquad (14.16)$$

The pressure p is here expressed in atmospheres, the heat of reaction Q_p in cal/degree.

96. Theoretical derivation of the Sackur–Tetrode formula. Although Sackur and Tetrode obtained the correct expression (14.12) of the chemical constant, the method of reasoning they used did not stand the test of later criticism, and cannot be considered as altogether valid. However, a rigorous derivation of this expression was given by O. Stern [1] in 1913. As this problem lies beyond the pale of pure thermodynamics, he had to appeal to the principles of statistics and of the quantum theory. But the statistical elements in Stern's argumentation are so simple that it can be given in its completeness even in a textbook of thermodynamics. The fundamental idea is to consider a vapor obeying the law of monatomic perfect gases in equilibrium with its condensed phase, and to calculate its pressures, on one hand, thermodynamically from eq. (14.05), on the other hand, statistically. The comparison of the two results leads to the expression for the chemical constant. This constant determines the entropy of the perfect gas and, therefore, it can depend only on the properties of the gaseous phase of our system remaining the same no matter what kind of condensed phase is in equilibrium with it. It is, therefore, permissible to consider the equilibrium even with an imaginary condensed phase which does not really exist but could exist, inasmuch as it is constructed in agreement with the laws of nature. Stern takes as the condensed phase Einstein's model of the solid body described in section 93 and assumes that the temperature T of the system is sufficiently high compared with $\Theta = h\nu/k$ to use the approximations (13.27).[2] We substitute them into eq. (14.05), taking the solid body also as monatomic ($g = 1$) and its volume as negligible ($v^{(c)} = 0$) and recalling that for a monatomic perfect gas $u = 3RT/2 + u_0$, $c_p = 5R/2$. If we drop the subscript

$$\log p = \tfrac{3}{2} + \tfrac{5}{2}\log T - 3[1 - \log(h\nu/kT)] - \frac{u_0 - u_0^{(c)}}{RT} + i$$

$$= -\tfrac{3}{2} - \tfrac{1}{2}\log T + 3\log(h\nu/k) - \frac{u_0 - u_0^{(c)}}{RT} + i. \qquad (14.17)$$

[1] O. Stern, Phys. Zs. 14, p. 629, 1913; Zs. Electrochemie 25, p. 99, 1919.

[2] Differently from the preceding section, ν is here the freqnency.

With this result the thermodynamic part of the investigation is concluded and we proceed to the statistical part. We have specified that the temperature is high, and this permits us to use the principles of statistics in their traditional form since, in this case, the differences between classical and quantum statistics disappear. All we need of the quantum theory is already contained in eq. (14.17), which embodies the properties of a quantized solid. In Einstein's model every atom of the solid body is regarded as a harmonic oscillator attached to the position of rest by a force F proportional to the distance r from it. The equation of motion of an atom is, then,

$$M\frac{d^2r}{dt^2} = -M\omega^2 r,$$

where M is its mass and $\omega = 2\pi\nu$ its angular frequency. The right side of the equation represents the force F, so that the potential energy of an atom at the distance r from its position of equilibrium is

$$\varepsilon_r = -\int_0^r F\,dr = M\omega^2 r^2/2. \tag{14.18}$$

These assumptions were sufficient for the theory of specific heats (section 93) but, in order to calculate the equilibrium of the solid with its vapor, we must specify them a little farther. How far does the field of the force F extend? The atoms are all considered as independent in their oscillations so that it cannot reach as far as the next atom. To satisfy this requirement we imagine, around every position of rest as a center, a sphere of the radius a. Inside each sphere there exists a radial force $F = -\omega^2 Mr$ while the space outside the spheres is field-free. The model of the solid body is reduced to a number of little spheres with fields of forces in them. The atoms which are inside the spheres belong to the condensed phase, while the free atoms outside form the vapor.

Let $d\tau$ be an element of space in one of the spheres situated at the distance r from the center, and let $z_r d\tau$ be the mean number of atoms in this element (i.e. the mean of many observations taken at different times). The only proposition from statistical mechanics which we need is Boltzmann's principle (4.69) which tells us that the mean numerical density z_r is proportional to an exponential function of the potential energy ε_r

$$z_r = C\exp\left(-\varepsilon_r/kT\right), \tag{14.19}$$

C being a constant of proportionality.

As the space outside the spheres is field-free, the potential energy ε_0 of the free atoms is the same as that of an atom at the border of the sphere $\varepsilon_0 = M\omega^2a^2/2$. Denoting the numerical density (i.e. number of atoms per unit volume) of the free atoms by z_0 we can apply Boltzmann's principle also to them

$$z_0 = C \exp(-\varepsilon_0/kT), \tag{14.20}$$

whence eliminating the constant C from the two equations

$$z_r = z_0 \exp[(\varepsilon_0 - \varepsilon_r)/kT].$$

If we integrate z_r over the whole volume of the sphere, we obtain the mean number of atoms in it. It is obvious that this number must be equal to 1. In fact, in a real solid the number of atoms is equal to the number of positions of rest. If a part of the solid is vaporized the positions of rest disappear with the atoms. We can write, therefore,

$$1 = \int z_r \, d\tau = 4\pi z_0 e^{\frac{\varepsilon_0}{kT}} \int_0^a e^{-\frac{M\omega^2r^2}{2kT}} r^2 dr. \tag{14.21}$$

In the thermodynamic eq. (14.17) small quantities of the order $x = h\nu/kT$ were neglected. To be consistent we must neglect terms of the same order also in the expressions derived from statistics. This remark shows the way of getting rid of the radius a. Since the Einstein model is not a real but an imaginary solid, the quantities ν and a can be selected at our discretion and we can choose them so that $y = M\omega^2a^2/2kT$ will be still large at the high temperature at which $x = h\nu/kT$ is very small, so that $\exp(-y)$ can be made smaller than x. The integral from 0 to a in (14.21) can then be replaced by the integral from 0 to ∞, since the two differ only by terms of that order. We obtain thus

$$1 = z_0(2\pi kT/M\omega^2)^{3/2} \exp(\varepsilon_0/kT).$$

The potential energy of 1 mol of the gaseous phase is $n_A\varepsilon_0$. It is the energy which would have to be expended to make n_A atoms free, if all the bound atoms were at rest in the centers of their respective spheres. This state of affairs prevails at the absolute zero of temperature when the atoms have no kinetic energy. The physical meaning of $n_A\varepsilon_0$ is, therefore, the difference in the zero point energies of the gaseous and the solid phases: $n_A\varepsilon_0 = u_0 - u_0^{(c)}$. Therefore,

$$z_0 = (2\pi M/kT)^{3/2}\nu^3 \exp[(u_0^{(c)} - u_0)/RT], \tag{14.22}$$

since $R = kn_A$ and $\omega = 2\pi\nu$. The number z_0 defines the vapor pressure according to eq. (1.15), $p = z_0 kT$. Substituting z_0 from (14.22) and taking the logarithm,

$$\log p = \tfrac{3}{2}\log 2\pi M + \tfrac{5}{2}\log k - 3\log h^2 - \tfrac{1}{2}\log T + \tfrac{3}{2}\log(h\nu/k) - \frac{u_0 - u_0^{(c)}}{RT}. \qquad (14.23)$$

Comparing this expression with (14.17), we find that in forming the difference the quantities p, T, ν, $u_0 - u_0^{(c)}$ are eliminated and we obtain for the chemical constant i precisely the expression (14.12) of Sackur-Tetrode.

In the preceding discussion we have not made use of the electric neutrality of atoms. All our considerations and formulas would apply, therefore, just as well to electrified particles attached to their respective spheres by electric forces, provided a gas consisting of such particles is subject to the law of perfect gases. The slight corrections which are necessitated by the existence of electronic and nuclear spins as well as the theory of chemical constants of diatomic and polyatomic gases will be dealt with in section 120.

CHAPTER XV

CRITICAL ANALYSIS OF NERNST'S POSTULATE[1]

97. Unattainability of the absolute zero. In the years following the discovery of Nernst's theorem the question was much discussed whether it really represented an independent and new principle of science or was contained, in some way, in the first and second laws of thermodynamics. The relation of the isothermal $T = 0$ to the system of adiabatics, $S = \text{const}$, played an important role in these discussions. The second law not only states that the entropy is a function of the state but implies also that it is a *unique* function of the state. No system can have two different values of the entropy at the same time. In fact, if this were possible in some state of the system, this state would be common to two adiabatics (say, $S = S_1$ and $S = S_2$, where $S_1 > S_2$) representing their intersection. This leads to a contradiction with the postulate contained in the second law that in an adiabatic process the entropy cannot decrease: starting from the entropy S_1 one could lead the process to the state of intersection and thence along the adiabatic S_2. It follows that the system of adiabatics $S = \text{const}$ is a family of surfaces which do not possess intersections or envelopes. However, it must be remembered that the adiabatic process is defined as one in which no heat is imparted to the system, its equation being

$$dQ = TdS = 0. \tag{15.01}$$

In addition to the solution $dS = 0$, or $S = \text{const}$, this equation has also the singular solution $T = 0$ which represents at the same time an isothermal and an adiabatic process. Taking the (p, V)-diagram of a simple system as an example, one is inclined, at first sight, to expect conditions as in Fig. 45: the lines of constant entropy form a non-intersecting family (of which we give only the two members $S = S_1$ and $S = S_2$), while the curve $T = 0$ cuts across. It seems possible to lead the system by a succession of reversible adiabatic

[1] With the kind permission of Yale University Press parts of this Chapter were patterned after the exposition by P. S. Epstein, Commentary on the Scientific Writings of J. W. Gibbs, Article *O*, Sections 6, 7.

processes from the state A to the state D of a different entropy, and this would be a contradiction with the second law of thermodynamics. On the other hand, this contradiction would not exist if the curve $T = 0$ were identical with one of the lines $S = \text{const}$, instead of being a stranger in their midst and cutting across their system.

There are, however, two reasons why it is not permissible to conclude from this argument that Nernst's postulate is a consequence of the second law. The first of them was realized early, being brought home forcibly by the example of the perfect gas which obeys the second law but contradicts Nernst's theorem. In the (p, v)-diagram of the perfect gas the line $T = 0$ is represented by the axes $p = 0$ and $v = 0$ which serve as asymptotes both of the system of isothermals $pv = \text{const}$ and of the system of adiabatics $pv^{\gamma} = \text{const}$. For this reason the line $T = 0$ cannot be reached by any finite and reversible adiabatic process so that the conditions illustrated by Fig. 45 do not apply. It is true that, in the case of the perfect gas, the isothermal $T = 0$ also belongs, mathematically speaking, to the system of lines of constant entropy, $S = \text{const}$, being its extreme member $S = -\infty$ in view of the entropy expression (4.18)

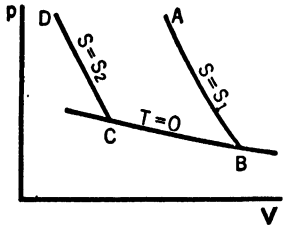

FIG. 45.—State $T = 0$ in relation to adiabatics.

$$s = c_p \log T - R \log p + s_0, \tag{15.02}$$

(where we suppose $p \neq 0$, $v = 0$). Nevertheless, this system does not satisfy Nernst's theorem which requires that *no change of entropy* be possible for $T = 0$. By changing the pressure from p_1 to p_2 we can change s in formula (15.02) by the finite amount $\Delta s_{T=0} = R \log (p_1/p_2)$, while it retains its singular value $-\infty$.

The example of the perfect gas is a conclusive proof that the second law of thermodynamics does not contain Nernst's theorem in its entirety. But attempts continued to show, at least, that certain consequences deduced from it could be also obtained from the second law. In this connection there was advanced by Nernst the principle of the *unattainability of the absolute zero of temperature.*[1] If one of the states $T = 0$ could be reached by a reversible adiabatic process, the diagram of the Fig. 45 would be an adequate illustration of the actual conditions. Pointing out that the succession of adiabatics AB, BC, CD could be

[1] W. Nernst, Die theoretischen und praktischen Grundlagen des neuen Wärmesatzes. Halle 1918.

used to decrease the entropy of the system, Nernst concludes that the assumption of attainability is in contradiction with the second law.

This conclusion was challenged by Einstein,[1] who questions that the part BC of the process (corresponding to $T = 0$) can be carried out. A reversible process is only an ideal, and there is in reality always a certain degree of frictional waste of work, developing heat. However, the slightest amount of heat production would throw the system off the curve $T = 0$. To bring out the gist of Einstein's objection, we may amplify it as follows. From the point of view of physics, a process can only then be considered as defined and meaningful when an experimental procedure is given by which it can be carried out. In general, the adiabatics and isothermals satisfy this requirement. In the case of a simple system, for instance, the adiabatic process is carried out by compressing (or expanding) the system while it is enclosed in a heat-insulating envelope, the isothermal process by the same procedure while the system is in thermal contact with a heat reservoir. The particular process $T = 0$ has the peculiarity that, while it is isothermal, no heat is transferred in it to the reservoir. Nernst treats it, therefore, as an adiabatic process. This is equivalent to dropping the heat reservoir altogether and imagining the system adiabatically insulated in all three branches of the Fig. 45. However, the lack of experimental differentiation between the compressions along the lines BA and BC makes the branch BC meaningless. In fact, no experimental direction is given (or, indeed, possible) to insure that a compression, starting from the point B, should cause the system to move in the curve BC and not in BA. This is the second reason why the argument making use of the diagram of Fig. 45 is fallacious.

These objections refer, however, only to the attempt to derive the principle of unattainability from the second law. If Nernst's postulate is accepted, unattainability becomes a matter of course since it states (in Planck's formulation) that $T = 0$ coincides with $S = 0$. The process $T = 0$ belongs, therefore, to the family $S = \text{const}$ and is identical with its extreme member. As the adiabatics $S = \text{const}$ do not intersect, it is obvious that $S = 0$ cannot be reached by any reversible process represented by one of the other adiabatics.

98. Solutions, supercooled liquids, and the statistical interpretation of Nernst's postulate. Of great practical and theoretical importtance is the question whether Nernst's postulate is a general law or admits exceptions for certain condensed systems. Some controversy

[1] A. Einstein, Structure de la matière (Second Solvay Congress of 1913). Published 1921.

arose with respect to solutions: Planck [1] maintains that his formulation of the theorem applies only to chemically pure substances while in the case of a solution or mixture one should add to the entropy the expression

$$s_0 = -R(N_1 + \ldots + N_f)\sum_{j=1}^{f} x_j \log x_j, \qquad (15.03)$$

where $x_1, x_2, \ldots$ represent the mol fractions of the components of the system and $N_1, N_2, \ldots$ their mol numbers. This term represents the entropy of mixing the components in the case of a mixture of perfect gases (compare section 50). According to Planck, a condensed solution or mixture should have the same value of the entropy constant since it can be converted into the gaseous phase by vaporization.

In this country Planck's views were advocated by Lewis and Gibson.[2] These authors went beyond Planck and questioned, on theoretical and experimental grounds, the applicability of Nernst's theorem to supercooled liquids even of a chemically homogeneous constitution. On the other hand, Nernst [3] had always claimed the general validity of his theorem and was supported by other authors.[4] The contradiction was resolved, and partly reconciled, by an investigation of O. Stern's [5] concerning the entropy of mixed crystals.

It will be best to say here a few words about the statistical aspect of the problem, as both the nature of the difficulty and its ultimate resolution are reduced in it to its simplest terms. We have seen (in section 30) that in statistical mechanics the entropy of a state is interpreted as proportional to the logarithm of its probability $S = k \log P$, which, in turn, is measured by the number of ways in which the state can be realized. If we consider a chemically homogeneous crystal at $T = 0$, every one of its Z atoms has a perfectly definite position of rest. We have discussed this case in section 30 and seen that two probability definitions are possible. If we regard permutations of identical atoms as independent realizations of the crystal (specific definition), we obtain $P_s = Z!$ and $S_0 = k \log Z!$. On the other hand, if (denying the possibility of telling whether the atoms were permuted or not) we consider all the permutations as one single realization (generic definition), we find $P_g = 1$ and $S_0 = 0$. *Nernst's theorem has, therefore, the generic probability definition as its statistical equivalent.*

[1] M. Planck, Thermodynamik (6th ed), p. 285, 1921.
[2] Lewis and Gibson, J. Am. Chem. Soc. 42, p. 1542, 1920.
[3] W. Nernst, Sitzungsberichte Berlin, p. 972, 1913.
[4] E. g. W. H. Keesom, Phys. Zs. 14, p. 665, 1913.
[5] O. Stern, Ann. Physik, 49, p. 813, 1916.

For a mixed crystal consisting of atoms of two kinds (Z_1 and Z_2 in number) the generic definition gives the probability by formula (4.66). By the use of the Stirling approximation ($\log Z! = Z \log Z$) and of mol fractions, $x_1 = Z_1/(Z_1 + Z_2)$, etc., it can be written as

$$P_{12} = x_1^{-Z_1} x_2^{-Z_2}, \tag{15.04}$$

so that the zero entropy of the mixed crystal appears to be of Planck's form

$$S_{12} = -R\,(N_1 + N_2)(x_1 \log x_1 + x_2 \log x_2), \tag{15.05}$$

since $kZ_1 = RN_1$, according to (1.14). If we call each of the realizations of the mixed crystal (differing by the arrangement of at least one pair of atoms of the two kinds) a *modification* of it, the number of modifications is identical with P_{12} and we meet, apparently, with the same difficulty which was encountered by Planck. However, the difficulty is removed by the following remark. The number of possible modifications only then measures the probability in a meaningful way if all these modifications belong to the same thermodynamical state. It was pointed out by Stern that this is not always the case. The rearrangement of atoms changes in a slight degree the internal energy and the other thermodynamical functions of the mixed crystal. Every modification has, therefore, a slightly different thermodynamical potential.

Suppose now that we have a very large number $\mathbf{Z}$ of copies of the same mixed crystal at the temperature T. Owing to the thermokinetic motions, the atoms will be continually rearranging themselves, changing the modifications to which the crystals belong. We may ask, therefore, how many of these copies are, at any given time, in the modification j having the thermodynamic potential Φ_j, and we shall show in the next section that their number is

$$\mathbf{Z}_j = \text{const} \cdot \exp\,(-\Phi_j/kT). \tag{15.06}$$

Correspondingly the ratio $\mathbf{Z}_j/\mathbf{Z}$ represents the probability of finding a given crystal in the modification j. Since the differences in the function Φ_j are very minute, all the numbers $\mathbf{Z}_j$ are practically equal at all temperatures which are not too low. This means that all the modifications are equally probable representing statistically equivalent realizations of our crystal. It is appropriate to count, as the probability of the crystal, the number of these realizations, as was done in formula (15.04), and this leads to the expression (15.05) for the entropy of mixing. On the other hand, at very low temperatures even very small differences in Φ_j begin to tell because of the factor

$1/T$ in the exponent. The numbers Z_j become unequal and, in the extreme case of the immediate vicinity of $T = 0$, the modification j_m with the lowest thermodynamical potential Φ_{min} dominates to such an extent that all the others are impossible. In the vicinity of the absolute zero the mixed crystal is, therefore, in the modification j_m. Since every modification can be realized in only one way, the probability of the crystal, instead of (15.04), becomes $P_{12} = 1$ and the zero entropy $S_0 = 1$, in agreement with Nernst's postulate. Offhand it is conceivable that several modifications could have the same thermodynamic potential, and its lowest value Φ_{min} might be shared by n of them. In this case, the probability at $T = 0$ would be $P_{12} = n$ and the entropy $S_0 = k \log n$. *The purport of Nernst's postulate is*, therefore (as far as mixed crystals are concerned), *that there is one and only one modification of lowest thermodynamic potential.*

Similar considerations apply to the entropies of supercooled liquids. In a liquid the positions of the atoms and molecules are irregular and the possibilities of arranging them more numerous than in a crystal. This makes their entropy, at high temperatures, larger than that of a crystal. At low temperatures, however, the regular crystalline modification is the most probable and, in the vicinity of $T = 0$, even the only possible arrangement of atoms.

From the theoretical point of view Nernst's postulate is, therefore, *completely vindicated* since there is no evidence that it admits of any exceptions. However, the differences in Φ_j on which the above argument depends are so very small that one can expect a perfectly regular arrangement only at extremely low temperatures which are, in many cases, below the range accessible to our experimental technique. Another important consideration is *the time element* since, under these conditions, all processes are extremely slow. For this reason one cannot be certain that the substances under investigation have reached the state of true thermodynamic equilibrium. In this sense, we may say that *the view of Planck and of Lewis and Gibson is justifiable from the practical standpoint of experimental measurements.* This is, in fact, borne out by the recent and very accurate observations [1] of Giauque and his collaborators. The method used by these authors is based on the fact that the absolute entropies of many diatomic and polyatomic gases can be calculated with great accuracy from spectroscopic data (compare section 119). They take the same substances in the solid state at very low temperatures and measure the

[1] Older work pointing in the same direction was due to Gibson, Parks, and Latimer (J. Am. Chem. Soc. **42**, p. 1542, 1920) and Gibson and Giauque (*ibidem* **45**, p. 93, 1923).

entropy difference attending their gradual transformation into gases by heating and subsequent vaporization. In this way it was found that hydrogen,[1] carbon monoxide,[2] nitrous oxide,[3] and ice[4] possess still appreciable entropies as solids at about 15° K. The lattice theory of solid hydrogen was treated by Pauling,[5] who showed that the crystals are built up of para- and ortho-molecules (compare section 118) whose distribution is entirely irregular at temperatures above 5° K. The interpretation which Giauque and co-workers give with respect to the other substances just mentioned is that their molecules are not uniquely oriented but even at temperatures as low as 15° K have still the choice between several orientations. Pauling[6] investigated the case of ice and finds the entropy $R \log (3/2) = 0.805$ cal deg^{-1} mol^{-1}, due to the statistical weight of the indeterminacy of orientation. This is in excellent agreement with the experimental value 0.82 cal deg^{-1} mol^{-1} found by Giauque and Stout.

99. Equilibrium of modifications of a mixed crystal. There remains to prove the formula (15.06) on which the conclusions of the preceding section rest. We shall do this by an argument which is thermodynamical in its main points. Its essential idea (but not its mathematical form) is due to Stern. The formula in question refers to the equilibrium of a very large number of copies of the same mixed crystal. In order to deduce it, we must provide an ideal experimental arrangement by which such an equilibrium can be secured. Let all these crystal copies be contained in an enormously large vessel where they are floating in a neutral gas medium removed from the action of gravity. Through their Brownian movements they will set themselves into thermal equilibrium with the medium and with one another. Provided the size of the crystals is small compared with their mean distance, such a suspension can be regarded as a perfect gas with extremely large molecules obeying all the laws valid for gases (compare section 146). In our particular case every modification of the crystal may be considered as a separate gas, so that we have a mixture of as many gases as there are modifications.

Any modification (1) can be converted through the internal rearrangement of its atoms into any other modification (2), and we can apply to this process the laws of chemical equilibrium of perfect gases.

[1] W. F. Giauque and H. L. Johnston, J. Am. Chem. Soc. 50, p. 3221, 1928.

[2] J. O. Clayton and Giauque, *ibidem* 54, p. 2610, 1932.

[3] R. W. Blue and Giauque, *ibidem* 57, p. 991, 1935.

[4] Giauque and Ashley, Phys. Rev. 43, p. 91, 1933; Giauque and Stout, J. Am. Chem. Soc. 58, p. 1144, 1936.

[5] L. Pauling, Phys. Rev. 36, p. 430, 1930.

[6] L. Pauling, J. Am. Chem. Soc. 57, p. 2680, 1935.

In the law of reaction (6.40) we have to substitute $\nu_1 = -\nu_2 = 1$, obtaining

$$G_1 - G_2 = 0, \tag{15.07}$$

while the equation of equilibrium (6.43) is reduced to

$$\varphi_1 - \varphi_2 = 0. \tag{15.08}$$

The difference between the system under consideration and the ordinary perfect gases of Chapter VIII lies in the fact that in the present case the thermodynamic potential consists of two parts

$$\varphi = \varphi_i + \varphi_e. \tag{15.09}$$

φ_i is the " internal " potential of the crystals themselves, φ_e the " external " part due to the Brownian motions. For φ_e we have to use the expression (8.08) of the thermodynamic potential in perfect gases, omitting the terms $u_0 - Ts_0$ which refer to the intrinsic properties of the " molecules " (here crystals) and are, therefore, included in φ_i. The total potential is, therefore,

$$\varphi = T(R \log p - c_p \log T + c_p) + \varphi_i. \tag{15.10}$$

At this stage of the reasoning we have to invoke another result of statistical mechanics, the fact that the " external " molal heat c_p (due to the movements of the crystals) depends only on the number of degrees of freedom of the " molecules " regarded as rigid bodies. It is, therefore, the same for all modifications: $c_{p1} = c_{p2}$. In substituting (15.10) into the condition (15.08), the terms with c_p will cancel out leaving

$$RT \log (p_1/p_2) = -(\varphi_{i1} - \varphi_{i2}). \tag{15.11}$$

φ_{i1} is the molal thermodynamic potential, i.e. it is referred to n_A crystals (n_A being the Avogadro number). It stands, therefore, in the following relation with the thermodynamic potential Φ_i of an individual crystal used in the preceding section $\varphi_{i1} = n_A \Phi_i$. Noting that $R = n_A k$, we obtain

$$\log (p_1/p_2) = -(\Phi_1 - \Phi_2)/kT. \tag{15.12}$$

p_1 and p_2 are the partial pressures in our vessel of the two gases consisting of the modifications (1) and (2). These pressures are proportional with the numbers $\mathbf{Z}_1$ and $\mathbf{Z}_2$ in which these modifications are represented in the vessel, according to the formula (1.15). The last equation becomes, therefore, identical with (15.06), and this is what we set out to prove.

We have obtained this result by applying to our imaginary suspension the laws of the classical perfect gas. It may be objected that these laws have doubtful validity at very low temperatures. However, we shall see in the next chapter that the approximation given by them is the better, the larger the weight of the molecules. Since, in our ideal experiments, we may attribute to the crystals any size, the accuracy may be considered as of any desired degree even in the immediate vicinity of the zero point.

CHAPTER XVI

DEGENERATE PERFECT GASES

100. Equation of state of the monatomic degenerate gas. Nernst's theorem was enunciated only for condensed systems, and it was realized, from the beginning, that the classical perfect gas fails to fulfill it. In fact, the entropy of the perfect gas has the form (4.18) which would need an infinite entropy constant in order to meet the requirement $s_{T=0} = 0$. The coefficient of expansion of the perfect gas is, according to (1.19), $\alpha = 1/T$, while the specific heats c_v and c_p are constants independent of temperature (section 15), in contradiction with the two immediate consequences (13.09) and (13.15) of the theorem which would require $\lim_{T=0} \alpha = 0$ and $\lim_{T=0} c = 0$. Beginning with Sackur and Tetrode (section 95) there were many attempts to subject the perfect gas to quantum conditions and to obtain a corrected equation of state. As long as these endeavors were based on the classical statistics of Boltzmann-Planck they failed, but the advent of new types of statistics led to a great success, the discovery of the correct laws of perfect gases which happen to be in agreement with Nernst's theory.

A textbook of thermodynamics is not the place to enlarge upon the statistical principles underlying the new theory of the perfect gases. We shall give only a brief reference to questions of statistics in section 104 of this chapter and shall take the equation of state as given, in the same way as we did not inquire into the statistical justification of the classical perfect gas. If we restrict ourselves to *monatomic* gases, the corrected equation of state can be written in the form

$$pv = RT\frac{P(\Theta)}{\Theta}. \tag{16.01}$$

It differs from the old equation of perfect gases (1.13) only by the factor $P(\Theta)/\Theta$ appearing on the right side. By $P(\Theta)$ is meant a certain function of the argument

$$\Theta = \frac{2\pi\mu k\, v^{\frac{2}{3}} T}{h^2\, n_A^{\frac{2}{3}}}, \tag{16.02}$$

where the letters have the same meaning as before. In particular, μ is the atomic weight, h Planck's quantum of action (6.554×10^{-27} erg sec), and n_A the Avogadro number. The function $P(\Theta)$ is so complicated that it cannot be given by an explicit formula but only implicitly. In order to define it we introduce two auxiliary functions $F(A)$ and $G(A)$ of a new argument A by the equations

$$\left.\begin{aligned} F(A) &= \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{A x^{1/2} e^{-x} dx}{1 - \delta \cdot A e^{-x}}, \\ G(A) &= \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{A x^{3/2} e^{-x} dx}{1 - \delta \cdot A e^{-x}}. \end{aligned}\right\} \tag{16.03}$$

We have to distinguish three types of perfect gases which differ, according to the value assigned to the constant δ and according to the range of variability of the variable A:

(1) The classical or Boltzmann-Planck gas

$$\delta = 0, \qquad 0 \leqq A \leqq \infty.$$

(2) The Fermi degenerate gas

$$\delta = -1, \qquad 0 \leqq A \leqq \infty.$$

(3) The Einstein-Bose degenerate gas

$$\delta = +1, \qquad 0 \leqq A \leqq 1.$$

When $\delta = +1$, A cannot be larger than 1 because otherwise the integrals (16.03) would be divergent.

In all three cases the connection between $F(A)$, $G(A)$, on one hand, and $P(\Theta)$, Θ, on the other, is the same, namely:

$$F(A) = \Theta^{-3/2}. \tag{16.04}$$

This relation expresses A in terms of Θ, so that $G(A)$ can now also be regarded as a function of Θ. Therefore, the second relation which we impose,

$$P(\Theta) = \Theta^{5/2} G(A), \tag{16.05}$$

amounts to defining $P(\Theta)$ as a function of Θ.

It should be noted that the functions $F(A)$ and $G(A)$ are not independent but there exists between them the relation

$$\frac{dG(A)}{dA} = \frac{F(A)}{A}, \tag{16.06}$$

which is readily obtained by multiplying the numerator and denom-

inator of the integral for $G(A)$ by e^x/A, then differentiating the result with respect to A and partially integrating with respect to x.

In the range $A \leqq 1$ the functions (16.03) can be represented by the following series

$$\left.\begin{aligned} F(A) &= A + \frac{\delta}{2^{3/2}} A^2 + \frac{\delta^2}{3^{3/2}} A^3 + \dots \\ G(A) &= A + \frac{\delta}{2^{5/2}} A^2 + \frac{\delta^2}{3^{5/2}} A^3 + \dots \end{aligned}\right\} \tag{16.07}$$

The opposite case of very large values of A, $(A \gg 1)$ is of interest only in connection with the Fermi gas, $\delta = -1$. The approximations for the two functions are, then, as follows

$$\left.\begin{aligned} F(A) &= \frac{4}{3\sqrt{\pi}} (\log A)^{3/2} \left[1 + \frac{\pi^2}{8(\log A)^2} + \dots \right], \\ G(A) &= \frac{8}{15\sqrt{\pi}} (\log A)^{5/2} \left[1 + \frac{5\pi^2}{8(\log A)^2} + \dots \right]. \end{aligned}\right\} \tag{16.08}$$

In the case ($\delta = 1$) of the Einstein-Bose gas, A cannot be larger than 1 and, for the classical gas ($\delta = 0$), no approximation is needed since $F(A) = G(A) = A$ are, then, the rigorous expressions for the functions.

It is clear from the formulas (16.07) and (16.08) that $F(A)$ is parallel with A in the sense of being small or large when A is small or large. On the other hand the equation (16.04) shows that Θ is in an inverse relation to $F(A)$ and, therefore, to A: when A is small, Θ is large, and vice versa. From the four equations (16.07), (16.04), and (16.05), we can eliminate by the method of successive approximations the three quantities A, $F(A)$, $G(A)$ and obtain the following approximate relation between $P(\Theta)$ and Θ:

$(\Theta \gg 1)$

$$P(\Theta) = \Theta \left[1 - \frac{\delta}{2^{5/2}\Theta^{3/2}} + \delta^2 \left(\frac{1}{8} - \frac{2}{3^{5/2}} \right) \frac{1}{\Theta^3} \right]. \tag{16.09}$$

The same procedure carried out with the formulas (16.08), (16.04), and (16.05) applies only to the case $\delta = -1$ of the Fermi gas

$(\Theta \ll 1)$

$$P(\Theta) = \frac{3}{5} \left(\frac{\pi}{6} \right)^{1/3} + 4 \left(\frac{\pi}{6} \right)^{5/3} \Theta^2 + \dots \tag{16.10}$$

We see from (16.09) that, for very large values of the variable Θ, the function $P(\Theta)/\Theta$ becomes closely equal to 1 so that eq. (16.01) takes the classical form $pv = RT$. By its definition (16.02) the quantity Θ is proportional to $v^{\frac{2}{3}}T$, it is large when the temperature is high or the density low. Under these conditions the gases of Einstein-Bose and Fermi do not deviate in their properties from the classical perfect gas: they are *non-degenerate.* As Θ decreases the deviation from the classical laws becomes more and more marked: the degree of degeneration increases. However, we shall postpone the quantitative discussion of the degree of degeneration until section 105.

101. The thermodynamic characteristics of the degenerate gas. From the equation of state (16.01) the internal energy can be obtained by means of the relation (4.23)

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = \left(\frac{\partial u}{\partial v}\right)_T, \tag{16.11}$$

or integrating with respect to dv,

$$u = \int \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv + f(T). \tag{16.12}$$

The function $f(T)$ is determined by the condition that the gas is non-degenerate at high temperatures. The internal energy must take, for $T \to \infty$, the classical value (3.18) without becoming infinite for $T = 0$. It is convenient to change the variable of integration from v to Θ, given by the relation (16.02) which can be also written

$$\tfrac{3}{2} \log \Theta = \tfrac{3}{2} \log T + \log v + \text{const.} \tag{16.13}$$

Since T is to be considered as constant with respect to the integration,

$$\frac{dv}{v} = \frac{3}{2}\frac{d\Theta}{\Theta}. \tag{16.14}$$

On the other hand, $T(\partial p/\partial T)_v = \Theta(\partial p/\partial \Theta)_v$. After these substitutions the integration can be readily carried out, giving, with a suitable disposal of the function $f(T)$,

$$u = \frac{3}{2} RT \frac{P(\Theta)}{\Theta} + u_0. \tag{16.15}$$

This is, in fact, identical with (3.18) in the limit $\Theta \to \infty$, since for a classical monatomic gas $c_v = \frac{3}{2} R$.

Knowing the internal energy u and the pressure p, we can calculate the entropy differential (4.15), $ds = (du + pdv)/T$. According to the expressions (16.01), (16.13), and (16.15) for p, v, and u, we can choose as variables T and Θ. The differential dv can be expressed in terms of dT and $d\Theta$: it follows from (16.13)

$$\frac{3}{2}\frac{d\Theta}{\Theta} = \frac{3}{2}\frac{dT}{T} + \frac{dv}{v}.$$

This change of variables reduces ds to the form

$$ds = \frac{3}{2} R \frac{dP(\Theta)}{\Theta} \tag{16.16}$$

depending only on Θ.

Nernst's postulate in the form (13.19) can be directly applied only in the case of the Fermi gas. In fact, in the case of the Einstein-Bose gas the variable A cannot be larger than 1, and the relation (16.04) shows that Θ cannot sink below a certain finite limit and is not defined in the vicinity of $T = 0$. We pointed out in section 1 that the postulate does not apply to the classical perfect gas. Therefore the validity of the simple entropy expression

$$s = \frac{3}{2} R \int_0^{\Theta} \frac{dP(\Theta)}{\Theta} \tag{16.17}$$

is restricted to the Fermi gas. The integration can be carried out by transforming back to the variable A with the help of the relations (16.04) and (16.05). The first of them can be written as $\log \Theta = -\frac{2}{3} \log F(A)$, or differentiating

$$\frac{d\Theta}{\Theta} = -\frac{2}{3}\frac{dF}{F}.$$

In this way the integrand is transformed into

$$\frac{dP(\Theta)}{\Theta} = -\frac{5}{3} G \frac{dF}{F^2} + \frac{5}{3}\frac{dG}{F} - \frac{2}{3}\frac{dG}{F}.$$

The first two terms give $\frac{5}{3} d(G/F)$ and we can write instead of the last $-\frac{2}{3} dA/A$, because of the relation (16.06). Hence

$$s = R\left[\frac{5}{2}\frac{G(A)}{F(A)} - \log A\right]. \tag{16.18}$$

The condition $s = 0$, at the limit $\Theta = 0$, or $A = \infty$ is taken care of because, for very large values of A, the formulas (16.08) give

$\frac{5}{2}G/F = \log A$. We shall show by a special investigation in section 103 that the form (16.18) of the entropy expression holds also in the case of the Einstein-Bose gas.

Finally, the formulas (16.01), (16.15), and (16.18) give for the molal thermodynamic potential $\varphi = u - Ts + pv$ the simple expression

$$\varphi = RT \log A + u_0, \tag{16.19}$$

which is true for both kinds of degenerate gases.

102. Chemical constant of degenerate gases. Their relation to Nernst's postulate. We have seen in section 1 that for high temperatures or low densities ($\Theta \ll 1$ and $A \gg 1$) the gases of Fermi and Einstein-Bose are non-degenerate, approximating in their properties the classical perfect gas. When the variable A is extremely large, the functions (16.07) are reduced to $F(A) = G(A) = A$, whence eq. (16.04) gives $A = \Theta^{-3/2}$. The entropy expression (16.18), therefore, takes the form

$$s = R(\tfrac{5}{2} + \tfrac{3}{2} \log \Theta), \tag{16.20}$$

or because of (16.02) and $R = n_A k$,

$$\left.\begin{aligned} s &= R \log v + \tfrac{3}{2} R \log T + R i' \\ &= \tfrac{5}{2} R \log T - R \log p + R i, \\ i &= \tfrac{5}{2} + \log \frac{(2\pi\mu)^{3/2} R^{5/2}}{h^2 n_A^4}. \end{aligned}\right\} \tag{16.21}$$

The entropy has the classical form (4.18), specialized for the monatomic gas ($c_v = \frac{3}{2}R$, $c_p = \frac{5}{2}R$), while the constant i exactly coincides with the Sackur-Tetrode expression (14.12). Putting the question as to the validity of Nernst's postulate we must remember that we so far obtained complete expressions for the energy and equation of state (valid down to the vicinity of $T = 0$) only in the special case of the Fermi gas. In deriving them we made explicit use of Nernst's theorem through eq. (16.17) so that there is no question but that it is fulfilled. It will be well, however, to check here the two immediate consequences from the theorem which we have derived in sections 90 and 91, that *the specific heat and the coefficient of thermal expansion must vanish* for $T = 0$.

For the specific heat we have from (16.15) and (16.10) the value

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{3}{2} R \frac{T}{\Theta} \left(\frac{\partial P(\Theta)}{\partial T}\right)_v = \frac{3}{2} R \frac{dP(\Theta)}{d\Theta} = 2\pi \left(\frac{\pi}{6}\right)^{3/5} R\Theta, \tag{16.22}$$

which is proportional to T, because of formula (16.02), and vanishes with T.

For the coefficient of thermal expansion, eqs. (1.02) and (1.05) give

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = -\frac{1}{v}\left(\frac{\partial p}{\partial T}\right)_v \Big/ \left(\frac{\partial p}{\partial v}\right)_T. \tag{16.23}$$

Since p differs from u only by the factor $2/3v$,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{2}{3}\frac{c_v}{v}, \tag{16.24}$$

so that α also vanishes for $T = 0$ in a linear way.

To elucidate the conditions in the case of the Einstein-Bose gas we need a separate investigation to which we now turn.

103. Condensation of the Einstein–Bose gas. It was pointed out in section 100 that in the Einstein-Bose case ($\delta = 1$) the variable A cannot be larger than 1. In view of this, Θ has a lower limit $\Theta_{\min}$ determined by eq. (16.04) with $A = 1$:

$$F(1) = \Theta_{\min}^{-3/2}. \tag{16.25}$$

Now $F(1) = 2.6123$, and the numerical value of the limit is, therefore, $\Theta_{\min} = 0.528$. Since the parameter Θ depends on v and T, according to eq. (16.02), we may ask what will happen if, keeping the temperature of the gas constant, we should compress it sufficiently to make Θ fall below the limit $\Theta_{\min}$ (or else decrease the temperature keeping the volume constant). To this question Einstein gives the answer that a part of the system will cease to be gaseous and will be precipitated out, forming a condensed phase in equilibrium with the remaining part of the gas. The condition of equilibrium is given by the equation (7.03)

$$\varphi = \varphi_{pr}, \tag{16.26}$$

where φ and φ_{pr} represent the thermodynamic potentials of the gaseous phase and of the precipitate. Since the expressions (16.18) and (16.19), derived for the entropy and thermodynamic potential of the Fermi gas, give the correct value of the chemical constant, it is desirable to conserve them for the Einstein-Bose gas. Under the conditions of condensation (saturated state) $\Theta = \Theta_{\min}$ and $A = 1$, so that eq. (16.19) gives $\varphi = u_0$. Consequently, $\varphi_{pr} = u_{pr} - Ts_{pr} + pv_{pr}$ must be also equal to u_0, for all temperatures and pressures compatible with $\Theta = \Theta_{\min}$. This requires $u_{pr} = u_0$, $s_{pr} = 0$, $v_{pr} = 0$ and means that in the solid phase the material is much in the same state which prevails at $T = 0$. It does not possess any thermokinetic energy, and

it has a perfectly regular arrangement of atoms and a negligible volume.

In support of Einstein's explanation we can point to the peculiar shape of the isothermals of the Einstein-Bose gas.[1] By means of (16.02) and (16.05) we obtain from (16.01) the expression for the pressure

$$p = \left(\frac{2\pi\mu}{n_A}\right)^{3/2} \frac{(kT)^{5/2}}{h^3} G(A), \tag{16.27}$$

and calculate from it the partial derivative

$$\left(\frac{\partial p}{\partial v}\right)_T = \frac{dp}{dA} \cdot \frac{dA}{dF} \cdot \frac{dF}{d\Theta} \cdot \left(\frac{\partial \Theta}{\partial v}\right)_T.$$

Because of (16.06) and (16.04), this gives

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{v^2} \frac{1}{\Theta^3 A} \frac{dA}{dF}. \tag{16.28}$$

It is easy to see from the definition (16.03) of the function $F(A)$ that (in the case $\delta = 1$) the derivative dF/dA becomes infinite for $A = 1$. Consequently, $(\partial p/\partial v)_T = 0$, for $A = 1$, $\Theta = \Theta_{\min}$. In the state of saturation the gas is, therefore, characterized by an infinite compressibility and its isothermals by horizontal tangents. These conditions are illustrated in Fig. 46, where the solid lines represent the isothermals and the dotted curve corresponds to $\Theta = \Theta_{\min}$. We have seen in the theory of the Van der Waals equation that the points $(\partial p/\partial v)_T = 0$ are those where a single phase of the gas begins to be completely unstable. The condensation of the ideal gas of Einstein-Bose is, therefore, closely analogous to the conditions in real gases.

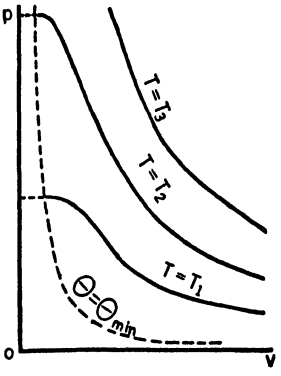

FIG. 46.—Isothermals in Einstein-Bose degenerate gas.

104. Statistics underlying the theory of degenerate gases. Rule of alternation.[2] We have introduced and treated eq. (16.01) of degenerate gases in a purely formal manner. It will be well to say now a few words about its origin and about the question of which gases of

[1] Compare P. S. Epstein, Commentary on the Scientific Writings of J. W. Gibbs, Article *O*, Section 10.

[2] For a detailed exposition of quantum statistical principles, see: P. S. Epstein, *ibidem*, Article *V*.

nature are subject to degeneration of the types of Fermi and of Einstein-Bose. Classical statistics and the statistics of the older quantum theory were dominated by Boltzmann's principle (4.70): If we have a single particle (or other system) which can assume different dynamical states, the probability of finding it in a state characterized by the energy ε_j is

$$P_j = C \exp(-\varepsilon_j/kT), \tag{16.29}$$

C being a constant. Nothing is changed if we consider Z particles of one and the same kind under joint external conditions (field of forces or vessel), determining a set of energy levels $\varepsilon_1, \varepsilon_2, \ldots \varepsilon_j, \ldots$ which any of the particles can assume. The mean number Z_j of particles occupying the energy level ε_j is again given by

$$Z_j/Z = C \exp(-\varepsilon_j/kT), \tag{16.30}$$

because in the classical theory the particles are regarded as statistically independent: the probability of a particle assuming any state is not influenced by the presence of the other particles and remains the same as if it were alone.

With the advent of wave mechanics the point of view had to be changed. In the case of a single particle, Boltzmann's principle (16.29) remains valid but Z particles forming a system of the kind mentioned above can no longer be regarded as statistically independent.[1] The primary particles of matter (the proton, neutron, and electron) fulfill the Pauli exclusion principle: *No more than one of Z identical particles can occupy any given quantum state.* (In the language of wave mechan-

[1] It was pointed out in section 30 that the fundamental difference between classical and quantum statistics lies in the question whether identical particles can be told apart. This question has an intimate relation to Heisenberg's *principle of indetermination* which states that the uncertainties Δx (of a coordinate of position) and Δp_x (of the conjugate momentum) are restricted by the inequality $\Delta x \cdot \Delta p_x \geqq h/4\pi$. In fact, when the uncertainty of position of each particle in a gas is small compared with the mean distance between the particles $(v/n_A)^{1/3}$, then there exists the conceptual possibility of keeping track of any particle and mentally identifying it as distinct from the others. Therefore, classical statistics must give a correct result when the condition $(v/n_A)^{1/3} >> \Delta x$ is satisfied. On the other hand, when the two quantities are of the same order of magnitude, there is no way of telling which particle is which, the concept of permutation loses its sense, and classical statistics can no longer be applied. The uncertainty of the momentum is, obviously, the mean momentum itself $\Delta p_x = \overline{p_x}$, since the particle may have any velocity. As long as classical statistics (equipartition) is valid $\overline{p_x^2} = M^2\overline{v_x^2} = MkT$. We obtain, therefore the condition $(MkT)^{1/2}(v/n_A)^{1/3} >> h/4\pi$, or using the notation (16.02), $\Theta >> 1/8\pi$. This is the deeper reason why degeneration is absent when Θ is large and sets in when this quantity becomes small.

ics the same thing is stated by saying that the primary particles have antisymmetric wave functions.) We cannot enter here into the details of the statistical calculations based on the exclusion principle and must be satisfied with their results: they lead to the modified formula

$$\frac{Z_j}{Z} = C\frac{Ae^{-\varepsilon_j/kT}}{1 - \delta \cdot Ae^{-\varepsilon_j/kT}} \tag{16.31}$$

($\delta = -1$), which represents the fundamental law of Fermi's statistics. The quantity A gives a measure of the deviation from the classical conditions of the formula (16.29). It is, therefore, obvious that A must be a function both of the particle density in the system and of its temperature. In fact, the sum of all Z_j is the total number of particles, $\Sigma Z_j = Z$, leading to the condition

$$\frac{1}{C} = \sum_j \frac{Ae^{-\varepsilon_j/kT}}{1 - \delta \cdot Ae^{-\varepsilon_j/kT}}. \tag{16.32}$$

Another condition follows from the energy relations. The total energy of the Z_j particles in the state j is $\varepsilon_j Z_j$ and, therefore, the total internal energy of the system $U = \Sigma \varepsilon_j Z_j + U_0$ or

$$U - U_0 = ZC\sum_j \frac{A\varepsilon_j e^{-\varepsilon_j/kT}}{1 - \delta \cdot Ae^{-\varepsilon_j/kT}}. \tag{16.33}$$

It is possible to eliminate C from these two equations and to obtain A as a function of U, Z, and T.

Let us now turn from primary particles to composite ones, for instance, to atomic nuclei built up of protons and neutrons. If antisymmetric wave functions are used for the protons and neutrons within the necleus, the translational motions of it, as a whole, are described as follows: (*a*) by antisymmetric wave functions, if the number of primary particles in the nucleus is odd, (*b*) by symmetric wave functions, if this number is even. Nuclei of the first kind have the same statistical properties as the primary particles themselves, they obey the exclusion principle and the formula (16.31) of Fermi's statistics (with $\delta = -1$). On the other hand, nuclei of the second kind possess entirely different qualities: the statistical calculation shows that in their case the number Z_j can be expressed by the formula (16.31) with $\delta = +1$ which characterizes the statistics of *Einstein-Bose.* The law that the statistics of Fermi applies to composite particles with an odd number of primary elements, and Einstein-Bose's to those with an even number, is known as the *rule of alternation.* Of course, this rule is theoretically valid also in the case of neutral *atoms* which

contain primary particles of three kinds: electrons in addition to protons and neutrons. The experimental test of the rule could not be carried out by observing the degeneration of gases (compare next section) but by study of molecular band spectra whose structure also depends on the statistical properties of the nuclei composing the molecule. In the present state of our knowledge the rule of alternation seems to hold without exception. Doubts exist only with respect to the sulfur nucleus, but the experimental data are insufficient to decide whether they are well founded. There was introduced into the theory of nuclear structure the hypothesis of the existence of another primary particle, the neutrino, which is supposed to have a very minute mass. This assumption proved very useful in the theory β-ray emission and of nuclear transformations, but it seems that the neutrino could be dispensed with as far as the rule of alternation is concerned.

The conditions (16.32) and (16.33) determining the quantity A are closely related to the integrals (16.03) of section 100. If the system is a gas, contained in a vessel of the volume V, the energy levels are determined by the vessel. It is shown in the quantum theory that in the interval of energy values between ε and $\varepsilon + \Delta\varepsilon$ there lie $2\pi V(2\mu/n_A h^2)^{3/2}\varepsilon^{1/2}\Delta\varepsilon$ levels, and, if V is sufficiently large, their distribution is practically continuous. By introducing the variable $x = \varepsilon/kT$ the sums (16.32) and (16.33) can be thrown into the form of integrals proportional to (16.03). The comparison shows

$$\left.\begin{aligned} \frac{1}{C} &= V(2\pi\mu kT/n_A h^2)^{3/2} F(A), \\ U - U_0 &= \tfrac{3}{2} ZkT\, G(A)/F(A). \end{aligned}\right\} \qquad (16.34)$$

Thus, the probability definition (16.31) leads directly to an energy expression equivalent with the formula (16.15).

The gases here discussed are *perfect* in the sense that their molecules (or atoms) have no extension and there are no forces of interaction between them. However, the statistical limitations imposed on *identical particles* by Pauli's exclusion principle or the requirements of Einstein-Bose have an effect upon the thermal and caloric equations of state which resembles the effect of force interactions (compare next section). It must be emphasized that no such limitations exist for non-identical particles. In a mixture of several degenerate perfect gases, there is no mutual influence between them, and each gas behaves as if it were alone and the others absent. This implies, in particular, that the formula

$$p = p_1 + p_2 + \ldots + p_\sigma, \qquad (16.35)$$

representing the total pressure as the sum of the partial pressures of the component gases (each calculated as if the rest were not present) remains valid.

105. Chances of observing the degeneration experimentally. Some of the laws of perfect gases have the same mathematical form for all three kinds of them (classical, Fermi, and Einstein-Bose). Such, for instance, is the equation of the adiabatic process: it follows from the expression of the entropy differential (16.16) that s = const, when Θ = const. According to (16.02) this can be written

$$Tv^{\frac{2}{3}} = \text{const}, \tag{16.36}$$

or multiplying by pv from eq. (16.01)

$$pv^{\frac{5}{3}} = \text{const}. \tag{16.37}$$

The relation between pressure and energy density resulting from (16.01) and (16.15)

$$p = \frac{2}{3}\,\frac{u - u_0}{v} \tag{16.38}$$

is also valid for the classical and both degenerate gases.

On the other hand, the pressure expressed in terms of the molal volume and temperature depends on the nature of the gas. Written out explicitly the expressions are

($\Theta \gg 1$)

$$p = \frac{RT}{v}\,(1 - \delta/2^{\frac{5}{2}}\Theta^{\frac{3}{2}})$$

or

$$p = \frac{RT}{v}\left(1 - \frac{\delta}{16}\,\frac{h^3 n_A^{\frac{5}{2}}}{(\pi\mu kT)^{\frac{3}{2}}}\,\frac{1}{v} + \ldots\right). \tag{16.39}$$

($\Theta \ll 1$ occurs only in the Fermi gas)

$$p = \frac{3}{5}\left(\frac{\pi}{6}\right)^{\frac{1}{3}}\frac{RT}{\Theta v} + 4\left(\frac{\pi}{6}\right)^{\frac{5}{3}}\frac{RT\Theta}{v}. \tag{16.40}$$

Substituting into the expression (16.02) for Θ the numerical values of the constants k, n_A, h, and v_0 (molal volume at normal conditions), we find

$$\Theta = 3.67\mu\left(\frac{v}{v_0}\right)^{\frac{2}{3}}T. \tag{16.41}$$

This gives for helium ($\mu = 4.00$) at 0° C and 1 atm, $\Theta = 4033$, so that the condition $\Theta \gg 1$ is fulfilled for the permanent gases of

nature. On the other hand, electrons in metals also form a gas (compare next chapter) of the atomic weight $\mu = 1/1821 = 0.000549$ and with a remarkably small molal volume, namely of the order $v/v_0 = 1/2000$. In such an electron gas the quantity Θ has at room temperature a value of the order of $\Theta = 0.004$, satisfying the opposite condition $\Theta \ll 1$. The two extreme cases represented, respectively, by the formulas (16.39) and (16.40) happen, therefore, to be sufficient for the treatment of all the degenerate systems occurring in nature.

For the permanent gases, eq. (16.39) must be used, and its form is analogous to the Van der Waals equation of state (1.21) which, in the case of not too small molal volume ($v \gg b$), can be written

$$p = \frac{RT}{v}\left[1 + \left(b - \frac{a}{RT}\right)\frac{1}{v}\right]. \tag{16.42}$$

Perfect gases have, of course, no extension of molecules ($b = 0$), but the Einstein-Bose gas ($\delta = 1$) acts as if its molecules were attracting one another, the Fermi gas ($\delta = -1$), as if they exercised repulsive forces. This behavior is in harmony with the statistical meaning of degeneration in the two cases (section 104).

The most promising gas for observations is helium: it is the monatomic gas of lowest atomic weight, and, because of this, has the highest degeneration. Moreover, it can be cooled to lower temperatures than any other gas. But even in helium the conditions are not favorable, the Van der Waals terms of eq. (16.40) are in it (under normal conditions) $b/v = 1.1 \times 10^{-3}$, $a/RTv = 6.8 \times 10^{-5}$ while the degeneration term of (16.39) has the much smaller value $-1/2^{5/4}\Theta^{3/4} = -6.9 \times 10^{-7}$. It is true that the ratio becomes more favorable at lower temperatures, but barring the immediate vicinity of the critical state the constant Θ remains fairly large even then. The effect is, therefore, completely obscured by the Van der Waals forces.

The velocity of sound can be measured with considerable accuracy even at very low temperatures and in a small volume of gas. The determinations of Keesom in helium at 4° K and 0.08 atm gave the value to be expected in a non-degenerate gas. It is easy to see the reason for this. Since the equation of the adiabatic (16.37) is the same as for the classical perfect gas, the expression (3.40) for the velocity of sound also remains valid. This gives (with $\gamma = \frac{5}{3}$)

$$a^2 = \frac{5}{3}\frac{pv}{\mu} = \frac{5}{3\mu}RT\,(1 - \delta/2^{5/4}\Theta^{3/4}). \tag{16.43}$$

Under the conditions of Keesom $\Theta = 24$ and $-1/2^{5/2}\Theta^{3/2} = -1.5 \times 10^{-3}$. The effect of the degeneration is only 0.15% and entirely within the errors of measurement.

Summarizing we can say that the observation of degeneration in atomic gases is hopeless. The only system in which the phenomenon is accessible to the experimental test is the electron gas which is treated in the next chapter.

CHAPTER XVII

ELECTRON AND ION CLOUDS

106. Thermodynamic properties of charged gases. As long ago as 1888 the pioneers of thermodynamics, Arrhenius and Ostwald,[1] applied the mass law to electrified particles (ions). We are indebted to them and their pupils for extensive experimental data which show conclusively that the thermodynamical theory of chemical equilibrium applies to ions just as well as to neutral atoms. The idea that a cloud of electrons can be also described by the laws of perfect gases proved useful in the theory of metallic conduction and associated phenomena. It was introduced by Drude [2] and Richardson,[3] who dealt with it from the statistical point of view, while the first thermodynamical treatment was due to H. A. Wilson.[4]

A part of the internal energy of such a gas must be of electric origin. Let us focus our attention on a portion of the gas so small that we can consider the outer electric potential Ω as constant over its volume τ. The potential Ω is produced, partly, by causes extraneous to the gas, partly by charges on the gas particles outside the volume τ. The contribution to the total electric energy of the portion within τ consists of two items: the mutual energy of this portion and of the rest of the system, and the electrostatic energy of the volume τ itself. The first item is proportional to the first power of the volume τ; the second goes mainly with τ^2 and only rarely contains a portion linear in τ. The latter case may arise when the charges within τ are of both signs so that there is a possibility of *pairing*, i.e. of positive charges hovering, by preference, in the vicinity of negative ones, and vice versa, a phenomenon which we shall discuss in section 115. At present we shall treat the case where pairing is either absent or negligible, so that the inner electric energy of the volume τ is quadratic in τ. If we select τ sufficiently small, the quadratic term becomes negligible com-

[1] W. Ostwald, Zs. phys. Chemie **2**, pp. 36, 270, 1888.

[2] P. Drude, Ann. Physik **1**, p. 566; **3**, p. 369, 1901.

[3] O. W. Richardson, Proc. Camb. Phil. Soc. **11**, p. 286, 1901; Philosophical Transactions (A) **201**, p. 497, 1903.

[4] H. A. Wilson, Philosophical Transactions (A) **202**, p. 258, 1903.

pared with the mutual electric (mentioned above) and the caloric terms which are both proportional to τ. Let us denote the charge per mol by $f = en_A$ (e being the charge on each particle).[1] The electric energy of the gas in the volume τ (due to the outer potential Ω) will then be $f\Omega$ per mol. This is the only part of the electric energy which has to be considered and added to the internal energy of caloric origin. For instance, if we assume that the caloric part has the expression (3.18), valid for a perfect gas, the internal energy becomes

$$u = c_v T + u_0 + f\Omega. \tag{17.01}$$

The additional term $f\Omega$ is independent of the condition of the gas in the volume τ. It is a constant with respect to it and not one of the parameters describing its state. The parameters, subject to change, defined within τ, are temperature, pressure, and specific volume, as in every simple system. It has been established by statistical reasoning and by experiment that the conditions concerning the equation of state and the caloric internal energy are in no way different in a charged gas from those in the uncharged. The equation

$$pv = RT, \tag{17.02}$$

together with (17.01) define the classical (or non-degenerate) perfect charged gas and describe the phenomena in clouds of ions and electrons to the same degree of approximation as the equations lacking the electric term describe the ordinary permanent gases.

Since $f\Omega$ must be considered as constant, with respect to changes in the volume τ, it may be regarded as forming part of the energy constant u_0: in fact, we have seen in section 98 that u_0 itself represents, in part, potential energy. Therefore, the entropy differential ds does not contain the electric potential so that we find for s precisely the same expression (4.18) as in uncharged gases. On the other hand, the thermodynamic potential φ becomes according to (5.41), (5.43)

$$\varphi = RT \log p - c_p T \log T + (c_p - s_0)T + u_0 + f\Omega. \tag{17.03}$$

107. Equilibrium in charged gases. The problem of equilibrium was treated in section 40 in its generality, but the conditions in charged systems are somewhat peculiar, and it will be necessary to say a word how they fit into the picture there given. The phases in a system consisting of charged gases may be determined by external conditions and separated by surfaces of discontinuity, for instance, when we

[1] f becomes identical with the Faraday F when the charge is monovalent and positive. In general, $f = \sigma F$, if σ is the valency; for the electron (whose charge is negative) $f = -F$.

consider the free electrons inside a heated metal, as one phase, and the electron cloud outside it, as another. However, when the electric potential Ω changes continuously with the position in the gas each small volume τ, considered in the preceding section, may be also regarded as a separate phase of the system because the electric conditions in it are different from those of the rest of the gas. In either case the potential is one of the essential characteristics of the phase, and this fact has an important bearing on the equilibrium. In section 40, we mentioned two possible cases, represented by eqs. (6.26) and (6.29), arising when there is no transfer of matter from one phase to another. Which of these applies to charged gases? The first equation is valid when the subsidiary condition (6.24) holds: when it is possible to change the volume of the individual phases at the expense of one another, while keeping the total volume of the system constant. Obviously this is not feasible in the system we are now considering. The expansion of any phase would push a part of it into a region of a different electric potential or, in other words, out of the phase. On the other hand, it is clear that the equilibrium will not be disturbed if we imagine each phase surrounded by a rigid heat-conducting envelope, i.e. if we assume the subsidiary conditions underlying the formulas (6.27) and (6.29). We must conclude, therefore, that a system composed of charged gases in an electric field possesses, in its state of equilibrium, a temperature T uniform for all its parts while the pressure is not uniform but "local," changing with the potential from phase to phase.

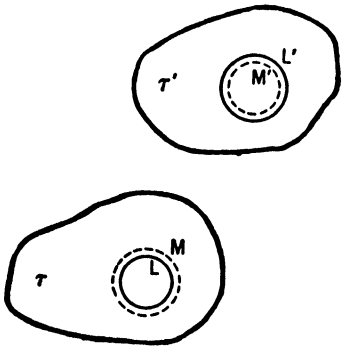

FIG. 47.—Equilibrium of charged gas in electric field.

The remaining condition of equilibrium (6.31) is derived from the analysis of processes of transfer of matter, from one phase to another and from one component to another, while the temperature of the system T and all the local pressures of the phases are kept constant. It applies to a charged system to the extent to which such processes are possible in it. Let us consider, for simplicity, a chemically pure gas (i.e. having molecules of one kind only) in equilibrium at the temperature T, regarding the small volumes τ and τ' (Fig. 47) as two of its phases with respective electric potentials Ω and Ω'. The equilibrium will not be disturbed if we imagine the small spherical surfaces L and L' within the phases hardened and transformed into rigid adiabatic

shells. If the spheres are taken so small that the electric potential due to the gas within them is negligible compared with the rest, we may imagine this part of the gas removed without prejudice to the equilibrium. Of course, we could have selected the spherical hole in τ larger by an infinitesimal amount and having the surface M (dotted line), and that in τ' slightly smaller with the surface M'. Let us adjust the radii in such a way that the spherical layer between L and M contain δN mols of the gas (in its original distribution), and that between L' and M' an equal number $-\delta N'$ (i.e. $\delta N = -\delta N'$), while the temperature and the local pressures remain the same. The same effect can be obtained by expanding the sphere in τ from L to M and contracting that in τ' from M' to L'. This last procedure provides the mechanism we were looking for, a process for transferring δN mols of the gas from the phase τ' to the phase τ without change of temperature or local pressures in any part of the system. We can, therefore, apply the formula (6.31) to it. Let the mol numbers and molal thermodynamic potentials in τ and τ' be N,φ and N',φ', respectively. Changes of Φ occur only in them, and the formula is reduced to $\varphi\,\delta N + \varphi'\delta N' = 0$, or because of the relation $\delta N + \delta N' = 0$,

$$\varphi = \varphi'. \tag{17.04}$$

It is well to say here a word about the phase rule. We found in section 43 that only three phases of a chemically pure substance can coexist. However, that applies only to uncharged systems in which temperature and pressure must be uniform throughout. On the other hand, let us envisage α phases of the charged gas we are discussing now. They are described by $\alpha + 1$ thermodynamical variables T, $p^{(1)}, \ldots p^{(\alpha)}$, and there exist between them $\alpha - 1$ relations (17.04). Even if the electric potential differences are prescribed, two of the variables can be chosen at random (no matter how large the number α is), for instance, the temperature and the pressure in one of the phases. If the electric potentials are not prescribed, there may exist still further degrees of freedom.

The relation (17.04) is valid not only for a chemically pure gas: by suitable use of semipermeable membranes it can be shown to hold for any component of a gas mixture. However, we shall be interested only in mixtures of perfect gases and, then, the following proposition is obvious: if the relation

$$\varphi_j = \varphi'_j \tag{17.05}$$

holds for the component j, when it is pure, it will continue to hold, when the component forms a part of a mixture. This follows from

the fact that perfect gases do not exercise forces on one another but behave as if the others were not present.

In the particular case of a non-degenerate perfect gas, eqs. (17.03) and (17.05) give

$$RT \log (p'_j/p_j) = -f(\Omega' - \Omega), \tag{17.06}$$

or

$$\frac{p'_j}{pj} = \exp\left[-f\frac{\Omega' - \Omega}{T}\right]. \tag{17.07}$$

This special form of the relation could have been obtained also in simpler ways, for instance, from Boltzmann's principle (4.69). However, we shall have to fall back upon the general form (17.05) in treating degenerate gases (section 111).

The other type of processes included in the equation of equilibrium (6.31) are chemical reactions taking place within the individual phases. In the interior of a phase the electric potential does not vary and merely plays the role of an additional energy constant. The conditions are, therefore, precisely the same in a charged gas as in an uncharged and eq. (6.31) remains valid. In particular, when we consider the case of a reaction of the type (6.46)

$$\nu_1 G_1 + \ldots + \nu_\beta G_\beta = 0 \tag{17.08}$$

between perfect gases, the equation of equilibrium has the form (6.49) of section 42:

$$\nu_1\varphi_1 + \ldots + \nu_\beta\varphi_\beta = 0. \tag{17.09}$$

Comparing it with (17.05), we see that the equation is satisfied in all the phases simultaneously so that we have equilibrium in every part of the system. For non-degenerate perfect gases we have to use for φ the expression (17.03) obtaining the following explicit form of the equilibrium condition

$$\sum_{j=1}^{\beta}\nu_j \log p_j = \log K_p - (\Omega/RT)\sum_{j=1}^{\beta}\nu_j f_j. \tag{17.10}$$

K_p is here exactly the same equilibrium constant as that defined by eq. (8.15) in the theory of ordinary gas mixtures (section 51). The sum $\Sigma\nu_j f_j = n_A\Sigma\nu_j e_j$ (where e_j is the charge on a molecule of the component j) represents the change of electric charge in the reaction. However, there is the law of conservation of electric charge, which cannot be created or destroyed, so that the sum $\Sigma\nu_j f_j = 0$. *The law of equilibrium has, therefore, precisely the same form* (8.17) *in a mixture*

of charged as of uncharged gases and can also be expressed in the equivalent formulations (8.18) and (9.60).

108. Remark on heavy gases in a gravitational field. The considerations of the preceding section can be transferred in their entirety to a system of heavy gases in a Newtonian gravitational field produced, partly, by external causes, partly, by their own masses. The only necessary change is to interpret Ω as a gravitational potential and to write, instead of $f_j = n_A e_j$, the molecular weights $\mu_j = n_A M_j$, (M_j being the masses of the molecules). The analogue to (17.06) is then

$$p'_j/p_j = \exp\,[-\mu_j(\Omega_0' - \Omega_0)/RT], \tag{17.11}$$

which is simply a slight generalization of the well-known barometric law of Laplace's. In a gravitational field the equation of chemical equilibrium takes the form

$$\sum_{j=1}^{\beta} \nu_j \log p_j = \log K_p - (\Omega_0/RT) \sum_{j=1}^{\beta} \nu_j \mu_j. \tag{17.12}$$

In most cases the sum $\Sigma \nu_j \mu_j$, representing the change of mass in the reaction, may be taken as zero. However, the law of conservation of mass does not hold for matter alone, and there are phenomena for which this sum is significant and may not be neglected (compare section 133).

109. Thermoelectric potential differences in the classical electron theory. As stated in section 106, the theory of electrons in metals achieved some signal successes by assuming that the free electrons form a perfect gas. In the older (classical) theory this gas was regarded as *non-degenerate*, with an osmotic pressure obeying the law (17.02) and eq. (17.07) resulting from that law. As an application of these ideas, let us consider *two bars* (1) and (2), *of two different metals* (Fig. 48), in contact at the junction J and forming an open chain. Suppose that, in their electrically neutral state at the temperature T, the two metals contain, respectively, z_1 and z_2 free electrons per unit volume. At the moment the two bars are brought in contact, there exists on both sides of the junction a difference of concentrations and, consequently, of osmotic pressures of the free electrons. As we know from section 65, the osmotic pressure tends to equalize the numbers z_1 and z_2 and drives the electrons from (1) to (2), if $z_1 > z_2$. How long will this so-called *thermoelectric*

FIG. 48. — Thermoelectric couple.

action continue? As the electrons are driven toward bar (2), there is set up an electric field: the potential of this bar will fall (because of the negative electronic charge) and that of bar (1) will rise. Equilibrium will be reached when the forces of the electric field just compensate the force of the thermoelectric (osmotic) action. Supposing that the system retains the uniform temperature T, we can calculate, for the state of equilibrium, the difference of electric potentials $\Omega_1 - \Omega_2$ between the two bars. We have only to apply the formula (17.07) of section 108, taking into account that $p_1/p_2 = z_1/z_2$, according to (1.15), and $R/f = -R/F = -k/e$ [1]

$$\Omega_{21} = \Omega_1 - \Omega_2 = \frac{kT}{e} \log \frac{z_1}{z_2}. \tag{17.13}$$

The assumption underlying this formula is as follows: the electron density z of each metal is completely determined by its nature and, possibly, by the temperature T, while the loss or gain of electrons necessary for charging up the system is entirely negligible at a small distance from the junction. In the immediate vicinity of the junction, metal (1) carries a positive charge, through loss of electrons, and metal (2) a negative one, through excess of them. The two opposite charges form an *electric double layer* accounting for the drop of potential.[2]

As long as the whole system is kept at the same temperature, the thermoelectric potentials are not accessible to measurement. In fact, their experimental determination would require a pair of wires going from the free ends of bars (1) and (2) to a suitable measuring instrument. If the two wires are of the same material (3) we can denote the thermoelectric differences with respect to the two bars by Ω_{31} and Ω_{32}. We see, then, from the expression (17.13) that

$$\Omega_{32} = \Omega_{31} + \Omega_{12}, \tag{17.14}$$

so that both wires are at the same potential. It is obvious that taking the wires of different materials will not remove the difficulty.

[1] See footnote on p. 267.

[2] Compare, however, footnote on p. 274.—It was pointed out by some authors that the energy necessary to form the double layer must be taken into account in setting up the conditions of equilibrium (see: P.W. Bridgman, Phys. Rev. **27**, p. 173, 1926). Theoretically this is true, but the terms arising from this cause are very small numerically and share with the capillary surface effects the property of decreasing in importance as the size of the system is increased (compare sections 39 and 81). Since capillary forces are neglected in this and the following chapters, consistency demands that the electric surface effects be treated on the same footing.

In the present connection, we are interested in the thermoelectric actions only in so far as they offer an interesting example of potential differences in electron clouds. We shall see in section 139 that it can be indirectly measured from the electromotive force of a thermocouple with two junctions kept at different temperatures. Without any doubt, the above theory explains the gist of the thermoelectric phenomena, but it is somewhat oversimplified. This appears from the experimental fact that thermoelectricity is *structure sensitive:* a slight distortion in the lattice structure of a conductor, due to mechanical strain, produces an appreciable change of its thermoelectric properties. As the theory stands today, it cannot account for the observations, quantitatively, but does give the correct order of magnitude.

It must be borne in mind that the formulas of this section apply (within the approximation of the theory) only to conductors in which the free electrons can be considered as forming a non-degenerate gas. As was shown in section 105, this situation prevails in *semi-conductors.* Experimentally, it is known only that such materials possess unusually large thermoelectric potential differences (compare Table 56 in section 139). This is unquestionably due to the wide range of the numbers z occurring in them. The thermoelectric conditions in metallic conductors will be considered in section 113.

110. Contact potentials and thermionic emission in the classical theory. Let us consider a conducting plate in vacuo: at its surface the density of free electrons changes abruptly. The forces of osmotic pressure (mentioned in the preceding section) tend, therefore, to drive the electrons out of the conductor into the empty space beyond, producing there a so-called thermionic cloud. We call the potential of the conductor Ω_1, the number of electrons in it (per unit volume) z_1, and the same quantities in the thermionic cloud at the surface of the conductor Ω'_1 and z'_1, and we apply the formula (17.13)

$$\Omega_1 - \Omega'_1 = \frac{kT}{e} \log \frac{z_1}{z'_1}. \tag{17.15}$$

The number z_1 is determined by the nature and physical state of the conductor, but the density z'_1 of the cloud may assume any value. What condition, then, makes the problem definite and fixes the potential difference $\Omega_1 - \Omega'_1$ and, through it, the number z'_1? The action of the osmotic pressure in producing the outer electron cloud is limited by the fact that *a definite amount of work W_1 is required in order to liberate one electron from the conductor,* which is performed by the electron

while it passes through the surface. Therefore, the left side of eq. (17.15) is determined by the relation

$$\Omega_1 - \Omega'_1 = W_1/e, \tag{17.16}$$

whence

$$z'_1 = z_1 \exp(-n_A W_1/RT) = z_1 \exp(-b_1/T), \tag{17.17}$$

where the quantity

$$b_1 = n_A W_1/R \tag{17.18}$$

is called the *thermionic work function.*[1]

It is generally accepted that the force resisting the loss of electrons and pulling them back into the conductor is the *image force.* As known from the theory of electricity, a perfectly conducting plane acts upon a point charge with a force equivalent to the attraction of the *reflected image* of the charge. If the distance of the point from the plane is x (its charge being e), the distance to its reflected image becomes $2x$ and the image force is $-e^2/4x^2$. The work necessary to remove the electron from the position $x = a$ to $x = \infty$ is, then, $e^2/4a$. The actual surface of the conductor is, of course, imperfect since it is constituted of atoms with interstices through which the electrons can pass into the outer space. Nevertheless, the above expressions for the image force and the work done against it remain approximately valid as long as x (or a) is not too small. To obtain the total work W_1 that must be supplied to an electron in order to get it free, one must attribute to a a value of the order of the atomic distances (10^{-8} cm). The equations

$$W_1 = e^2/4a, \qquad \Omega_1 - \Omega'_1 = e/4a \tag{17.19}$$

give then, in fact, the correct order of magnitude for the potential difference, namely, a few volts.

Sometimes the question is asked how the electron cloud builds up this difference of potentials. This question is illegitimate and based on a misconception resulting from the fact that the term "potential difference" is used in the above formulas in a sense slightly different from that given it in most textbooks on electricity.[2] As under-

[1] Not to be confused with the "work function" Ψ defined in section 34.

[2] The difference of electric potentials $\Omega_2 - \Omega_1$ between the points (2) and (1) is determined by the work W_{12} which must be supplied to a test body (of the charge e) in order to move it from (1) to (2). Two different definitions are possible: either, $\Omega_2 - \Omega_1 = \lim (W_{12}/e)$, when e approaches 0; or $\Omega_2 - \Omega_1 = W_{12}/e$, when e is finite. Most textbooks on electricity do not distinguish between the two definitions. The second, obviously, takes in the work of any field induced by the test body and is, therefore, unsuited for many theoretical purposes. However, it is the definition which must be used in connection with Boltzmann's principle and thermodynamics, since ε_{pot} in eq. (4.69) is the energy imparted to a particle *under the actual conditions.* In this sense (17.19) represents the actual difference of potential between the conductor and the outer space.

stood here, the potential difference (17.19) exists from the start and is not, to any material extent, built up by the electrons leaving the conductor: the potential added by the electron cloud (so called, space charge potential) is usually so small as to be negligible.

If a second conducting plate is placed at a short distance from the first facing it in vacuo, it will also set itself in equilibrium with the electron cloud and through it with the first plate. Two potential differences relating to the plates are of interest. On the one hand, the difference $\Omega_1 - \Omega_2$ between the potentials *in the interiors of the two conductors* depends (according to the theory of section 107) only on their internal properties. It has, therefore, the same expression as when the plates are in direct contact, and is identical with the thermoelectric potential difference discussed in the preceding section. On the other hand, there is the so-called mutual *contact potential* $\Omega'_1 - \Omega'_2$ of the two substances. It is defined as the difference of potentials between two points *in the electronic cloud* which are, respectively, close to the surfaces of the two plates. The potential Ω'_1 at the surface of the first plate is given by the eq. (17.16), that at the second plate by the analogous formula $\Omega_2 - \Omega'_2 = W_2/e$. Subtracting the two equations, we find

$$\Omega'_1 - \Omega'_2 = \Omega_1 - \Omega_2 - (W_1 - W_2)/e. \tag{17.20}$$

Substituting for $\Omega_1 - \Omega_2$ and $W_1 - W_2$ from the formulas (17.13) and (17.18), we obtain for *the contact potential in the classical theory*

$$\Omega'_1 - \Omega'_2 = -\frac{k}{e}[b_1 - b_2 - T \log (z_1/z_2)]. \tag{17.21}$$

The second term in the brackets is usually very small compared with the first.

The work function b can be measured either photoelectrically or by thermionic currents. If we let light of a high frequency ν fall upon a metal plate, it emits photoelectrons having a kinetic energy E_{kin}. Einstein's photoelectric equation

$$h\nu = E_{\text{kin}} + W' \tag{17.22}$$

expresses the hypothesis that the energy of an absorbed photon $h\nu$ is imparted to the photoelectron. The part W' of it is spent in getting through the surface of the metal, the remaining part appears as kinetic energy. As the incident frequency ν is decreased, E_{kin} becomes smaller and smaller and vanishes altogether for a certain limiting value

$$h\nu_0 = W'. \tag{17.23}$$

Light of lower frequency cannot produce any photoelectric effect, and this permits the experimental determination of W'. If we identify W' with W_1 of eq. (17.16), we find from (17.20) for the contact potential[1]

$$\Omega'_1 - \Omega'_2 = -\frac{h}{e}(\nu_{01} - \nu_{02}) + \frac{k}{e} T \log (z_1/z_2). \qquad (17.24)$$

The method of *thermionic emission* for measuring b is based on the formula from the kinetic theory of gases

$$n = z\,(RT/2\pi\mu)^{1/2}, \qquad (17.25)$$

giving the connection between the number z of molecules per unit volume in a perfect gas and the number n of those which pass from one side to the other of any plane per unit time and unit area. μ means the molecular weight of the gas, in our case that of the electron $\mu_e = 1/1821$. This expression holds also for the electrons going in either direction at the surface of the metal. However, of those going outward the number rn are reflected at the surface, if r is the coefficient of reflection. Only the remaining $(1 - r)n$ electrons come out of the metal itself. The thermionic current is observed by making the heated metal plate the cathode of a vacuum tube and applying a strong field between the cathode and the anode. The electron cloud in the vacuum is swept away by the field, but the conditions within the metal are not appreciably changed and the electrons leaving it are still the same in number, carrying with them the current

$$J = e(1 - r)n, \qquad (17.26)$$

or substituting from (17.25) and (17.17)

$$J = A'T^{1/2}e^{-b/T}, \qquad (17.27)$$

where

$$A' = (R/2\pi\mu)^{1/2} z_1 e(1 - r).$$

This is Richardson's formula for the thermionic current. It was deduced by its author [2] from kinetic considerations and by H. A. Wilson [3] from thermodynamics. For the reasons pointed out at the end of the preceding section its validity cannot be claimed for metals but is restricted to semi-conductors.

[1] It can be made plausible by statistical reasoning that $W_1 = W'$ is, in fact, the correct identification. The data on semi-conductors are not precise enough to test the accuracy of formula (17.24).

[2] See footnote on p. 266.

[3] See footnote on p. 266.

111. The degenerate electron gas. We have seen in section 105 that the free electrons in metals must be regarded as a completely degenerate gas. This fact was first pointed out by Pauli,[1] while extensive study of metallic electrons, on the basis of Fermi's statistics, is due to Sommerfeld.[2] The formulas of Chapter XVI, however, need a small correction before they can be applied to electrons. It is caused by the *electron spins* which obey the following rule: the spins of any two electrons in the cloud are either parallel or anti-parallel. We have, therefore, two types of electrons with respect to the spin which we shall call, for short, the first kind and the second kind. The statistical weight and the intrinsic energy of either kind of electron are the same, so that our gas is a mixture of equal parts of two components. According to the remarks made at the end of section 105, the formulas of Chapter XVI apply to each component separately, and it is easy to infer from them the equations for the mixture. The specific volume of each component is $2v$, twice the specific volume of the mixture, while the partial pressure of each kind of electrons is $p/2$, one-half of the total pressure. All we have to do is to substitute in all equations $2v$, instead of v, and $p/2$, instead of p. As this leaves the product pv unchanged, the only correction which the laws of degenerate gases require in the case of electrons is a redefinition of the quantity Θ (replacing v by $2v$)

$$\Theta = \frac{2^{5/3}\pi\mu\, k\, v^{2/3} T}{h^2\, n_A^{2/3}}, \tag{17.28}$$

instead of (16.02), where μ is the atomic weight of the electron $\mu_e = 1/1821$. Substituting the numerical values of the constants

$$\Theta = 0.403 \times 10^{-5}\, v^{2/3} T. \tag{17.29}$$

There is reason to assume that in monovalent metals there are as many free electrons as atoms. The molal volume of the free electrons coincides then with that of the metallic material itself. For instance it is $v = 10.26$ cm^3 mol^{-1} in the case of silver, giving $\Theta = 1.91 \times 10^{-5} T$. In other metals the values of Θ are of the same order of magnitude and must be considered as small even at the highest temperatures (about 2300° C) accessible to thermionic measurement. It is, therefore, permissible to use the expansion (16.10) and to obtain from (16.01)

$$pv = \frac{RT}{\Theta}\left[\frac{2}{5}\left(\frac{9\pi}{16}\right)^{1/3} + 4^{-2/3}\left(\frac{2\pi}{3}\right)^{2/3}\Theta^2\right]. \tag{17.30}$$

[1] W. Pauli, Zs. Physik 41, p. 81, 1927.
[2] A. Sommerfeld, Zs. Physik 47, pp. 1, 43, 1928.

When Θ^2 is negligible, the gas is completely degenerate. Its pressure then becomes independent of temperature, being determined by the specific volume alone which, in turn, is fixed by the nature of the metal. We shall introduce the notation

$$\frac{RT}{\Theta}\left(\frac{9\pi}{16}\right)^{1/3} = f\Omega_i, \tag{17.31}$$

where Ω_i is called the *inner potential.* Hence its numerical value is

$$\Omega_i = -\ 25.85\, v^{-2/3} \text{ electron-volt.} \tag{17.32}$$

For instance, in the case of silver $\Omega_i = -\ 5.48$ e.-v. With the abbreviation (17.31), eq. (17.30) takes the form

$$pv = f\left[\frac{2}{5}\,\Omega_i + \frac{\pi^2}{3\cdot 2}\left(\frac{k}{e}\right)^2 \frac{T^2}{\Omega_i}\right],$$

while the expression for the energy follows from (16.15) and (17.01): $u = \frac{3}{2}pv + f\Omega + u_0$. The entropy is determined by (16.17) and becomes for small values of Θ, according to (16.10),

$$s = \frac{2^{1/3}\pi^{5/3}}{3^{2/3}}\, R\Theta = f\frac{\pi^2}{2}\left(\frac{k}{e}\right)^2 \frac{T}{\Omega_i}, \tag{17.33}$$

while the molal heat has the expression

$$c = \frac{\pi^2}{2}\,\frac{k}{e}\,\frac{RT}{\Omega_i} = 1.619 \times 10^{-5}\, v^{2/3} RT. \tag{17.34}$$

Finally, the thermodynamic potential is expressed by

$$\varphi = f\left[\Omega_i + \Omega - \frac{\pi^2}{12}\,\frac{k^2T^2}{e^2\Omega_i}\right] + u_0. \tag{17.35}$$

The electronic spin has an important bearing also on the *entropy expression for high temperatures.* In Θ of eq. (16.20), $2v$ must be substituted for v, and this is equivalent to adding the term $R \log 2$ to the entropy constant, or $\log 2$ to the chemical constant. The entropy (16.21) and the thermodynamic potential (17.03) of the *non-degenerate electron gas* retain, therefore, the form of their expressions, but the constant s_0 has an increased value. The chemical constant (14.15) of the electron gas becomes (with $\mu = 1/1821$):

$$j_{10,\,atm} = -\ 6.180 \tag{17.36}$$

or $j_{10} = 0.826 - 1$.

A similar increase of the chemical constant occurs also in the case of gaseous atoms having an angular momentum and can be calculated

in a quite analogous way. It will be better, however, to postpone this calculation until section 120, where it will be treated together with the chemical constant of diatomic and polyatomic gases.

112. Thermionic emission and thermoelectricity from the modern point of view. We are now going to apply the results of the preceding section to the equilibrium of a metal with the thermionic cloud outside it. While the free electrons within the metal are in a degenerate state, those forming the outer cloud are completely non-degenerate. In fact, after deriving the conditions of equilibrium, under this assumption, we shall justify it by showing that the density of the cloud is extremely low and the value of the quantity Θ in it very high. We substitute into the condition (17.04), $\varphi = \varphi'$, the expressions (17.03) for the outer cloud, and (17.35) for the metal. Noticing that $c_p = \frac{5}{2}R$, we find (with $f = -en_\Delta$)

$$\log p = j + \tfrac{5}{2}\log T - b/T, \tag{17.36'}$$

with the abbreviation

$$b = -\frac{e}{k}\left[\Omega' - \Omega - \Omega_i + \frac{\pi^2}{12}\frac{k^2T^2}{e^2\Omega_i}\right], \tag{17.37}$$

where the potentials Ω' and Ω refer to the outer cloud and to the metal, respectively. Neglecting second order terms,

$$b = \frac{e}{k}(\Omega_i + \Omega - \Omega'). \tag{17.37'}$$

With the help of (1.15) we throw (17.36') into the form

$$z = \frac{1}{k}T^{3/2}\exp(j - b/T), \tag{17.38}$$

and obtain from (17.25) and (17.26) the thermionic current

$$\left.\begin{aligned} J &= A(1-r)T^2e^{-b/T}, \\ A &= e\,(n_\Delta/2\pi\mu k)^{1/2}\exp j \\ &= 120.2 \text{ amp cm}^{-2}\text{ deg}^{-2}. \end{aligned}\right\} \tag{17.39}$$

This formula was first derived by Dushman [1] from a semi-classical hypothesis of thermionic emission. Its derivation in terms of the degenerate electron gas was due to R. H. Fowler.[2]

The work function b receives, according to eq. (17.37'), an interpretation different from that of section 110. The work which the electron

[1] S. Dushman, Phys. Rev. **20**, p. 109, 1922; **21**, p. 623, 1923.
[2] R. H. Fowler, Proc. Roy. Soc. (A) **122**, p. 36, 1929.

has to do in getting through the metal surface is still determined by the image force w which, in turn, fixes the *outer* potential difference $\Omega - \Omega'$ as in eq. (17.17). However, the electrons bring with them the energy $-e\Omega_i$ depending on the inner potential (which has the nature of a quantized kinetic energy, as is shown in the statistical version of the theory). Only the difference $bk = e(\Omega - \Omega' + \Omega_i)$ has to be supplied by thermokinetic or photoelectric forces. The connection of the thermionic work function with the photoelectric threshold frequency remains, therefore the same as in the classical theory, namely,

$$h\nu_0 = kb.$$

Our knowledge of the inner potential Ω_i is not exclusively theoretical: its existence and order of magnitude can be inferred from other phenomena, for instance, from experiments on the diffraction of electron beams falling on the surface of the metal. The values of Ω_i found by such measurements are not at all accurate, as they are affected by an uncertainty of $\pm$ 5 volts, but theoretical results obtained from formula (17.32) do not lie far outside these limits. A few numerical data are given in Table 36.[1]

TABLE 36

Metal	Photoelectric		Thermionic		$-\Omega_i$ (calc.)	$\Omega - \Omega'$ (calc.)	$\Omega - \Omega'$ (obs.)
	kb/e (volt)	$t°$ C	kb/e (volt)	$t°$ C			
Ag	4.73	20	4.08	925	5.48	10.2	18 ± 5
"	4.56	600					
Al	2.5–3.6	....	....	....	(5.57)	(8.6)	18 "
Au	4.82	20	4.32	1050	5.50	10.3	17 "
"	4.73	740					
Cu	4.1–4.5	....	4.38	....	7.00	11.3	17 "
Fe	4.72						
Hg	4.53	20					
Ni	5.01	....	....	....	(7.35)	(12.4)	18 "
Pb	3.5–4.1	....	....	....	(3.9)	(7.9)	11 "
Pd	4.96	....	4.99				
Pt	6.30	....	6.27				
Rh	4.57	20	4.58				
"	4.93	240					
W	4.58	....	4.52				

[1] Taken from Hughes and DuBridge (Photoelectric Phenomena, pp. 76, 235, New York, 1932) and slightly revised. A more complete list will be found in the article by J. A. Becker, Rev. of Mod. Physics 7, p. 123, 1935.

The inner potentials Ω_i in Table 36 are calculated on the assumption that there is one free electron per atom. This is sound in the case of metals of the first group (Ag, Au, Cu) but less certain in other cases.

From the tabulated values of b one can determine z by means of eq. (17.38) and find the molal volume and the quantity Θ in the thermionic cloud at different temperatures. For instance, in the case of tungsten (neglecting the change of b with temperature) these data are as follows:

TABLE 37

$t°$ C.	20°	300°	600°	1000°	1500°	2000°	2300°	3000°	3800°
v...	1.1×10^{82}	4.6×10^{36}	3.4×10^{26}	5.2×10^{19}	1.6×10^{15}	3.4×10^{12}	2.5×10^{11}	4.8×10^{9}	5.1×10^{8}
Θ...	6.0×10^{78}	7.6×10^{31}	1.9×10^{15}	7.8×10^{10}	1.0×10^{8}	2.1×10^{6}	4.3×10^{5}	3.7×10^{4}	1.0×10^{4}

We see from this table that Θ has exceedingly high values in the electron gas outside the metal, so that the assumption of its being non-degenerate is entirely justified.

In comparing Dushman's formula (17.39) with experiments, it must be remembered that it has its theoretical limitations. The thermionic work function is not strictly a constant but has a slight temperature dependence. This is due, in the first place, to the neglected terms of the expression (17.35) and to the thermal expansion of the metal which changes the molal volume v in it and also may affect the image force, and through it, the potential difference $\Omega - \Omega'$. In the second place, the picture of electrons being completely free is only an approximation; in reality, there are some mutual forces between them and the metal ions which also could account for small deviations from the constancy of b. Finally, the factor $(1 - r)$, which is supposed[1] to be of the magnitude 0.95, is again slightly temperature dependent. On the other hand, the measurement of thermionic currents involves an extremely difficult experimental technique whose accuracy cannot be pushed beyond a certain limit. In view of this situation, the agreement must be considered as quite satisfactory. The results for A, as obtained experimentally,[2] do not agree with the theoretical value 120.2, as shown in Table 38. This is probably due to the work function b depending on T and containing a linear term $(b = b' + \alpha T.)$ Therefore, the formula (17.39) can be rewritten in the same form but with the new constants $b' = b - \alpha T$, $A' = A \exp \alpha$. From the analysis of the measurements one obtains directly b', A' and not b, A, but, knowing the theoretical value of A, one can calculate α and the true work function b.

[1] L. Nordheim, Proc. Roy. Soc. (A) 117, p. 626, 1928.
[2] L. A. DuBridge, Proc. Nat. Acad. 14, p. 788, 1928.

TABLE 38*

Material	Authority	kb'/e (in volt)	kb/e	A'/A	$\beta \times 10^4$
W	BuBridge	4.61	5.53	0.99×10	4.56
Th-W	"	4.61	2.63	1.05×10^{-3}	1.76
Pt	"	5.08	6.27	0.57×10^{3}	3.41
K	"	0.645	2.21	1.37×10^{12}	24.70
Cu (liqu)	"	4.55	3.54	1.65×10^{-4}	6.91
Zr, Hf	Zwikker	3.85	4.84	0.57×10^{3}	4.08
BaO	Detels	2.48	1.47	1.89×10^{-4}	6.79

* See: S. Dushman, Rev. Modern Physics, 2, p. 381, 1930.

A curious and not entirely explained result of DuBridge's is that, in the same metal but for different conditions of its surface, the observed log A' is a linear function of the observed b' (i.e. $\log A' = \beta b' + \text{const}$). The coefficients β are listed in Table 38.

With respect to thermoelectric forces between two metals (1) and (2), the qualitative considerations of section 4 remain valid. The equilibrium of the electrons in the two metals is determined by the same condition $\varphi_1 = \varphi_2$. The only difference is that we have to substitute for the thermodynamic potential in either metal the expression (17.35) since we consider both clouds as degenerate. Thus the potential difference becomes

$$\Omega_1 - \Omega_2 = (\Omega_{i1} - \Omega_{i2}) - \frac{\pi^2}{12}\frac{k^2}{e^2} T^2 \left(\frac{1}{\Omega_{i1}} - \frac{1}{\Omega_{i2}}\right). \qquad (17.40)$$

The expression $\Omega_{i1} - \Omega_{i2}$ is independent of the temperature. It represents a potential difference existing between the two metals *under all circumstances*. It cancels out of every closed circuit and cannot be observed by galvanometric or electrometric methods. Therefore, only the second term need to be taken into account for the *thermoelectric* difference:

$$\Omega_{21} = 0.611 \times 10^{-8} T^2 \left(\frac{1}{\Omega_{i1}} - \frac{1}{\Omega_{i2}}\right) \text{volt}, \qquad (17.41)$$

where Ω_{i1}, Ω_{i2} are expressed in volts. This formula was first given by Sommerfeld.[1] For the reasons outlined in section 109, we can hardly expect from it more than the correct order of magnitude. Experi-

[1] A. Sommerfeld, note on p. 277. This formula does *not* represent the e.m.f. in a thermoelectric circuit, which is given at the end of section 139.

mental data and a thermodynamical discussion of thermoelectricity will be given in section 139.

As to the *contact potential of metals*, it can be obtained directly from the formula (17.37), substituting for $\Omega_1 - \Omega_2$ the expression (17.40),

$$\Omega'_1 - \Omega'_2 = -\frac{k}{e}(b_1 - b_2) = -\frac{h}{e}(\nu_{01} - \nu_{02}).$$

This relation was tested by Millikan, Lukirsky and Prilezaev, and Olpin [1] and was confirmed in the case of metals with very clean surfaces.

113. Ionization in the solar atmosphere. In their systematic study of solar radiation the astronomers succeeded in analyzing spectroscopically the light coming from the different altitude layers of the chromosphere. They found that the emission of the lower levels mostly consists of arc lines (characteristic of the neutral atoms), while the spark lines (belonging to the ionized atoms) appear higher up and grow in intensity with altitude at the expense of the spark lines. This result seemed puzzling because the lower layers of the sun are hotter and, in the laboratory, the spark lines are enhanced by raising the temperature. The reason for this discrepancy was explained by M. N. Saha,[2] who pointed out the influence of the pressure on the degree of ionization and applied the thermodynamical equations of chemical equilibrium to the problem. There are charged particles of both signs in the solar chromosphere, but at the temperatures and pressures prevailing there the phenomenon of *pairing* (mentioned in section 106) is quite negligible. Therefore, the form of the equations of equilibrium is not appreciably changed either by the charges on the electrons and ions or by the gravitational field of the sun (section 108). These conditions also exclude degeneration so that we can apply the equation of chemical equilibrium (14.16) for classical perfect gases. The reactions which we have to consider as taking place are those of the *single and double ionization of atoms* by splitting off one or two electrons. In the symbols of section 42

$$G_+ + G_- - G_n = 0 \quad \text{and} \quad G_{++} + 2G_- - G_n = 0, \qquad (17.42)$$

where G_+ and G_{++} refer to the positive ions, G_- to the electron and G_n to the neutral atom. The formula (14.16) needs a slight correction;

[1] R. A. Millikan, Phys. Rev. 7, p. 355, 1916; P. Lukirsky and S. Prilezaev, Zs. Physik 49, p. 236, 1928; Olpin, Phys. Rev. 36, p. 251, 1930. For a discussion from the point of view of the statistical theory see: Mitchell, Proc. Roy. Soc. (A) 146, p. 442, 1934; 153, p. 513, 1936.

[2] M. N. Saha, Phil. Mag. 40, pp. 472, 809, 1920.

there must be added log 2 to the chemical constant of the electron (section 111). However, this is not all: it will be shown in section 120 that a similar term log g belongs to the chemical constants of the atoms and ions (because of the statistical weight of the angular momenta of these particles. Since the atomic weights of the atom and the ion are practically the same, we can write $\frac{3}{2}\Sigma\nu_h \log_{10} \mu_h = \frac{3}{2}\nu \log_{10} \mu_e = -4.892\nu$, where μ_e means the atomic weight of the electron. For monatomic gases $c_p = \frac{5}{2}R$, and the heat of reaction becomes, according to (3.28), $Q = \Sigma\nu_h\chi_h = \Delta U_0 + \frac{5}{2}\nu RT$. If we continue to measure the *pressure in atmospheres* but take as the unit of heat of reaction not the erg but the electron-volt (1 erg/mol = 0.9646×10^{12} e.-v.), the equations of equilibrium become for the two reactions (17.42)

$$\left.\begin{aligned} \log (p_+ p_-/p_n) &= -6.180 + \log_{10}(g_+/g_n) \\ &\quad + \tfrac{5}{2}\log_{10} T - \frac{5037\Delta U_0}{T}, \\ \log (p_{++} p_-^2/p_n) &= -12.360 + \log_{10}(g_{++}/g_n) \\ &\quad + 5\log_{10} T - \frac{5037\Delta U_0}{T}. \end{aligned}\right\} \tag{17.43}$$

The values of ΔU_0 and g for the most important ingredients of the solar atmosphere are given in Table 39. The data of this table refer to the *normal states of the particles*; the statistical weights of the nuclear spins are not included in g because they are the same in the neutral atom and the ion and cancel out of the reaction.

TABLE 39

Particle	g	ΔU_0 (in e.-v.)	Particle	g	ΔU_0 (in e.-v.)	Particle	g	ΔU_0 (in e.-v.)
H	2	13.53	Ca	1	6.09	Zn	1	9 36
H_+	1		Ca_+	2	11.82	Zn_+	2	17.86
He	1	24.46	Ca_{++}	1		Zn_{++}	1	
He_+	2		Sr	1	5.67	Cd	1	8.96
Na	2	5.12	Sr_+	2	10.98	Cd_+	2	16.84
Na_+	1		Sr_{++}	1		Cd_{++}	1	
Rb	2	4.16	Ba	1	5.19	Hg	1	10.38
Rb_+	1		Ba_+	2	9.96	Hg_+	2	18.67
Cs	2	3.87	Ba_{++}	1		Hg_{++}	1	
Cs_+	1	23.4						
Cs_{++}	2							

We see from eqs. (17.43) that the ratio p_+/p_n not only is an increasing function of the temperature but also depends on the pressure of the free electrons, being inversely proportional to it. This pressure is an appreciable fraction of the total pressure and rapidly decreases with the general attenuation of the chromosphere as the level is raised. The equation, therefore, gives a qualitative explanation of the observations described above. Moreover, it accounts for the observed fact that, the lower the ionization potential, the lower also the level at which the appearance of the spark lines sets in. On the other hand, it is very difficult to calculate p_+/p_n quantitatively because the pressure of the electrons p_- depends on many factors. All the elements of the mixture which constitutes the solar atmosphere contribute to it, but even if we had atoms of one kind only the degree of ionization would depend on the excited states and its computation would be a difficult problem.[1] However, if our object is only to obtain a check of the thermodynamical formulas (17.43), we can get around this difficulty by choosing one of the elements of the solar chromosphere as a standard. Suppose we have measured, for different levels of the sun, the intensities of the arc lines and the spark line of this standard substance and inferred from these measurements the relative abundance $p_+^{(s)}/p_n^{(s)}$ of its ions and neutral atoms. Writing eq. (17.43) for the standard element and for any other element, we eliminate p_- and obtain

$$\log_{10}\frac{p_+}{p_n} - \log_{10}\frac{p_+^{(s)}}{p_n^{(s)}} = \log_{10}\left(\frac{g_+ g_n^{(s)}}{g_+^{(s)} g_n}\right) - 5037\,\frac{\Delta U_0 - \Delta U_0^{(s)}}{T}. \quad (17.44)$$

The theory was tested by similar devices and received a fair confirmation, but it was pointed out by H. N. Russel [2] that great accuracy in the agreement cannot be expected. The gases of the solar chromosphere are not strictly in a condition of thermodynamical equilibrium since they are exposed to the one-sided radiation coming from the lower and hotter regions of the photosphere.

114. Ion concentrations in electrolytes. Galvanic cells. The theory of dilute solutions also offers an important field of applications for the results of sections 106 and 107. A large class of solutes, the electrolytes, undergo a partial or complete dissociation into electrically charged components (ions). This is particularly characteristic of acids and salts in aqueous solutions: when their molecules dissociate,

[1] It was treated by Milne, R. H. Fowler, and C. G. Darwin. The most comprehensive review of the whole field of ionization in the solar atmosphere is due to A. Pannekoek (Handbuch der Astrophysik, Vol. III 1, pp. 257–350. Berlin 1930).

[2] H. N. Russel, Astrophys. J. 79, p. 317, 1934.

the hydrogen or the metal acquires a (single or multiple) positive charge and is called the *cathion*, or *positive ion*, the acid radical gets a negative charge and constitutes the *anion* or *negative ion*. As an example we take cadmium sulfate which, dissolved in water, dissociates according to the formula

$$Cd^{++} + SO_4^{--} - CdSO_4 = 0,$$

where the superscript $++$ indicates a bivalent positive ion (i.e. one carrying two elementary charges).

We know from section 68 that non-electrolytic dilute solutions behave like perfect gases. If the conditions of equilibrium are not changed by the electric charges of the ions, we should expect the laws derived in that section, especially the mass law (9.60), to apply also to electrolytic solutions. For instance, the above reaction would give

$$x_{++}x_{--}/x_n = K(T),$$

where x_{++}, x_{--}, x_n are the respective mol fractions of the positive and negative ions and of the neutral (undissociated) salt. In the more general case, when the molecule is ionized into $\nu_1, \nu_2, \ldots \nu_r$ positive and negative ions, their total number being $\nu_e = \nu_1 + \ldots + \nu_r$, the equation takes the form

$$\nu_1 G_1 + \nu_2 G_2 + \ldots + \nu_r G_r - G_n = 0 \tag{17.45}$$

and the mass law has the expression

$$\sum_j \nu_j \log x_j - \log x_n = \log K. \tag{17.46}$$

This equation is of the same type as those considered in section 52, and we can draw from it the conclusion that a certain fraction of the salt molecules is *ionized* (dissociated into ions). In fact, experiments show that the equilibrium constant K is fairly large in these reactions, so that solutions of low concentration are almost completely ionized.

The hypothesis that dilute electrolytes are completely dissociated into ions was first advanced by Arrhenius, who adduced in its support their high osmotic pressures and low freezing points. Moreover, he showed that the electric conductivity is in agreement with this assumption, being nearly proportional to the molality of the dissolved salt. The work of Arrhenius and his successors had a great influence on the development of thermodynamics, on one hand, and laid the foundations of the science of electrochemistry, on the other. The laws of electrolytic conduction, as developed by Kohlrausch, afforded a means

of determining the mol fractions x_j of the individual ions and gave a rough confirmation of the formula (17.46). However, as the technique of these measurements grew more and more accurate, it was found that *the law* (17.46) *is rigorously valid only for a limited class of substances*, the so-called *weak electrolytes*. To this group belong a number of organic acids and their salts. On the other hand, the common inorganic acids and their salts form the class of *strong electrolytes* which exhibit appreciable deviations from the formula (17.46) even in very low concentrations.

At first, it was doubtful whether these discrepancies were due to the inadequacy of the formula itself or to the failure of the conduction measurements to give the correct mol fractions. The investigations based on the freezing method, described in section 78, were undertaken to decide this question. They led to the result that eq. (17.46), actually, *is not valid for strong electrolytes*, or in other words, the ionic clouds of strong electrolytes do not obey the laws of perfect gases. As was shown in section 77, the form of the mass law can always be retained if the numbers x_j are replaced by the effective mol fractions or activities a_j:

$$\sum_{j=1} \nu_j \log a_j - \log a_n = \log K. \tag{17.47}$$

Putting for the neutral salt $a_n = x_n$ and making use of the notations of section 79, especially of the activity function γ defined by (11.32), we can write (for dilute solutions)

$$\sum_{j=1}^{r} \nu_j \log x_j - \log x_n = \log K - \nu_e \log \gamma. \tag{17.48}$$

The data from conduction measurements turn out to be in excellent agreement with those obtained by the freezing method: when the proper values of γ are substituted, the formula (17.48) is confirmed with great accuracy. The theoretical reasons for the abnormal behavior of strong electrolytes will be discussed in the next section.

The notion of electrolytic ionization affords an insight into the mechanism producing the e.m.f. (*electromotive force*) *of galvanic cells* which were treated in section 37 from the more formal point of view of energy relations. In all the constructions mentioned there the chemical reaction is between two metallic salts, MR and $M'R$ (with the same radical R) which ionize in aqueous solutions according to equations similar to

$$MR = M_+ + R_-, \qquad M'R = M'_+ + R_-, \tag{17.49}$$

and in which the reaction $M'R + M \rightarrow MR + M'$ is exothermic.

The current is, in part, due to the negative radical ion R_- traveling through the cell from the vicinity of the positive to the negative plate.[1] We are now able to say what force drives the ions and produces the current: it is the force of osmotic pressure. In fact, the R_- ions react at the negative plate with the metal M of which it consists. Therefore, their concentration and partial osmotic pressure P_- sinks below the value P'_- which it has at the positive plate. When the resistance of the outer circuit is very large, an electric difference of potentials $\Omega' - \Omega$ builds up which almost completely compensates the e.m.f. (electromotive force) of osmotic pressure.

According to (17.06) we have then (since $f = -F$)

$$\Omega' - \Omega = \frac{RT}{F} \log (P'/P), \tag{17.50}$$

provided the cloud of R_- ions in the solution can be regarded as a perfect gas. The explanation for the movement of the M'_+ ions to the positive plate is also osmosis (since in equilibrium the total osmotic pressure must be everywhere the same), but the calculation of their concentrations would lead us too far into electrochemistry.

It is essential for the operation of the cells described in section 37 that its electrodes consist of two different metals; they are, therefore, called electrode cells. There exist cells of a different kind, known as *concentration cells*, an example of a modern concentration cell is as follows:[2]

Ag	AgCl (solid)	KCl solution (m)	K–Hg amalgam	KCl solution (m')	AgCl (solid)	Ag

The first half of this chain (from Ag to the amalgam K–Hg) represents an electrode cell with the reaction AgCl + K = KCl + Ag, which is strongly exothermic. If this half chain were *left to itself*, the molality m of KCl in the chamber filled with potassium chloride solution would increase producing a current in the direction to the left (i.e. from K–Hg to Ag). In fact, in this case, the K_+ ions move to the left and replace some of the silver in the AgCl paste (the reduced silver being deposited on the Ag electrode). At the same time the Cl_- ions move to the right and react with the potassium metal in the amalgam. In both processes KCl is produced and added to the solution. On the other hand, if *an electric current is sent through* the half

[1] In the example of the Weston cell (Fig. 11, p. 95) the radical (R_-) is SO_{4--}, the negative plate (M) consists of Hg and the positive (M') of Cd.

[2] MacInnes and Parker, J. Am. Chem. Soc. 37, p. 1445, 1915.

chain in the direction to the right all processes are reversed and the molality of potassium chloride solution must decrease. Now, the second half of the concentration cell is of the same construction and of opposite orientation: the resultant current will be, therefore, the difference of the currents produced in the two half chains and will flow through both of them. If we assume $m' > m$ (see below), it will have the direction from K–Hg to Ag, in the first half, and from Ag to K–Hg, in the second. Therefore, the molality in the first KCl chamber will increase at the expense of that in the second. There is no current when $m' = m$: the driving power is due to the difference of osmotic pressures in the two chambers.

All this is also characteristic of the general case when the reaction is given by eq. (17.45). The essential feature of every concentration cell are two chambers C' and C filled with the same solution in different concentrations. In the beginning, when the chambers are freshly filled, the solutions are electrically neutral (as a whole, containing equal positive and negative charges) so that the osmotic forces are entirely uncompensated by electric potentials. Under the ordinary conditions of construction, there is no tendency for potential differences to build up, and the solutions can be regarded as neutral during the whole length of their operation. Owing to these forces, the ions pass from the chamber of higher osmotic pressure into that of lower in numbers proportional to the coefficients ν_i of eq. (17.45) as is implied in the electric neutrality of the solutions. We shall calculate E, the e.m.f. of such a cell, only for the case of low concentrations when the electrolyte (in both chambers) can be considered as completely ionized. The change of thermodynamic potential which the ions undergo in being transferred from the chamber C to the chamber C' is then (referred to 1 mol of the neutral electrolyte) $\Delta\Phi = \sum \nu_h(\overline{\varphi}'_h - \overline{\varphi}_h)$. The left side, according to (5.35), is the (negative) non-mechanical work done by the system $\Delta W = -W' = EJ$, where J is the total charge of the ions pertaining to 1 mol. On the right side, we substitute the activities from formula (11.17)

$$JE = -RT\sum_{h=1}^{r}\nu_h \log (a'_h/a_h). \tag{17.51}$$

If we denote the valency of the ion h by σ_h (taking it positive or negative, according to the sign of the charge)

$$J = F\sum_h |\sigma_h|\cdot\nu_h.$$

Further, making use of the abbreviation (11.32), we can write

$$E = -(RT/J)\{\nu_e \log(\gamma'/\gamma) + \sum_h \nu_h \log(x'_h/x_h)\}. \qquad (17.52)$$

The measurement of electromotive forces of concentration cells offers a method for the determination of relative activity functions of electrolytes. Numerical data for the activity function will be given in the next section.

115. Strong electrolytes. All the results so far obtained in this chapter rest on the following hypothesis made in section 106: the mutual electric energy of the particles in a small volume τ is proportional to the *square* of the number of particles in it and, therefore, negligible. However, this argument is sound only as long as the electric forces do not affect the uniformity of distribution of the particles, and it ceases to be strictly applicable in the case of mixtures of positive and negative ions. Owing to the mutual attraction, each ion has the tendency to hover in the neighborhood of other ions of the opposite sign. The mean distance between unlike ions is smaller than that between like ones. This gives rise to energy terms, proportional to the number of particles, which may become significant under certain circumstances. It had been suspected for a long time that these additional electric terms may account for the abnormalities in strong electrolytes mentioned in sections 79 and 114. If this point of view is accepted, the sharp line of division between dissociated and undissociated molecules disappears: the distances between the ions can assume all values and are distributed according to the laws of probability. The transition from association to dissociation is gradual, and all ions can be considered as free, in this sense.

The problem was formulated with complete clarity and partially treated by Milner.[1] It was made better amenable to quantitative evaluation by Debye and Hückel,[2] who gave a simple method for the approximate calculation of the effect at low concentrations.

Let us consider a neutral solution containing ions of several kinds, the type (j) being represented by N_j mols. We denote their valency by σ_j, which is positive or negative, according to the sign of the charge on this ion. The total charge in the solution is then

$$F\sum_j \sigma_j N_j = 0, \qquad (17.53)$$

[1] Milner, Phil. Mag. **23**, p. 551, 1912; **25**, p. 742, 1913.
[2] P. Debye and E. Hückel, Phys. Zs. **24**, pp. 185, 305, 1923.

where $F = en_A$ is the Faraday constant or the charge per 1 mol of monovalent ions. We denote farther by

$$z_j = N_j n_A / V, \tag{17.54}$$

the *mean density*, i.e. the number of ions of the type j per unit volume. Let us now focus our attention on a " preferred ion " of the kind (1) and let us ask how the other ions are distributed around it. The answer is given by the Boltzmann principle (4.69). Suppose that, at a point P, its electric potential is Ω_1; in the time average, the density of j-ions at this point will be $C \exp(-e\sigma_j\Omega_1/kT)$. Let the potential Ω_1 be counted "from infinity", i.e. from a distant point where the field of the preferred ion does not make itself felt ($\Omega_1 = 0$) and the density has the normal value z_j; then the constant of proportionality has the value $C = z_j$. The total density of electric charge at the point P, produced by ions of all kinds, is, therefore,

$$\rho_e = e\sum_j \sigma_j z_j \exp(-e\sigma_j \Omega_1/kT). \tag{17.55}$$

The potential Ω_1 is produced by the preferred ion, in part directly, in part indirectly through the action of the " atmosphere " of other ions which hover about it. Assuming the validity of the Coulomb law and, on the average, a spherically symmetrical distribution of the atmosphere, Ω_1 must satisfy Poisson's equation in the form

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Omega_1}{dr}\right) = -\frac{4\pi}{D}\rho_e, \tag{17.56}$$

where D is the *dielectric constant* of the solvent. Eliminating ρ_e from (17.55) and (17.56), we obtain a differential equation for the determination of Ω_1. We restrict ourselves to the case when the exponent $-\sigma_j e\Omega_1/kT$ is so small that its square can be neglected. Because of (17.53), the term of zero order vanishes, leaving

$$\frac{d^2\Omega_1}{dr^2} + \frac{1}{r}\frac{d\Omega_1}{dr} = -\kappa^2\Omega_1, \tag{17.57}$$

$$\kappa^2 = \frac{4\pi e^2}{DkT}\sum_j \sigma_j^2 z_j = \frac{4\pi e^2 n_A}{DkTV}\sum_j \sigma_j^2 N_j. \tag{17.58}$$

The integral of eq. (17.57) is

$$\Omega_1 = \frac{A_1}{r}e^{-\kappa r}. \tag{17.59}$$

The coefficient A_1 must be determined from the "boundary conditions." Let a_1 be the mean distance of nearest approach of the other ions to the preferred ion: within the little sphere of the radius a_1 the field is not influenced by the ionic atmosphere and the potential in this region may be taken as obeying the simple Coulomb law

$$\Omega'_1 = \frac{\sigma_1 e}{Dr} + \Omega_{01}, \tag{17.60}$$

while outside this region it follows the law (17.59). At the surface of the sphere $r = a_1$, there must be continuity of potential ($\Omega'_1 = \Omega_1$) and of dielectric displacement ($d\Omega'_1/dr = d\Omega_1/dr$). This leads to

$$A_1 = \frac{\sigma_1 e \exp(\kappa a_1)}{D(1 + \kappa a_1)}, \quad \Omega_{01} = -\frac{\sigma_1 e \kappa}{D(1 + \kappa a_1)}. \tag{17.61}$$

Without the ionic cloud about the preferred ion, its potential (against infinity) would be represented merely by the first term of the expression (17.60). Therefore, Ω_{01} *gives us the potential difference,* built up through mutual interaction, *of the ion with respect to the mean potential in the solution.* In a similar way the other ions assume the potentials

$$\Omega_{0j} = -\frac{\sigma_j e}{D} \frac{\kappa}{1 + \kappa a_j}. \tag{17.62}$$

In arriving at this formula, a dual capacity was attributed to every ion. On the one hand, it acted as a "preferred ion" collecting an atmosphere around it; on the other, it formed part of the atmospheres of all the other ions. It is clear that it is not always permissible to separate and superpose these two functions of the ion, as is done in Debye-Hückel's theory. The superposition implies, ultimately, a linearity of the equations controlling the electric field and comes back to the same restriction which was made in eq. (17.57). It seems, therefore, risky trying to improve the theory by taking into account terms of higher order in the exponent of (17.56), as has been done by some authors.[1] The question needs a closer investigation whether the theory is not restricted by its very method to cases in which $(\sigma_j e \Omega_1/kT)^2$ can be neglected. Another idealization of the theory lies in the schematic character of the "boundary conditions" which lead to the formula (17.62). In view of them, the dependence of the potential Ω_{0j} on the ionic radius a_j can hardly be considered as entirely trustworthy.

[1] Gronwall, LaMer, and Sandved, Phys. Zs. 29, p. 358, 1928.

We shall show in section 138 that the change of internal energy of the solution produced by the potentials (17.62) is a rather complicated one. The work function Ψ, however, can be calculated without much trouble. In order to do so, it will be well to bring out the thermodynamical significance of our results. An ion of the charge $\sigma_j e$ acquires the potential Ω_{0j}: let us consider an imaginary, ideal way of producing such a distribution of charges and potentials. Suppose that e is not constant but that the charge of every ion can be changed and built up from 0 to the normal value.[1] The work which must be done in order to increase all the charges from $\sigma_j e$ to $\sigma_j(e + de)$ (e being the same for every ion) is known from the theory of electricity to be $DW_e = -\Sigma\Omega_{0j}\sigma_j\, de$, where the summation is extended over all the ions. Since there are $n_A N_j$ ions of the kind j, $DW_e = -n_A\sum_j \sigma_j N_j \Omega_{0j}\, de$. The total work of building up the distribution *at constant temperature and constant volume* is, therefore,

$$W_e = -n_A \int_0^e \sum_j \sigma_j \Omega_{0j} N_j\, de. \tag{17.63}$$

It was shown in section 36 that the non-mechanical work done in a reversible process, at T = const, V = const, is oppositely equal to the increase of the work function. This increase, due to the electric charges and potentials of the ions, we denote by $\Psi_e = -W_e$. The expression (17.63) is somewhat simplified if we use, instead of the individual ionic radii a_j of eq. (17.62), a mean radius a. In fact, the accuracy of the theory is hardly sufficient to justify such distinctions and, moreover, the term $\kappa a_j = \kappa a$ in the denominator is altogether neglected in our ultimate applications. According to the definition (17.58) of κ we can write, then,

$$\Psi_e = -W_e = -\frac{kTV}{4\pi}\int_0^\kappa \frac{\kappa^2 d\kappa}{1+\kappa a}. \tag{17.64}$$

The partial thermodynamic potential can be obtained directly from the work function by means of eq. (5.39)

$$\bar{\varphi}_{eh} = \left(\frac{\partial \Psi_e}{\partial N_h}\right)_{V,T} = -\frac{kTV}{4\pi}\frac{\kappa^2}{1+\kappa a}\left(\frac{\partial \kappa}{\partial N_h}\right)_{V,T} = -\frac{n_A \sigma_h^2 e^2}{2D}\frac{\kappa}{1+\kappa a}. \tag{17.65}$$

This is the increase of the thermodynamic potential due to the electric fields of the ions. If we define the activity coefficient of the ions h as $\log \alpha_h = \bar{\varphi}_{eh}/RT$ (section 78), this means that we compare the

[1] R. H. Fowler, Statistical Mechanics, p. 318, Cambridge, 1927.

activities in strong electrolytes with the theoretical ones in dilute solutions *at the same volume*, whereas experimentally they are compared *at the same pressure*. This difference, however, is of slight significance in view of the very small compressibility of water and other condensed solvents.[1]

In very dilute solutions κ is comparatively small, and κa in the denominator can be neglected. From (17.58)

$$\log \alpha_h = - \frac{\sigma_h^2 e^3}{(DkT)^{3/2}} \left(\frac{\pi n_A}{V} \sum_j \sigma_j^2 N_j \right)^{1/2},$$

or in terms of molalities ($V = 1000$, $N_j = m_j$)

$$\log \alpha_h = - \frac{\sigma_h^2 e^3}{(DkT)^{3/2}} \cdot \left(\frac{\pi n_A}{1000} \sum_j \sigma_j^2 m_j \right)^{1/2}. \qquad (17.66)$$

In water at the temperature of 25° C the dielectric constant is $D = 78.8$ leading to the expression

$$\log_{10} \alpha_h = - 0.356 \, \sigma_h^2 \left(\sum_j \sigma_j^2 \nu_j \right)^{1/2} m^{1/2},$$

if we denote by m the molality of the neutral electrolyte originally dissolved ($m_j = \nu_j m$). Hence the *activity function*, defined by eq. (11.32), is given by

$$\log_{10} \gamma = - \frac{0.356}{\nu_e} \left(\sum_j \sigma_j^2 \nu_j \right)^{3/4} m^{1/2}, \qquad (17.67)$$

while the coefficient becomes 0.345 for the temperature 0° C. This is the so-called *limiting law for very dilute electrolytes* due to Debye and Hückel.

The agreement of the limiting law with the measured activities is very good for ions of low valency as appears from Table 40.

The very accurate measurements by Neumann,[2] on silver chloride and barium sulfate, show, however, that the limiting law is not rigorous even for low-valency salts. In plotting the measured γ against $m^{1/2}$ this author finds curious oscillations of the curves around the theoretical value (17.67). The deviations, although very small, seem outside the limit of experimental error. High-valency electrolytes

[1] The pressure increase due to the effect here considered is only a small fraction of 1 mm Hg. According to (9.42), (11.35), and (17.67), in water of 25° C it is: $\Delta p - \Delta p_0 = - 0.006 \nu_e m \log \gamma = 0.12 (\Sigma \sigma_j \nu_j m)^{3/2}$ mm Hg.

[2] E. W. Neumann, J. Am. Chem. Soc. **54**, p. 2195, 1932; **55**, p. 879, 1933.

were investigated by La Mer and co-workers,[1] who found large discrepancies with the limiting law.

TABLE 40

ACTIVITY FUNCTIONS OF STRONG ELECTROLYTES

Type	$\sigma_1 = 1$,	$\sigma_2 = 1$,	$\nu_1 = 1$,	$\nu_2 = 1$	
m	0.001	0.002	0.003		0.005
γ (theor)	0.964	0.949	0.938		0.932
HCl (exp)	0.965	0.953	.....		0.929
HNO_3 "	.....	0.953	.....		0.930
$AgNO_3$ "	.....	.....	0.940		
$AgClO_3$ "	.....	.....	0.940		
KCl "	.....	.....	.....		0.926

Type	$\sigma_1 = 2$,	$\sigma_2 = 1$,	$\nu_1 = 1$,	$\nu_2 = 2$	
m	0.001	0.002	0.003		0.005
γ (theor)	0.881	0.836	0.803		0.753
$CaCl_2$ (exp)	0.888	0.850	.....		0.785
$BaBr_2$ "	.....	.....	0.829		0.800
H_2SO_4 "	0.876	0.825	.....		0.734

Type	$\sigma_1 = 2$,	$\sigma_2 = 2$,	$\nu_1 = 1$,	$\nu_2 = 1$	
m	0.001	0.002	0.003		0.005
γ (theor)	0.746	0.661	0.601		0.519
$BeSO_4$ (exp)	0.754	0.670	.....		0.534
$CdSO_4$ "	0.754	0.671	0.621		0.540
CaS_2O_3 "	0.754	0.674	.....		0.540

When the solutions are not very dilute (presumably, $m > 0.005$, for low-valency salts), the term κa in (17.65) can no longer be neglected. In fact, the measured activity functions usually fall, at the higher concentrations, below the values of formula (17.67). However, in the present state of the theory the dependence on a is not accurately enough known to make its quantitative discussion worth while.[2]

[1] La Mer and Mason, J. Am. Chem. Soc. 49, p. 410, 1927; La Mer and Cook, *ibidem* 51, p. 2622, 1929; La Mer and Goldman, *ibidem* 51, p. 2632, 1929.

[2] A review of the work done on the theory of strong electrolytes by *statistical methods* will be found in an article by O. Halpern (J. Chem. Physics 2, p. 85, 1934). A critical discussion of the foundations of the theory was given by R. H. Fowler, (*loc. cit.*)

CHAPTER XVIII

THEORY OF SPECIFIC HEATS

116. General considerations. We had occasion to give the expressions for the specific heats of a few ideal systems, such as perfect gases (non-degenerate and degenerate) and the Einstein model of a solid. Purely thermodynamical reasoning does not enable us to say much about the heat capacities of the real substances of nature except that they must vanish at $T = 0$. The internal energy of a system completely determines its equation of state through eq. (13.22), but the reverse is not true: the knowledge of the equation of state is not sufficient for calculating the energy since eq. (16.12)

$$u = \int \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv + f(T) \tag{18.01}$$

still contains an unknown function of the temperature which usually gives the major contribution to the specific heat. However, heat capacities are of such fundamental importance as material for the applications of thermodynamics that a textbook of this branch of science would be incomplete if it did not contain some information on the status of our theoretical knowledge about them, even if this knowledge is obtained by non-thermodynamical methods. It seems appropriate, therefore, to include a chapter partially devoted to the way in which the kinetic theory of matter approaches the problem of specific heat.

The fundamental tool of the kinetic treatment is eq. (4.70) of the Boltzmann principle. It is true that there are other types of statistics which we have described in section 104. However, as it was stated there, they apply only when many identical particles are distributed over energy states determined largely by joint external conditions. On the other hand, in such systems as an assembly of rotating molecules, each particle rotates around its own center of gravity and its quantum states are determined by conditions peculiar to itself as if it were alone and not part of a system. The same thing applies to the other systems occurring in the theory of specific heats, for instance,

linear oscillators. There is, therefore, little occasion to use the statistics of Fermi or Einstein-Bose, and the Boltzmann principle reigns supreme as far as these investigations are concerned. If a particle can assume the quantum states 0,1,2, . . . with the respective energies $\varepsilon_0, \varepsilon_1, \varepsilon_2, \ldots$ the principle postulates that the number of particles in the state l be $Z_l = C \exp(-\varepsilon_l/kT)$. The sum of the numbers Z_l represents, obviously, the total number Z of particles in the system

$$Z = C\sum \exp(-\epsilon_l/kT) = CY. \tag{18.02}$$

The expression $Y = \Sigma \exp(-\epsilon_l/kT)$ is usually called the *sum of states*. *Every quantum state of the particle must be represented in it by a term.* If the same energy level ε_l belongs to several (g_l) different quantum states, the corresponding term must be repeated g_l times. It is, therefore, more convenient to write it in the form

$$Y = \sum_l g_l \exp(-\varepsilon_l/kT). \tag{18.03}$$

We call the integer g_l, as in section 111, the *statistical weight* of the level l.

The energy of all the particles in the state l is $\varepsilon_l g_l Z_l = C g_l \varepsilon_l \times \exp(-\varepsilon_l/kT)$, and the total energy of the system

$$U = C\sum_l g_l \varepsilon_l \exp(-\varepsilon_l/kT). \tag{18.04}$$

The sum in this expression can be obtained by differentiating Y with respect to $-(1/kT,)$ i.e. $U = -Ck\partial Y/\partial(1/T)$. Eliminating C with the help of (18.02)

$$U = -Zk \frac{\partial \log Y}{\partial(1/T)}. \tag{18.05}$$

If we refer our considerations to 1 mol of matter, the number of particles is $Z = n_A$ (Avogadro's number $n_A = R/k$), and the molal internal energy becomes

$$u = -R\,\partial \log Y/\partial(1/T). \tag{18.06}$$

We may consider this as the fundamental formula of the statistical theory of specific (molal) heats, since they can be derived from u by the formula $c = \partial u/\partial T$ or

$$c = \frac{R}{T^2} \frac{\partial^2 \log Y}{\partial(1/T)^2}. \tag{18.07}$$

Comparing (18.06) with the relation (5.56), we find as the thermodynamical interpretation of the sum of states

$$\psi = - RT \log Y, \tag{18.08}$$

where ψ is the molal work function defined as $\psi = u - Ts$. Therefore, the entropy has the expression

$$s = - \left(\frac{\partial \psi}{\partial T}\right)_v = \frac{u}{T} + R \log Y. \tag{18.09}$$

When the temperature T is very low, all the terms of the sum of states (18.03) become negligible compared with those of the lowest energy ε_0. The sum is reduced to $Y = g_0 \operatorname{esp}(-\varepsilon_0/kT)$, whence $RT \log Y = - n_A \varepsilon_0 + RT \log g_0$ and $s = R \log g_0$. It may seem, at first sight, that this result is in contradiction with Planck's formulation (13.19) of Nernst's postulate. However, these formulas are no longer valid in the vicinity of $T = 0$. The expression (18.03) refers to the rotational and oscillatory motions of the molecules, and its use implies the assumption that the probabilities of these motions can be evaluated apart from the translational movements. This ceases to be true under conditions of temperature and density in which the statistics of Fermi or Einstein-Bose begin to play a role for the translational degrees of freedom. We refer, in this connection, to the remarks made in section 111 with respect to the entropy of the electron gas. In that example the statistical weight is $g_0 = 2$, as there exist two kinds of spin. In the non-degenerate state the entropy contains, therefore, the term $R \log 2$ (entropy of mixing), but in the degenerate gas this term disappears because the two kinds of electrons are regularly and uniquely arranged over the quantum states.

117. Diatomic gases. The classical kinetic theory inevitably leads to the principle of equipartition of energy (4.71): each degree of freedom takes up the kinetic energy $\frac{1}{2}RT$ per mol. It is assumed that the molecule of a monatomic gas has only 3 (translational) degrees of freedom, the molecule of a diatomic gas 5 (3 translational, 2 rotational). The corresponding molal heats are $c_v = \frac{3}{2}R$ and $c_p = \frac{5}{2}R$, respectively. If the gas does not strictly obey the equation $pv = RT$, the resulting correction is taken care of by eq. (18.01) or by its derivative with respect to T

$$c_v = T \int \left(\frac{\partial^2 p}{\partial T^2}\right)_v dv + f'(T), \tag{18.10}$$

while c_p can be obtained from (4.27). The main success which the classical theory has to its credit lies in the sphere of *monatomic* gases,

whose specific heats it represents accurately. It is not so satisfactory in application to diatomic substances (compare section 15). For the more perfect permanent gases of nature the agreement is fair in the region of room temperatures, but there are large deviations both for low and very high temperatures.

The following treatment is based on the theorem of mechanics that the kinetic energy of any system (molecule) can be represented as a sum of the two terms: the kinetic energy of the center of gravity and the energy of the motion within the system (molecule) relatively to the center of gravity. Correspondingly, the internal energy (as also the entropy and the specific heat) may be divided into two parts. It happens, moreover, that the contributions of the rotations and vibrations (though not rigorously additive) are separable with a sufficient degree of approximation [1]

$$u = u_t + u_r + u_{vi}. \tag{18.11}$$

The first belongs to the translational motions and is calculated by the classical formula

$$u_t = \tfrac{3}{2}RT + u_0, \tag{18.12}$$

since the center of gravity is completely determined by the three coordinates of translation, assuming that degeneration of the type of Chapter XVI is negligible (compare preceding section). The second and third parts are due to the rotational motion of the molecule as a whole or to the vibrations of the atoms inside it. They are computed with the help of the quantum eqs. (18.03) and (18.06).

As to the *rotational heat* c_r, a good approximation is often afforded by the so-called *dumb-bell model.* The diatomic molecule is considered as consisting of two material points at an invariable distance from each other rotating around their center of gravity in a joint plane. Quantum dynamics gives for the energy levels of the dumb-bell model

$$\varepsilon_j = \frac{h^2}{8\pi^2 K} j(j+1), \tag{18.13}$$

where K is the moment of inertia of the molecule. At the same time the statistical weight of the level ε_j is $g_j = 2j + 1$ (provided the nuclei have no spins).

[1] Occasionally, more rigorous expressions are used in which the rotational and vibrational energies cannot be separated (compare section 119). This is, however, unnecessary as far as the accuracy of caloric measurements is concerned. In addition to the items of eq. (18.11), sometimes the energy of electronic configurations (excited states) is also of importance.

Two cases must be distinguished with respect to the values of the quantum integers j. (A) When the molecule is *asymmetrical*, consisting of two different atoms, it can assume all integral values ($j = 0,1,2, \ldots$). (B) When the molecule is *symmetrical*, built up of two identical atoms, only *even* integral values are permissible [1] ($j = 0,2,4, \ldots$). This distinction was recognized even in the old quantum theory and was there interpreted as follows: the asymmetrical molecule must be rotated through the angle 2π until it returns to the initial position; the cycle of the symmetrical molecule is only half as large, for after being turned by the angle π it is in a position which cannot be told from the initial. The interpretation of quantum dynamics is somewhat different: when we have two identical atoms (without nuclear spins) they obey the statistics of Einstein-Bose [2] and admit only quantum states with symmetrical wave functions; these happen to be those with even numbers j. No such restriction exists for the asymmetrical molecule.

In either case, we can express the sum of states (18.03) by the single formula ($j = 1,2,3 \ldots$)

$$Y_r = \sum_{j=0}^{\infty} (2\sigma j + 1) \exp [-\tau\sigma j(\sigma j + 1)], \tag{18.14}$$

$$\tau = h^2/8\pi^2 KkT, \tag{18.15}$$

if we introduce the *symmetry number* σ, which is, respectively, equal to 1 and 2, for asymmetrical and symmetrical molecules.

For *high temperatures*, τ is very small and (18.14) yields the equipartition value. In fact, putting $n = 0$ in eq. (18.22), below, we find in this case

$$Y_r = 1/\tau\sigma$$

or $\log Y_r = -\log (1/T) + \text{const.}$ Hence (18.07) gives $c_r = R$, corresponding to the two degrees of freedom of the dumb-bell model. On the other hand, for very *low temperatures*, only the first two terms of the sum are significant, $\log Y_r = (2\sigma + 1) \exp [-\tau\sigma(\sigma + 1)]$, whence $c_r = R(2\sigma + 1)\sigma^2(\sigma + 1)^2\tau^2 \exp [-\tau\sigma(\sigma + 1)]$. Therefore, the formula (18.14) represents a gradual rise (with temperature) of the rotational molal heat from zero to the equipartition value, a behavior which is in qualitative agreement with the observed facts.

[1] We consider here only nuclei *without spins*. The case of atoms with nuclear spins will be treated in the next section.

[2] Nuclei without spins are, necessarily, built up of an even number of primary particles.

When quantitative accuracy is desired, the dumb-bell model often turns out to be oversimplified. For one thing, nuclear spins of the two atoms will introduce changes in the statistical weights, as we shall see in the next section. For another, the molecule may be capable of several electronic configurations (excited states) causing a multiplication of energy levels. The spectroscopy of the band spectra makes available a material of large and rapidly increasing volume relating to the rotational and vibrational energy states. For a great many gases the levels ε_l have been accurately measured and tabulated. If a simple formula is not available, the procedure usually followed is to substitute into the sum of states (18.03) the spectroscopically measured levels (or exact theoretical expressions where they are known) and to obtain the specific heats by numerical calculation.

In view of this, we shall mention here specifically only a particularly simple case, that of the *doublet structure* of the energy levels. It is not restricted to the rotational energy of molecules but has a quite general application and was first treated by Schottky.[1] Suppose that the energy levels occur in pairs ε_l and $\varepsilon_l + \Delta\varepsilon$ (the increment $\Delta\varepsilon$ being constant and independent of l) with the relative statistical weights $g_0 : g_1$. Every term of Y (18.03) will then appear to be multiplied by the same factor $Y_d = g_0 + g_1 \exp(-\Delta\varepsilon/kT)$. Writing for short

$$\Theta = \Delta\varepsilon/k, \quad \gamma = \tfrac{1}{2}\log(g_1/g_0), \tag{18.16}$$

we find

$$Y_d = g_0 + g_1 \exp(-\Theta/T) = 2g_0 \exp\left(\gamma - \frac{\Theta}{2T}\right)\cosh\left(\frac{\Theta}{2T} - \gamma\right).$$

Correspondingly, $\log Y$ will contain the additional term

$$\log Y_d = -\frac{\Theta}{2T} + \log\cosh\left(\frac{\Theta}{2T} - \gamma\right) + \tfrac{1}{2}\log(4g_0g_1), \tag{18.17}$$

whence the *doublet heat* is calculated from (18.07)

$$c_d = R\frac{(\Theta/2T)^2}{\cosh^2\left(\frac{\Theta}{2T} - \gamma\right)}. \tag{18.18}$$

This expression is valid, of course, even when no other energy spectrum exists, i.e. when each particle is capable only of the two energy states ε_0 and $\varepsilon_0 + \Delta\varepsilon$. In the special case of the rotational doublets, $\Delta\varepsilon$ is not strictly constant. Its formula was worked out by

[1] W. Schottky, Phys. Zs. 23, p. 448, 1922.

Hill and Van Vleck [1] and shows a slight dependence on j. It seems, however, that in most cases the simple formula (18.18) gives an approximation, sufficient within the accuracy of heat measurements (section 119). The presence of the term c_d produces a characteristic hump in the specific heat curve as exemplified in Fig. 54. The conditions are not very different when each energy level, instead of splitting into two components, splits into several or many closely spaced sublevels (multiplet structure): the analytical expressions are more complicated but the result is a hump in the curve of specific heat not unlike the doublet hump.

It is well known that the energy levels of the linear oscillators are given by the formula

$$\varepsilon_{vi} = h\nu_0(v + \tfrac{1}{2}), \qquad v = 0,1,2, \ldots$$

ν_0 being its characteristic frequency. The *vibrational levels* of diatomic molecules are not quite so simple as that but in most cases they can be sufficiently well represented by an expression of the form

$$\varepsilon_{vi} = h\nu_0[(v + \tfrac{1}{2}) - x(v + \tfrac{1}{2})^2], \tag{18.19}$$

(anharmonic oscillator) where x is a constant. A theoretical foundation for this formula was given by Kratzer [2] and in a different way by Morse.[3] We repeat that, strictly speaking, the vibrational energy is not entirely independent from the rotational but there exist mixed roto-vibrational terms, which are, however, negligible as far as the computation of specific heats is concerned. The fact that ε_j and ε_{vi} are simply additive means that, by taking into account the levels (18.19), each term of the sum Y_r (18.14) is multiplied by the same expression Y_{vi}. Since the statistical weight of each vibrational energy level is 1, we can write

$$Y_{vi} = \Sigma \exp\left\{-\frac{h\nu_0}{kT}[(v + \tfrac{1}{2}) - x(v + \tfrac{1}{2})^2]\right\}. \tag{18.20}$$

In other words, the rotational and vibrational sums of states are multiplicative, $Y = Y_r \cdot Y_{vi}$, whence $\log Y = \log Y_r + \log Y_{vi}$ and $c = c_r + c_{vi}$. The rotational and vibrational heats are additive, within our approximation, and can be evaluated separately.

It must be noted that the sum of states with the energy levels

[1] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, p. 250, 1928. On the basis of this work a correction to (18.18) was calculated by G. Gregory (Zs. Physik **78**, p. 789, 1932).

[2] A. Kratzer, Zs. Physik **3**, p. 289, 1920.

[3] Ph. M. Morse, Phys. Rev. **34**, p. 57, 1929.

(18.19) would be divergent if v could increase to infinity. This means either that the number of states is finite, being cut short by the dissociation of the molecule, or that the expression (18.19) represents an approximation valid only for low order terms. There is no practical difficulty connected with this because the terms decrease rapidly even at high temperatures and no ambiguities arise in the numerical calculations. For a few gases the expression (18.19) does not hold with sufficient precision; recourse is then taken to the empirical energy levels tabulated by spectroscopists. On the other hand, when the coefficient x is small compared with 1, it is possible to obtain a fair approximation neglecting it altogether, and extending the summation to infinity.[1] In this case it can be readily carried out and gives the result

$$\left.\begin{aligned} Y_{vi} &= 1/2 \sinh (\Theta/2T), \\ c_{vi} &= R\Theta^2/4T^2 \sinh^2 (\Theta/2T), \end{aligned}\right\} \tag{18.21}$$

where the "characteristic temperature" Θ is an abbreviation for $\Theta = h\nu_0/k$. *At any event the law of equipartition of energy does not apply to expressions of the type* (18.19) or (18.20). The vibrational specific heats, therefore, rise steadily without reaching a limiting value even at the highest attainable temperatures.

The constant $h\nu_0$ in (18.20) is always considerably larger numerically than τkT of (18.15). Therefore, the vibrational heats come into play at much higher temperatures than the rotational. The gases mentioned in the beginning of this section as apparently confirming the classical theory are those for which the rotational degrees of freedom have reached complete equipartition at room temperature while the vibrational degrees are not yet appreciably excited.

Exercise 104. Take a sum slightly more general than (18.14)

$$Y = 2\sum_{j=0}^{\infty} (\sigma j + n + \tfrac{1}{2}) \exp [-\tau(\sigma j + n)(\sigma j + n + 1)]\, \Delta j.$$

$\Delta j = 1$ is the increment which j receives from term to term. Write $\sqrt{\tau}\,\sigma j = x_j$; if τ is very small, $\Delta x_j = \sqrt{\tau}\,\sigma \Delta j$ is also very small, and the summation can be replaced by an integration with respect to x_j. Show that the result of the integration is $Y = (1/\sigma\tau) \exp [-n(n+1)\sigma]$, or when σ is extremely small,

$$Y = 1/\sigma\tau. \tag{18.22}$$

118. Hydrogen (Protium, H^1H^1). The decline of rotational specific heats at low temperatures was first observed in hydrogen.[2] Its

[1] W. Nernst and K. Wohl, Zs. techn. Physik **10**, p. 611, 1929.

[2] A. Eucken, Preuss. Akad. d, Wiss., p. 141, 1912.

complete theory was developed in slow steps which were highly instructive. The simple dumb-bell model is here inadequate because of the nuclear spin of the hydrogen atom. There exist two modifications of the molecule: para-hydrogen in which the spins of the two nuclei are anti-parallel, and ortho-hydrogen in which they are parallel. The total spin of the para-hydrogen is zero and it is indifferent to a magnetic field, while ortho-hydrogen is capable of assuming in such a field three quantized orientations. Therefore, the factors $(2j + 1)$ in the sum of states (18.14) represent correctly the statistical weights of those energy levels which belong to para-hydrogen while those corresponding to ortho-hydrogen must be multiplied by three. It happens that the levels of the two modifications divide neatly, para-hydrogen being capable only of even quantum numbers j, and ortho-hydrogen only of odd. The corrected sum of states as first given by Hund [1] is, therefore,

$$Y = Y_s + 3Y_a, \tag{18.23}$$

$$Y_s = \sum_{j=0}^{\infty} (4j + 1)e^{-\tau 2j(2j+1)}, \quad Y_a = \sum_{j=0}^{\infty} (4j + 3)e^{-\tau(2j+1)(2j+2)}. \tag{18.24}$$

This is in complete agreement with the band spectrum data where the lines corresponding to odd levels are three times as strong as those corresponding to even levels. Hund gave also the theoretical explanation of the selectivity of the two modifications with respect to even and odd levels. It lies in the requirement of wave mechanics that the wave functions representing the states of the molecule must be anti-symmetric with respect to the two nuclei (compare section 104). These wave functions consist of two factors which characterize, respectively, the spins and the rotational motions. It is clear, therefore, that the arrangement of the spins will influence the selection of the rotational states. When the spins are anti-parallel, the interchange of the two nuclei produces the same effect as a reversal of the spins: para-hydrogen is, therefore, anti-symmetric in the spins and must have a symmetric rotational function (which happens to be the one with even j). On the other hand, when the spins are parallel an interchange of the nuclei does not produce any effect: ortho-hydrogen is symmetric with respect to the spins and has an anti-symmetric rotational function (the one with odd j). We shall, therefore, drop the prefixes para- and ortho- and speak instead of symmetrical and anti-symmetrical hydrogen (meaning symmetry with respect to the rotations).

[1] F. Hund, Zs. Physik 42, p. 93, 1927.

Yet the specific heats calculated from the sum of states (18.23) do not agree with those obtained from measurements.[1] The reason for this has been cleared up by Dennison [2] and lies in the fact that the two modifications of hydrogen are very slow in reaching equilibrium. The theory of wave mechanics permits one to foresee that transitions between the two modifications of hydrogen are extremely unlikely, and this is borne out by the complete absence of band lines corresponding to such transitions. When heat is added to hydrogen, it immediately distributes itself over the rotational levels *within each modification separately*, but it takes a very long time for the equilibrium ratio of the two kinds of molecules to be established. The number of molecules of symmetrical hydrogen is proportional to Y_s, that of antisymmetrical to $3Y_a$; we give the equilibrium ratio of these numbers for several temperatures using the value $\sigma T = 82.6$ deg. which follows from the spectroscopical value [3] $K = 4.80 \times 10^{-41}$g cm^2.

Temperature	$Y_s : 3Y_a$
$T = \infty$	1.00 : 3.00
293°.1 K	1.00 : 2.98
78	1.00 : 1.07
20.4	1.00 : 0.0145

While at high temperatures symmetrical hydrogen accounts for only one-quarter of the gas, it is practically pure in equilibrium at the temperature of boiling hydrogen. Under usual conditions, the determination of specific heats takes only a fraction of an hour, and the actual ratio $Y_s : 3Y_a$ in the gas is that corresponding to room temperature and not to the temperature of measurement. In other words, symmetrical and anti-symmetrical hydrogen behave like two independent gases in the permanent ratio of about 1 : 3. The appropriate procedure is, therefore, to calculate separately, by means of eq. (18.07), the specific heats of the two modifications: c_s from Y_s, and c_a from Y_a. The rotational heat of the actual gas is then

$$c_r = \tfrac{1}{4}c_s + \tfrac{3}{4}c_a. \qquad (18.25)$$

The result is indeed in excellent agreement with experiment, as will

[1] Experimental determinations were due to: F. A. Giacomini, Phil. Mag. **50**, p. 146, 1925; J. H. Brinkworth, Proc. Roy. Soc. (A) **107**, p. 510, 1925; Partington and Howe, *ibidem*, **109**, p. 286, 1925; Cornish and Eastman, J. Am. Chem. Soc. **50**, p. 627, 1928; Scheel and Heuse, Ann. Physik **40**, p. 473, 1913; A. Eucken, Sitzungsber. Berlin, p. 141, 1912.

[2] D. M. Dennison, Proc. Roy. Soc. (A) **115**, p. 483, 1927.

[3] Compare: R. T. Birge, I.C.T. V, p. 409, 1929.

be seen from Fig. 49, where the dashed curve is calculated from eq. (18.25).

An investigation by Bonhoeffer and Harteck [1] showed that, under ordinary conditions, the time necessary for reaching equilibrium of para- and ortho-hydrogen is about ten months. However, it can be enormously shortened, in fact, reduced to a few minutes, by letting the gas be absorbed in carbon. In this way it is possible to prepare almost

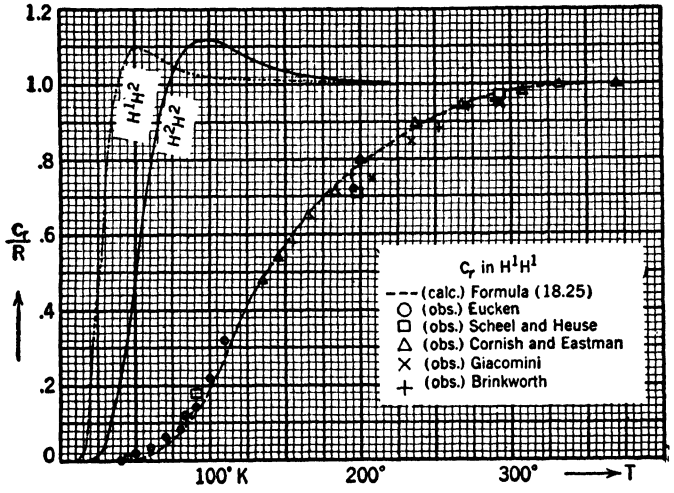

FIG. 49.—Specific heats of hydrogen and deuterium.

pure symmetrical hydrogen which keeps for several months when stored in a glass container.

119. Deuterium, N_2, O_2, Cl_2, NO, Cl. Limitations of space do not permit us to give an exhaustive account of the work on specific heats of gases, and we restrict ourselves to a few typical examples.

As to *rotational heats*, the situation in hydrogen repeats itself in many other gases. Most of them possess a symmetric and an antisymmetric modification of the molecule, so that the complete sum of states is

$$Y_r = g_s Y_s + g_a Y_a. \tag{18.26}$$

The ratio of statistical weights $g_a : g_s$ is, in general, not the same as in hydrogen (where it is 3 : 1). The two modifications interact but little and behave, under the conditions of measurement, like two

[1] Bonhoeffer and Harteck, Sitzungsber. Berlin, p. 103, 1929; Zs. phys. Chem. (B) 4, p. 113, 1929.

independent gases. The experimental specific heats are, therefore, represented by the formula

$$c_r = \frac{g_s c_s + g_a c_a}{g_s + g_a}. \tag{18.27}$$

The *vibrational heats* are usually calculated from expressions of the sum of states of the form (18.20).

(1) *Deuterium* (H^2H^2).

The nucleus of deuterium (deuteron or the heavy isotope of hydrogen) possesses a double spin (with the quantum number 1, as compared to $\frac{1}{2}$ of the proton). As shown in the quantum theory, the molecule is then capable of 6 symmetrical and 3 antisymmetrical spin configurations. Moreover, the deuteron obeys the Einstein-Bose statistics, being built up of an even number (2) of protons. Therefore, the symmetrical spin states combine with the symmetrical rotational states, etc., and we have $g_s = 6$, $g_a = 3$. The specific heats of deuterium have been calculated with great accuracy (even taking into account mixed vibro-rotational terms) by Johnston and Long.[1] Their results are represented by the solid curve of Fig. 49. The decline takes place at lower temperatures than in the case of protium, caused by the, roughly, two times larger moment of inertia. The dotted curve of Fig. 49 refers to the mixed proton-deuteron molecule H^2H^1 as given by the same authors.

The data given below for several gases are mostly taken from Trautz and Ader,[2] in whose paper can be found the references to the older work on the subject.

(2) *Nitrogen*, N_2 (Fig. 50).

The rotational heat (determined by $K = 39.65 \times 10^{-40}$, $\sigma T = 2.873$, $g_a : g_s = 2 : 1$) reaches the full equipartition value at 29° abs.

The vibrational levels are represented by [2, 3]

$$\Theta_{vi} = k^{-1}\varepsilon_{vi} = 3374.24(v + \tfrac{1}{2}) - 20.66(v + \tfrac{1}{2})^2. \tag{18.28}$$

(3) *Oxygen*, O_2 (Fig. 51).

[1] H. L. Johnston and E. A. Long, J. Chem. Phys. **2**, p. 389, 1934.

[2] M. Trautz and H. Ader, Zs. Physik **89**, pp. 1, 12, 15, 1934. The experimental data included in Figs. 50, 51, 52 are taken from the following papers: Eucken and v. Lüde, Zs. phys. Chem. **5**, p. 413, 1929; Eucken and Mücke, *ibidem* **18**, p. 167, 1932; P. S. Henry, Proc. Roy. Soc. **133**, p. 492, 1931; Shillings and Partington, Phil. Mag. **9**, p. 1020, 1930.

[3] Compare also: Giauque and Clayton, J. Am. Chem. Soc. **55**, p. 4875, 1933.

The equipartition of the rotational heat is reached at temperatures still lower than in the case of nitrogen. The vibrational levels are [1]

$$\Theta_{vi} = k^{-1}\varepsilon_{vi} = 2310.7(v + \tfrac{1}{2}) - 16.26(v + \tfrac{1}{2})^2. \quad (18.29)$$

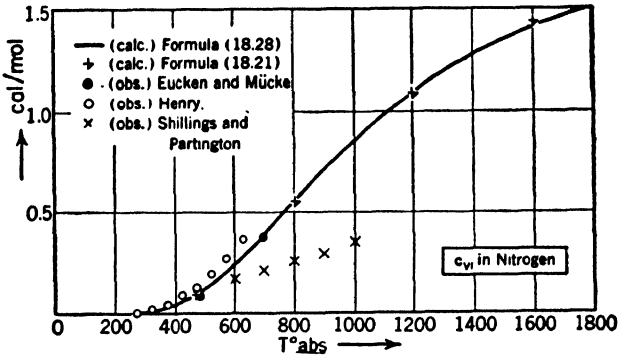

FIG. 50.—Vibrational specific heat of nitrogen.

The specific heat of O_2 has been calculated also by Johnston and Walker,[2] who used the rigorous spectroscopic expressions for the energy levels (including the mixed vibro-rotational terms). Their

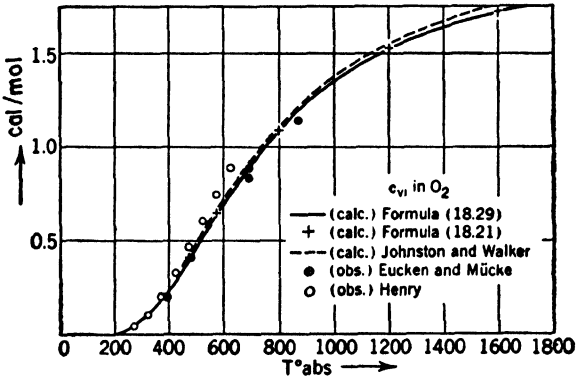

FIG. 51.—Vibrational specific heat of oxygen.

data are represented by the dashed curve in Fig. 51. It will be seen that the difference is appreciable only at very high temperatures.

(4) *Air* (Fig. 52).[1]

The constitution of air is 78.06% N_2, 21.0% O_2, 0.94% Ar.

(5) *Chlorine*, Cl_2 (Fig. 53).[1]

[1] Trautz and Ader, *loc. cit.*

[2] Johnston and Walker, J. Am. Chem. Soc. 55, pp. 172, 187, 1933.

The conditions in Cl_2 are complicated by the existence of the two isotopes Cl_{35}, Cl_{37} which form three kinds of molecules. The band spectra, however, show that the amount of $Cl_{37}Cl_{37}$ is small and that chlorine can be taken as consisting of 60% $Cl_{35}Cl_{35}$ and 40%

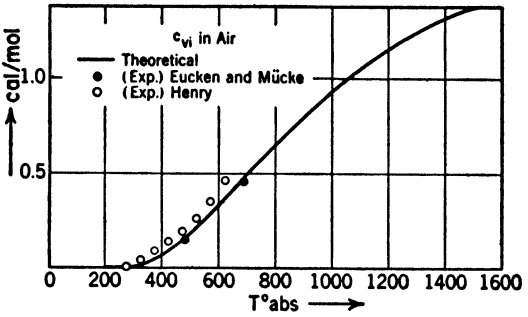

FIG. 52.—Vibrational specific heat of air.

$Cl_{35}Cl_{37}$.[1] The rotational heat of chlorine is of only academic interest as it reaches equipartition at 1°.5 abs. The vibrational levels of $Cl_{35}Cl_{35}$ are given by[2]

$$\Theta_{vi} = k^{-1}\varepsilon_{vi} = 807.81(v + \tfrac{1}{2}) - 5.72(v + \tfrac{1}{2})^2. \qquad (18.30)$$

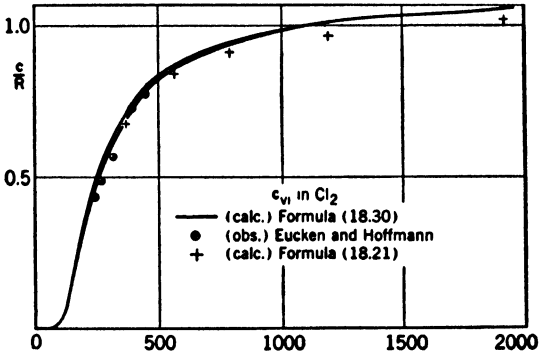

FIG. 53.—Vibrational specific heat of chlorine.

In the case of $Cl_{35}Cl_{37}$ the two coefficients must be multiplied $(36/37)^{\frac{1}{2}}$ and $(36/37)$, respectively:[2]

$$\Theta_{vi} = k^{-1}\varepsilon_{vi} = 796.26(v + \tfrac{1}{2}) - 5.57(v + \tfrac{1}{2})^2. \qquad (18.31)$$

[1] A. Elliott, Proc. Roy. Soc. (A) **127**, p. 638, 1930.
[2] Trautz and Ader, *loc. cit.*

(6) *Nitric oxide* (NO) does not offer much new with respect to the rotational and vibrational heats. In fact, c_r reaches equipartition below 30° abs. and c_{vi} comes into play only above room temperature. In the intermediate range NO is interesting because it offers an example of doublet heat c_d as given by the formula (18.18). From spectroscopic data the doublet difference is $\Delta\varepsilon_0 = 354$ cal/mol, whence $\Theta = 178$ deg. As mentioned in section 117, it is not strictly constant. The measurements were carried out by Eucken and d'Or,[1] who also calculated the theoretical values from the approximate formula (18.18), with $\gamma = 0$. Accurate calculations of the specific heat of NO were carried out by Johnston and Chapman,[2] who used the rigorous spectroscopic expressions of the energy levels. We give the values of c_d inferred from their results in the last column of Table 41. It will be seen that the approximation given by formula (18.18) is pretty good and certainly sufficient in view of the not very accurate experimental data.

TABLE 41

SPECIFIC HEATS OF NO

T	c_d/R (obs.)	c_d/R (calc.)	
		Eucken and d'Or	Johnston and Chapman
50°.0 C	....	0.34	0.325
75.0	....	0.44	0.429
100.0	....	0.39	0.395
127.0	0.27	0.31	0.314
133.3	0.31	0.29	0.295
150.0	0.28	0.25	0.258
173.8	0.22	0.20	0.21
193	0.17	0.17	0.18
218	0.14	0.14	0.15
298.1	0.14	0.09	0.10

(7) *Atomic chlorine* (Cl) offers another example of doublet heat (18.10). From spectroscopical data $\Delta\varepsilon = 2 \times 580$ cal/mol, $\Theta = 1299$, $\gamma = \frac{1}{2}\log\frac{1}{2}$. The calculation [3] leads to the curve shown in Fig. 54.

There are more gases whose complete curves of specific heats have been accurately calculated, but limitations of space do not

[1] A. Eucken and L. d'Or, Nachrichten Göttingen, p. 107, 1932.
[2] Johnston and Chapman, J. Am. Chem. Soc. 55, p. 159, 1933.
[3] W. Nernst and K. Wohl, Zs. techn. Physik 10, p. 608, 1929.

permit us to extend the number of examples, and we can only give here an incomplete list of references: H_2O has been treated by Trautz and Ader (*loc. cit.*); CO and N_2 by Johnston and Davis (J. Am. Chem. Soc. 56, p. 271, 1934); OH by Johnston and Dawson (*ibidem* 55, p. 2744, 1933). The work previous to 1930 can be found in I. C. T. and in other Tables of Constants.

Figures 50–53 contain also the values calculated by Nernst and Wohl (*loc. cit.*) with the help of the approximate formula (18.21).

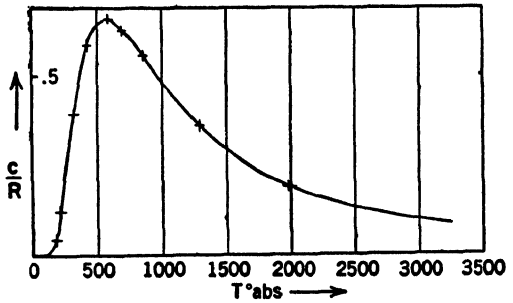

FIG. 54.—Doublet specific heat of atomic chlorine (theoretical).

The very good agreement shows that this simple way of computation can be used to great advantage when the coefficient x of the formula (18.19) is small compared with unity (and, presumably, T not too high). The values of the characteristic temperature Θ, for the common diatomic gases, as used by them, are given in Table 42.

TABLE 42

CHARACTERISTIC TEMPERATURES

Gas	Θ	Gas	Θ	Gas	Θ	Gas	Θ
H_2.....	5950	O_2.....	2220	HF.....	4130	Li_2.....	495
F_2.....	1610	S_2.....	1030	HBr.....	3660	Na_2.....	225
Cl_2.....	888	Se_2.....	570	HO.....	5110	K_2.....	130
Br_2.....	465	Te_2.....	360	NO.....	2680	NaK.....	175
F_2.....	305	N_2.....	3374	CO.....	3060		
ClJ.....	545						

120. The chemical constant of gases. The notion of the chemical constant was introduced in section 95. It is that part of the entropy of a perfect gas which is left undetermined by the first and second laws

of thermodynamics. Its determination completes the definition of the thermodynamic functions, especially of the thermodynamic potential $\varphi = u - Ts + pv$, and so makes definite the equations of equilibrium (6.50). In section 95 we showed that it has the Sackur-Tetrode expression (14.12) in the case of molecules having only translational degrees of freedom. Generally, the thermodynamic potential of a non-degenerate perfect gas can be divided into two parts

$$\varphi = \varphi_t + \varphi_i,$$

where φ_t refers to the translational and φ_i to the inner (rotational, vibrational, etc.) degrees of freedom of the molecules. To φ_t applies the expression which was derived for a monatomic gas consisting of material points, i.e. (5.41), (5.43) with $c_p = 5R/2$. On the other hand, the inner motions do not contribute to the term pv and consequently φ_i is identical with the work function ψ_i whose connection with the sum of states is given by (18.08):

$$\varphi = u_{0t} + RT[\log p + \tfrac{5}{2}\log T - \log Y - j_t], \qquad (18.32)$$

where j_t is the expression (14.13).

(A) *Monatomic gases* do not possess rotational or vibrational degrees of freedom. The sum of states $Y = Y_e$ refers here only to the energy levels of electronic configurations. The term $RT \log Y_e$ contains, however, a contribution to the zero point energy. In fact, factoring off the first exponential in the sum (18.03) we may write $Y_e = \exp(-\varepsilon_0/kT)\, g_e$ or $\log Y_e = -(\varepsilon_0/kT) + \log g_e$. The quantity g_e can be thrown into the form

$$g_e = \sum_l g_l \exp(-\Theta_l^e/T), \qquad (18.33)$$

where $\Theta_l^e = (\varepsilon_l - \varepsilon_0)/k$. Consequently,

$$\varphi = u_0 + RT(\log p - \tfrac{5}{2}\log T - j),$$

$$j_{10} = -1.589 + \tfrac{3}{2}\log_{10}\mu + \log_{10} g_e, \qquad (18.34)$$

(provided the pressure is expressed in atmospheres). g_0 represents the statistical weight of the fundamental state due to the moment of momentum of the atom. The quantities Θ_l^e are usually so large that the higher terms of (18.33) are negligible even at fairly high temperatures. Only in rare cases are the terms with $l = 1$, $l = 2$ appreciable. Data relating to a number of atoms are contained in Table 43.[1]

[1] Taken from K. Wohl, Landolt-Bornstein, Second Supplement, p. 1254, 1930.

TABLE 43

Atom	Symbol of level	g_l	Θ_l^e	Atom	Symbol of level	g_l	Θ_l^e
Noble gases	$^1S_0$	1			$^3P_2$	5	
H, Cu, Ag, Au, alkali metals	$^2S_{1/2}$	2		O	$^3P_1$	3 (9)	228
					$^3P_0$	1	324
Zn, Cd, Hg, earth alkalis	$^1S_0$	1		F	$^2P_{3/2}$	4	
					$^2P_{1/2}$	2	580
C	^3P	9		Cl	$^2P_{3/2}$	4	
Si	$^3P_0$	1			$^2P_{1/2}$	2	1 260
	$^3P_1$	3 (9)	110	Br	$^2P_{3/2}$	4	
	$^3P_2$	5	320		$^2P_{1/2}$	2	5 270
Sn	$^3P_0$	1		J	$^2P_{3/2}$	4	
	$^3P_1$	3	2 420		$^2P_{1/2}$	2	10 900
	$^3P_2$	5	4 900	Fe	$^5D_4$	9	
Pb	$^3P_0$	1			$^5D_3$	7	595
	$^3P_1$	3	11 200		$^5D_2$	5	1 010
	$^3P_2$	5	15 200		$^5D_1$	3	1 270
N, P, As, Sb, Bi	$^4S_{3/2}$	4			$^5D_0$	1	1 400

(B) *Diatomic gases.* The concept of the chemical constant can be extended to diatomic and polyatomic gases only within the approximation with which $\log Y_r$, pertaining to the rotational states, can be regarded as additive to $\log Y$ due to the other degrees of freedom. We have seen in the preceding section that this approximation is, indeed, quite sufficient for thermodynamical purposes. The range of temperatures is restricted to those above equipartition of the rotational energies when $Y_r = (1/\sigma\tau)$, according to (18.22) or

$$Y_r = -\log(h^2/8\pi k) + \log K - \log\sigma + \log T.$$

In practice, moreover, it is assumed that the molecule is in its fundamental electronic state, so that g_e reduces to g_0 and the remainder of $\log Y$ becomes $\log g_0 + \log Y_{vi} = \log g_0 - \psi_{vi}/RT$. Eq. (18.32), therefore, takes the form

$$\varphi = u_{0i} + \psi_{vi} + RT[\log p - \tfrac{7}{2}\log T - j],$$

where ψ_{vi} can be calculated either from the approximate equations (18.21), with the data of Table 42, or from the more accurate formula (18.20). Since the numerical value of $-\log_{10}(h^2/8\pi^2 k)$ is 38.402, we find for the chemical constant the expression

$$j_{10} = 36.813 + \tfrac{3}{2}\log_{10}\mu + \log_{10} K - \log_{10}\sigma + \log_{10} g_0. \qquad (18.35)$$

TABLE 44

CHEMICAL CONSTANTS OF DIATOMIC GASES

Gas	$10^{40}K$	σ	g_0	j	Gas	$10^{40}K$	σ	g_0	j
H_2	0.480	2	1	−3.355	HF	1.35	1	1	−1.10
F_2	25.3	2	1	0.285	HCl	2.646	1	1	−0.419
Cl_2	114	1.57	1	1.45	HBr	3.303	1	1	0.197
Br_2	330 ?	1.42	1	2.49 ?	HJ	4.309	1	1	0.609
J_2	742.6	2	1	2.995	HO	1.500	1	$2(\Theta_1^e=173)$	−0.561
ClJ	575 ?	1	1	2.89 ?	CO	14.9	1	1	0.159
O_2	19.3	2	3	0.531	NO	16.35	1	$2(\Theta_1^e=182)$	0.862
S_2	67 ?	2	3?	1.08 ?	Na_2	179.5	2	1	1.262
Te_2	860 ?	2	3	3.09 ?	K_2	184	2	1	1.619
N_2	13.8	2	1	−0.175	NaK	66	1	1	1.324

The fractional symmetry numbers (for Cl_2 and Br_2 in Table 44) represent the mean values for the isotopes.

(C) *Polyatomic gases.* Without entering into the derivation we only state here the final result for the expression of the thermodynamic potential [1]

$$\varphi = u_{0i} + \psi_{vi} + RT[\log p - 4\log T - j],$$

$$j_{10} = 56.563 + \tfrac{3}{2}\log\mu + \tfrac{3}{2}\log\overline{K} - \log\sigma + \log g_0, \qquad (18.36)$$

where $\overline{K} = (K_1K_2K_3)^{1/3}$ is the geometrical mean of the three moments of inertia possessed by the molecule.

A few numerical values are given in Table 45.

TABLE 45

CHEMICAL CONSTANTS OF POLYATOMIC GASES

Gas	j	Gas	j
CO_2	0.73±0.05	H_2O	−1.91
N_2O	0.68	NH_3	−1.66
C_2H_2	0.008	CH_4	−1.94

In conclusion it must be pointed out that the above expressions are still incomplete in so far as they do not contain *the statistical weights g_n of the nuclear spins.* Strictly speaking, one should add to

[1] A. Eucken, Phys. Zs. 30, p. 118, 1929; 31, p. 361, 1930.

the expressions (18.34), (18.35), and (18.36) the term $\log g_n$. However, at temperatures at which the symmetrical and antisymmetrical modifications of the molecules (sections 118, 119) have practically reached the ratio $g_s : g_a$, corresponding to $T = \infty$, this term is the same in the molecules and in an equivalent number of free atoms so that it drops out of the equations of chemical equilibrium. At room temperature this condition is satisfied for all gases except hydrogen, for which it is true from about 70° C on. In Chapter XIX we shall discuss problems of transmutation of matter in which the term $\log g_n$ may play a role. We mention, therefore, that in the atom of ordinary hydrogen (protium) $g_n = 2$, in the deuteron $g_n = 3$, in the helium atom $g_n = 0$.

121. Heat capacity of a reacting gas mixture. The diagrams of section 119 give the specific heats of several gases up to temperatures of 2000° abs. Under these circumstances dissociation may be already appreciable and must be taken into account. It will, therefore, be well to discuss how chemical reactions, taking place in a gas mixture, affect its heat capacity. We shall restrict ourselves to conditions under which the equation of perfect gases $pv = RT$ gives a sufficient approximation, permitting us to use the equilibrium theory of Chapter VIII.

Let us consider a mixture composed of the gases 1, 2, . . . β in the respective mol numbers N_1, N_2, . . . N_β, and let us suppose the following reactions to be possible in the mixture

$$\left.\begin{aligned} \nu_1 G_1 + \ldots + \nu_\beta G_\beta &= 0, \\ \nu'_1 G_1 + \ldots + \nu_\beta' G_\beta &= 0, \\ \text{etc.} & \end{aligned}\right\} \tag{18.37}$$

The condition of equilibrium for the first reaction is represented by the mass law (8.18)

$$\sum_i \nu_i \log x_i = \log K(p,T) \tag{18.38}$$

Substituting the definition of the mol fraction $x_i = N_i/N$ (where $N = N_1 + \ldots + N_\beta$), we can write

$$\sum_i \nu_i \log N_i - \nu \log N = \log K, \tag{18.39}$$

with the abbreviation $\nu = \nu_1 + \ldots + \nu_\beta$. According to eqs. (8.19) and (8.21)

$$\left(\frac{\partial \log K}{\partial T}\right)_p = \frac{Q}{RT^2}, \tag{18.40}$$

Q being the heat of the reaction

$$Q = \sum_l \nu_l \chi_l. \tag{18.41}$$

In the same way we find for the other reactions

$$\sum_l \nu'_l \log N_l - \nu' \log N = \log K', \tag{18.42}$$

$$\left(\frac{\partial \log K'}{\partial T}\right)_p = \frac{Q'}{RT^2}, \tag{18.43}$$

and so on.

We are now ready to calculate the heat capacity at constant pressure. The total heat function of the gas mixture is

$$\mathbf{X} = \sum_{l=1}^{\beta} N_l \chi_l,$$

and according to (3.26)

$$C_p = \left(\frac{\partial \mathbf{X}}{\partial T}\right)_p = \sum_{l=1}^{\beta} \left[N_l \left(\frac{\partial \chi_l}{\partial T}\right)_p + \chi_l \left(\frac{\partial N_l}{\partial T}\right)_p \right]. \tag{18.44}$$

The mol numbers change only inasmuch as the molecules of the mixture take part in the reactions (18.37). Each of the variations δN_l, therefore, must be expressible in the form

$$\delta N_l = \nu_l \, \delta\alpha + \nu'_l \, \delta\alpha' + \ldots, \tag{18.45}$$

where the quantities α, α', . . . are independent of the coefficients ν. Hence

$$\left(\frac{\partial N_l}{\partial T}\right)_p = \nu_l \left(\frac{\partial \alpha}{\partial T}\right)_p + \nu'_l \left(\frac{\partial \alpha'}{\partial T}\right)_p + \ldots \tag{18.46}$$

Noting (18.46) and the relation $(\partial \chi_l / \partial T)_p = c_{pl}$ and writing for short

$$N\overline{c_p} = \sum_{l=1}^{\beta} N_l \, c_{pl}, \tag{18.47}$$

we have

$$C_p = N\overline{c_p} + Q\left(\frac{\partial \alpha}{\partial T}\right)_p + Q'\left(\frac{\partial \alpha'}{\partial T}\right)_p + \ldots$$

In the case of a mixture of neutral, non-reacting gases this reduces simply to

$$C_p = \sum_l N_l \, c_{pl}.$$

The process of change of the mol numbers is supposed to take place in such a way that the equations of equilibrium (18.39) and (18.42) are always fulfilled. We can, therefore, obtain $(\partial\alpha/\partial T)_p$ by differentiating the first of them and taking into account that the contribution of this reaction to $(\partial N_l/\partial T)_p$ is the first term of (18.46), namely, $\nu_l(\partial\alpha/\partial T)_p$:

$$\left(\sum_{l=1}^{\beta}\frac{\nu_l^2}{N_l}-\frac{\nu^2}{N}\right)\cdot\left(\frac{\partial\alpha}{\partial T}\right)_p=\frac{Q}{RT^2}. \tag{18.48}$$

With the abbreviations

$$F(x)=\left(\sum_l\frac{\nu_l^2}{x_l}-\nu^2\right)^{-1},\quad F'(x)=\left(\sum_l\frac{\nu'^2_l}{x_l}-\nu'^2\right)^{-1}, \tag{18.49}$$

etc., we obtain as the final expression

$$C_p=N\left[\overline{c_p}+F(x)\frac{Q^2}{RT^2}+F'(x)\frac{Q'^2}{RT^2}+\ldots\right]. \tag{18.50}$$

The mol fractions x refer here, of course, to the state of chemical equilibrium. They can be obtained either theoretically, by the solution of the simultaneous eqs. (18.38), (18.42), etc., or empirically from measurements of the density and other properties of the gas mixture.

For the heat capacity *at constant volume*, we must start from the internal energy of the mixture

$$U=\sum_l N_l\,u_l, \tag{18.51}$$

whence

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V=\sum_l\left[N_l\left(\frac{\partial u_l}{\partial T}\right)_V+u_l\left(\frac{\partial N_l}{\partial T}\right)_V\right]. \tag{18.52}$$

For δN_l we have again to use the expression (18.45). Noting that $(\partial u_l/\partial T)_V=c_{vl}$, $\Sigma\nu_l u_l=\Delta U$, and introducing the abbreviation

$$N\overline{c_v}=\sum_l N_l\,c_{vl}, \tag{18.53}$$

we obtain

$$C_V=N\overline{c_v}+\Delta U\left(\frac{\partial\alpha}{\partial T}\right)_V+\Delta U'\left(\frac{\partial\alpha'}{\partial T}\right)_V+\ldots$$

In view of the relation (8.19), $\log K=\log K_p(T)-\nu\log p$, the equation of equilibrium (18.39) can be transformed by substituting for the pressure its expression from the equation of state, $p=NRT/V$:

$$\sum_l\nu_l\log N_l=\log K_p-\nu\log T+\nu\log(V/R). \tag{18.54}$$

Introducing the abbreviations

$$f(x) = \left(\sum_i \nu_i^2/x_i\right)^{-1}, \quad f'(x) = \left(\sum_i \nu'^2_i/x_i\right)^{-1}, \qquad (18.55)$$

and taking into account the relation $\chi_i = u_i + RT$, we obtain by differentiating (18.54) with respect to T

$$\frac{1}{f(x)}\left(\frac{\partial \alpha}{\partial T}\right)_v = N\left(\frac{Q}{RT^2} - \frac{\nu}{T}\right) = N\frac{\Delta U}{RT^2}.$$

The expression for the heat capacity (18.52) is, therefore,

$$C_V = N\left[\overline{c_v} + f(x)\frac{(\Delta U)^2}{RT^2} + f'(x)\frac{(\Delta U')^2}{RT^2} + \ldots\right]. \qquad (18.56)$$

An interesting application of this theory is due to McCollum,[1] who investigated the heat capacity of nitrogen tetroxide (N_2O_4). On the one hand, he made calorimetric determinations of C_p at tempertures between 30° and 100° C. On the other hand, he calculated C_p from a formula equivalent to (18.50). The equilibrium in N_2O_4 was treated in section 52: the only reaction in it (8.22) has the coefficients $\nu_1 = 2$, $\nu_2 = -1$, $\nu = 1$. As was shown there, the mol fractions can be expressed in terms of the degree of dissociation ξ as follows: $x_1 = 2\xi/(1 + \xi)$, $x_2 = (1 - \xi)/(1 + \xi)$. Hence we find for the (single) functions $F(x)$ and $f(x)$

$$F(x) = \tfrac{1}{2}\xi(1 - \xi), \qquad f(x) = \xi(1 - \xi)/(1 + \xi)(2 - \xi).$$

McCollum used empirical values of ξ. The excellent correspondence between measurement and calculation which he obtained is shown in Fig. 55.

122. Velocity of sound in gases and gas mixtures. Determinations of the velocity of sound in gases have been often used as a simple and, apparently, accurate method of measuring their specific heats. As was mentioned in section 18, the square of the velocity of sound in a pure gas is supposed to be given by the formula

$$a^2 = \left(\frac{dp}{d\rho}\right)_s = -\frac{v^2}{\mu}\left(\frac{dp}{dv}\right)_s, \qquad (18.57)$$

[1] McCollum, J. Am. Chem. Soc. 49, p. 28, 1927.

ρ being the mass density and μ the molecular weight. If the gas follows the equation $pv = RT$, this expression takes the form (3.40)

$$\left.\begin{aligned} a^2 &= \gamma RT/\mu, \\ \gamma &= \frac{c_p}{c_v} = 1 + \frac{R}{c_v}. \end{aligned}\right\} \tag{18.58}$$

It was pointed out that these relations apply without regard to whether c_p, c_v, γ are constants or functions of temperature.

However, the specific heats c_v measured by the sonic method in oxygen and in air [1] at high temperatures (from 100° to 1000° C) are considerably below those determined by other methods. In a similar way, the sound velocities in NO give the same specific heat at low temperatures as at 0° C,[2] instead of the increase tabulated in Table 41 of section 119. This fact seemed to indicate that the changes of state, produced by the sonic waves, are too rapid to allow the equilibrium of the molecular degrees of freedom to be established. In fact, the dispersion of sound waves in gases (CO_2) had already been observed a few years earlier [3] and was interpreted as a lag in the molecular adjustment.[4] Extensive work on the subject was done by Kneser,[5] who was able to show that it is the vibrational energy which requires periods up to 10^{-2} sec to assume its equilibrium value, while the rotational degrees of freedom respond much more quickly. At low frequencies the ratio γ of the formula (18.58) was experimentally equal to $1 + R/(c_t + c_r + c_{vi})$, at high frequencies, to $1 + R/(c_t + c_r)$.

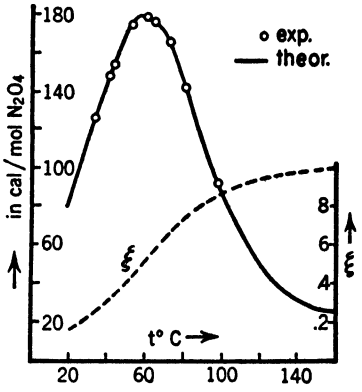

FIG. 55.—Specific heat of nitrogen tetroxide.

These investigations were greatly influenced by a paper of Einstein's [6] which suggested sonic measurements as a method of deter-

[1] W. C. Shillings and J. R. Partington, Phil. Mag. 9, p. 1020, 1930.
[2] Partington and Shillings, Phil. Mag. 45, p. 416, 1923.
[3] G. W. Pierce, Proc. Am. Acad. 60, p. 271, 1925.
[4] K. F. Herzfeld and F. O. Rice, Phys. Rev. 31, p. 691, 1928.
[5] H. O. Kneser, Ann. Physik 11, pp. 761, 778, 1931; 16, p. 337, 1933; H. O. Kneser and V. O. Knudsen, Ann. Physik 21, p. 682, 1935.
[6] A. Einstein, Sitzungsber. Berlin, p. 380, 1920.

mining the rates of reaction in gas mixtures. While this paper was indirectly responsible for the research on dispersion in pure gases, the results of this research defeated its original purpose. The observations in mixtures are too difficult to interpret when possible abnormalities of the components themselves must be taken into account.[1] For this reason, we shall calculate here the velocity of sound in mixtures only for low frequencies when the question of lag does not arise.

The velocity of sound in a gas mixture of the total mass M can be written

$$a^2 = (dp/d\rho)_S = - V^2(dp/dV)_S/M, \tag{18.59}$$

since the mass density is $\rho = M/V$. Let us envisage a mixture of a given initial constitution. If its reacting components are always in equilibrium, the total volume is completely determined by the temperature and pressure. The system is, therefore, simple in the sense of section 2: its entropy differential, $dS = (dU + pdV)/T$, can be regarded as a function of pressure and volume, and the equation of the adiabatic can be written

$$T\,dS = \left(\frac{\partial U}{\partial p}\right)_V dp + \left(\frac{\partial \mathbf{X}}{\partial V}\right)_p dV = 0,$$

since $(\partial \mathbf{X}/\partial V)_p = (\partial U/\partial V)_p + p$, in view of the definition of the heat function $\mathbf{X} = U + pV$. Because of (3.12) and (3.26)

$$\left(\frac{\partial U}{\partial p}\right)_V = C_V\left(\frac{\partial T}{\partial p}\right)_V, \qquad \left(\frac{\partial \mathbf{X}}{\partial V}\right)_p = C_p\left(\frac{\partial T}{\partial V}\right)_p,$$

whence

$$C_V\left(\frac{\partial T}{\partial p}\right)_V dp + C_p\left(\frac{\partial T}{\partial V}\right)_p dV = 0,$$

and

$$\left.\begin{aligned}(dp/dV)_S = - \gamma(\partial p/\partial T)_V/(\partial V/\partial T)_p = \gamma(\partial p/\partial V)_T,\\ \gamma = C_p/C_V.\end{aligned}\right\} \tag{18.60}$$

This equation holds generally for any simple system. When we apply it to a gas mixture, *the heat capacities in the ratio* γ *are*, of course,

[1] C. E. Teeter, J. Chem. Physics 1, p. 251, 1933. This paper contains a good review of the experimental and theoretical work about measuring rates of dissociation in nitrogen tetroxide by the sonic method.

those calculated in the preceding section. From the equation of state, $pV = NRT$,

$$\left.\begin{aligned}\left(\frac{\partial p}{\partial T}\right)_V &= \frac{p}{T}\left[1 + \frac{T}{N}\left(\frac{\partial N}{\partial T}\right)_V\right],\\ \left(\frac{\partial V}{\partial T}\right)_p &= \frac{V}{T}\left[1 + \frac{T}{N}\left(\frac{\partial N}{\partial T}\right)_p\right].\end{aligned}\right\} \tag{18.61}$$

We transform this with the help of the relations (18.43), (18.46), and (18.54), obtaining

$$a^2 = \frac{pV}{M}\gamma\frac{1 + \nu f(x)\dfrac{\Delta U}{RT} + \nu' f'(x)\dfrac{\Delta U'}{RT} + \dots}{1 + \nu F(x)\dfrac{Q}{RT} + \nu' F'(x)\dfrac{Q'}{RT} + \dots}. \tag{18.62}$$

It will be noted that the last factor is much less affected by the heats of reaction than γ: it is linear in Q/RT, etc., while C_V, C_p contain the squares of these large numbers.

Experimental work concerning the velocity of sound has been published by several authors.[1] While the results are not quite consistent in their bearing on the rate of the reaction and the speed with which equilibrium is established, it seems that indications of a lag in reacting gas mixtures are to be found only in the measurements of absorption of sound. There is no convincing proof of the existence of dispersion, and the formula (18.62) appears to represent the observed velocities fairly well. This would mean that chemical equilibrium is, practically, reached after the lapse of only 10^{-4} sec.

123. Solids. Einstein's model of a solid body was described in section 93. It treats the atoms of the solid as harmonic oscillators, all independent and having the same frequency ν. For the energy levels of the three-dimensional harmonic oscillator the quantum theory gives

$$\varepsilon_{n_1 n_2 n_3} = h\nu(n_1 + n_2 + n_3 + \tfrac{3}{2}),$$

where n_1, n_2, n_3 are the quantum numbers of the three degrees of freedom. The sum of states is

$$Y = \sum_{n_1 n_2 n_3} \exp\left[-x(n_1 + n_2 + n_3 + \tfrac{3}{2})\right] = \frac{e^{-\frac{1}{2}x}}{(1 - e^{-x})^3} \tag{18.63}$$

($x = h\nu/k$). The energy and entropy can be derived from it by eqs.

[1] Compare the review in the paper of Teeter's (*loc. cit.*)

(18.06) and (18.09), and are those given in section 93. In particular, the mean energy of the oscillator is, per degree of freedom,

$$\bar{\varepsilon}_\nu = \frac{kTx}{e^x - 1} + \frac{h\nu}{2}. \tag{18.64}$$

As was mentioned before, the agreement of Einstein's formulas with the measured specific heats is not very close. The reason for this discrepancy was pointed out in a later paper [1] of his: the model does not represent the actual conditions accurately enough because, in reality, the atoms of a crystal do not oscillate independently of one another with the same frequency but form a coupled system. The forces of interaction influence the characteristic frequencies so that they all become different and are drawn out into a spectrum. More accurate theories were given from this point of view by Debye[2] and independently by Born and Von Karman.[3] Debye's theory is particularly simple: he assumes that the $3Z$ frequencies of a body containing Z atoms can be calculated as if it were a homogeneous elastic continuum. In other words, these frequencies correspond to the fundamental tone and to the first $3Z - 1$ overtones of its elastic spectrum. The following considerations support this assumption. In the region of high temperatures prevails equipartition and the energy depends only on the number of frequencies (or degrees of freedom) and not on their values. On the other hand, at low temperatures, the high order overtones are not appreciably excited; according to eq. (18.64) their mean energy becomes very small. All depends then on the low order frequencies, and for these the approximation by a continuum is quite adequate because their wave length is large compared with the atomic distances. Therefore, we should expect accurate results both at low and at high temperatures.

The calculations are easily carried through in the case of *isotropic* elementary materials. If we take the solid in the shape of a cube with the edge l,[4] the theory of elasticity gives the following expressions for the frequencies of the standing longitudinal and transverse waves

$$\nu = a_1(n_1^2 + n_2^2 + n_3^2)^{1/2}/2l, \quad \nu = a_2(n_1^2 + n_2^2 + n_3^2)^{1/2}/2l, \tag{18.65}$$

where a_1 and a_2 are the velocities of the longitudinal and transverse wave systems. Every triple of integral numbers n_1, n_2, n_3 determines a state of the body (standing wave) in each of the two wave systems,

[1] A. Einstein, Ann. Physik **35**, p. 679, 1911.
[2] P. Debye, Ann. Physik **39**, p. 789, 1912.
[3] M. Born and Th. Von Karman, Phys. Zs. **13**, p. 297, 1912; **14**, pp. 15, 65, 1913.
[4] R. Ortvay, Ann. Physik **42**, p. 745, 1913.

the corresponding frequencies being given by eqs. (18.65). It is easy to see that the number of all longitudinal states with frequencies smaller than a given value ν is

$$Z_1(\nu) = \frac{4\pi V}{3a_1^3}\nu^3, \tag{18.66}$$

where $V = l^3$ is the volume of the cube. In the transverse system the number must be doubled: every transverse wave has two degrees of freedom because of the two possible states of polarization

$$Z_2(\nu) = \frac{8\pi V}{3a_2^3}\nu^3. \tag{18.67}$$

Exercise 105. If we imagine the numbers n_1, n_2, n_3 plotted in three orthogonal directions, their integral values will represent a cubic lattice. The number $Z_1(\nu)$ is the number of lattice points within the surface given by the first eq. (18.65). Show that the expression (18.66) holds when l is very large. n_1, n_2, n_3 are positive.

If the solid were really a continuum, there would be no upper limit to its characteristic frequencies. But it has, actually, atomic structure, and the total number of its possible states must be equal to the number of its degrees of freedom, namely $3Z$. Debye, therefore, makes the assumption that the elastic spectrum is cut off at an upper limit ν_0 determined by the condition

$$Z_1(\nu_0) + Z_2(\nu_0) = 3Z.$$

Substituting (18.66) and (18.67) we find

$$4\pi V\left(\frac{1}{a_1^3} + \frac{2}{a_2^3}\right) = \frac{9Z}{\nu_0^3}.$$

The number of characteristic states in the frequency interval from ν to $\nu + d\nu$ is

$$dZ_1(\nu) + dZ_2(\nu) = \frac{9Z}{\nu_0^3}\nu^2 d\nu.$$

Each of these states is a harmonic oscillation whose mean energy is given in the quantum theory by the expression (18.64). The contribution of the frequency interval $d\nu$ to the internal energy is, therefore, $9\mathfrak{E}_\nu Z\nu^2 d\nu/\nu_0^3$. The total internal energy is obtained by integrating this expression from 0 to ν_0 and is, per mol,

$$u = \frac{9Rh}{\nu_0^3 k}\int_0^{\nu=\nu_0} \frac{\nu^3 d\nu}{e^\alpha - 1} + u_0. \tag{18.68}$$

The specific heat results from differentiation with respect to T (contained in x). If we introduce the abbreviation $h\nu_0/k = \Theta$,

$$c = 9R\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^4 e^x dx}{(e^x-1)^2} \tag{18.69}$$

This formula shares with Einstein's (18.64) the property that the individual characteristics of the substance are all contained in the single constant Θ, the *characteristic temperature.* If we plot c against T/Θ (the reduced temperature) we obtain for all bodies one and the same universal curve. In the limiting case of very low temperatures ($T/\Theta \ll 1$) the integral can be regarded as constant and equal to $4\pi^4/15$. The formula becomes then

$$c = \frac{12\pi^4}{5} R\left(\frac{T}{\Theta}\right)^3 = 462.2\left(\frac{T}{\Theta}\right)^3 \frac{\text{cal}}{\text{deg}} = 1.934 \times 10^{10}\left(\frac{T}{\Theta}\right)^3 \frac{\text{erg}}{\text{deg}}. \tag{18.70}$$

The agreement with experiments can be judged from Fig. 56 [1] giving the measured c_v. The value of Θ for each substance is here

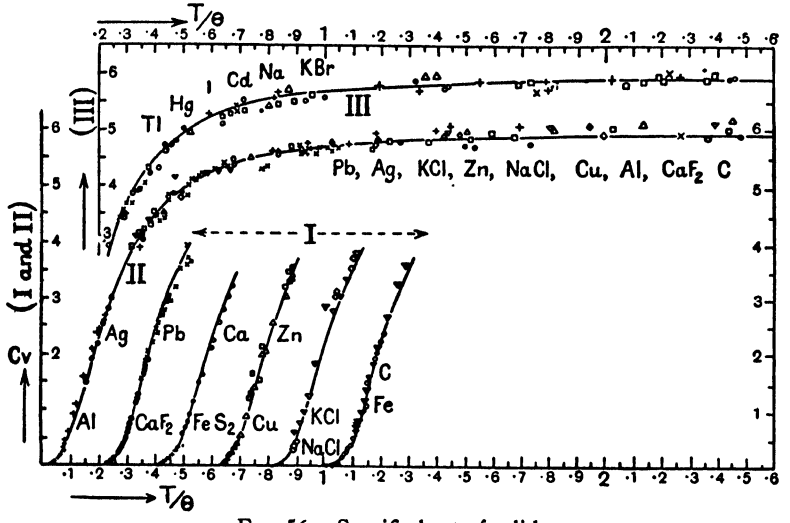

FIG. 56.—Specific heat of solids.

chosen so as to give the best fit for that substance with the continuous curve representing eq. (18.69). Curve II is in the normal position; the others are displaced because the experimental material was too large to be accommodated in a single curve. The key to the substances is contained in Table 46.

[1] Taken from E. Schrödinger, Phys. Zs. 20, pp. 420, 450, 474, 497, 523, 1919.

TABLE 46

KEY TO FIG. 56

Substance	Chemical symbol	Temperature range	Θ	Points in Fig.		
				I	II	III
Lead	Pb	14–573	88	×	×	
Thallium	Tl	23–301	96			○
Mercury	Hg	31–232	97			□
Iodine	I	22–298	106			×
Cadmium	Cd	50–380	129–160			+
Sodium	Na	50–240*	159			△
Potassium bromide	KBr	79–417	177			●
Silver	Ag	35–873	215		●	
Platinum	Pt	.....	225			
Calcium	Ca	22–62	230	○		
Sylvine	KCl	23–550	217.6	▽	▽	
Zinc	Zn	33–673	235	□	□	
Rocksalt	NaCl	25–664	287	◇	◇	
Copper	Cu	14–773*	315	△	△	
Aluminum	Al	19–773	392		+	
Iron	Fe	32–95 *	454	○		
Fluorspar	CaF_2	17–328	499	○	○	
Iron pyrites	FeS_2	22–57 *	645	+		
Diamond	C	30–1169	1860–2230	▼	▼	

* Rises above the curve after these temperatures.

The formula (18.69) was derived on the assumption that the substance is isotropic and elementary. Within this scope, it represents the facts on the whole very well although a few exceptions are known. But Fig. 56 shows that it applies, in some measure, also to substances of a more complicated structure, presumably because they do not deviate greatly from isotropy.

The approach of Born and Von Karman permits to treat the more general cases, at least, by approximation. If the substance is an element in an anisotropic system of crystallization, the elastic waves propagate in it with three different velocities and form three sets of overtones. Born [1] finds that the specific heat is then the arithmetical mean of three terms of the Debye type (18.69), each with a different characteristic temperature. If the substance is a chemical compound containing r different kinds of atoms, there still exist, in addition to the spectrum of overtones, $r - 1$ characteristic frequencies represent-

[1] M. Born, Dynamik der Krystallgitter, 1915.

ing the oscillations of these atoms with respect to one another. The molal heat is, therefore, expressed by three Debye terms and $r - 1$ terms of the Einstein type (13.25). Unfortunately, these expressions are so unwieldy that their comparison with experimental results is difficult.

The *third power law* at very low temperatures remains valid also in the general case because the Debye terms satisfy it and the Einstein terms become negligible. While a great many substances fulfill the third power law down to the very lowest attainable temperatures,[1] other metallic and non-metallic solids show marked deviations in the region of the temperature of liquid hydrogen and below. The measured specific heats lie, in this case, above those predicted by Debye's formula. It was suggested that in metallic substances the discrepancy may be due to the specific heats of the free conduction electrons (compare sections 102 and 111). In fact, in the case of silver the influence of the free electrons seems well authenticated by recent measurements in the laboratory of Leiden.[2] In Fig. 57 is plotted the difference between the measured c and the value predicted by the third power law (18.70). It shows both the linear dependence required by the Sommerfeld formula for free electrons (17.34) and the correct absolute value on the assumption that there is one electron to every atom of silver.

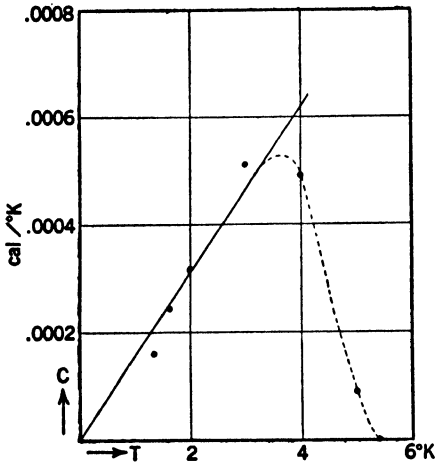

FIG. 57.—Electronic specific heat in silver.

The only other (non-supraconductive) metal investigated in the same temperature region is zinc, and here the free electrons do not give a sufficient explanation of the trend of specific heats. Even after correcting for them, there remains a hump-like residual curve with a maximum at 4° abs., not unlike in its shape to that of Fig. 54. Indeed, it was suggested that they are due to the same cause, doubling of the lowest quantum level of the zinc atom. However, the relation

[1] Compare in this connection, the work of Simon and collaborators (Ann. Physik 68, p. 241, 1922; Zs. phys. Chemie 123, p. 383, 1926; Zs. Physik 38, p. 227, 1926).

[2] W. H. Keesom and J. A. Kok, Physica 1, p. 770, 1934.

of the position of the hump and its height is such that only a small fraction of the zinc atoms could possess the double level, a circumstance which makes the explanation doubtful. There are some solids (such as gadolinium sulfate,[1] samarium sulfate,[2] orthohydrogen [3]), in which the doubling or tripling of the atomic and molecular levels gives a complete explanation of the anomalies of specific heats according to (18.18) or to similar formulas. We reproduce here the very instructive curve measured by Giauque and McDougall in gadolinium sulfate (Fig. 58).

In other cases (e.g. tin and silicon [4]) there were observed humps in the curves of specific heats lying at somewhat higher temperatures whose detailed explanation is still lacking. Simon suggested that they may be due to a doubling of the energy levels according to the formula (18.18). It should be mentioned, however, that electrons which are not completely free and cannot cause electric conduction may nevertheless contribute to the specific heats, sometimes even in a larger measure than the free electrons. At extremely low temperatures the specific heat due to them is proportional to T, in non-magnetic materials, and to $T^{3/2}$, in ferromagnetic ones.[5] At somewhat higher temperature this cause, being essentially a multiplet action (compare section 117), should produce a hump similar to that of formula (18.18).

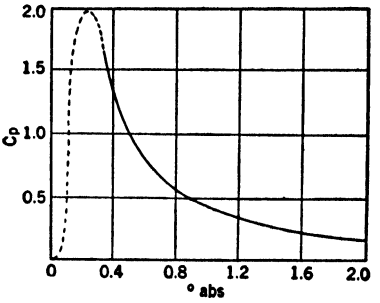

FIG. 58.—Anomaly of specific heat in gadolinium sulfate.

Recent work by Jaeger and co-workers (on metals at high temperatures) drives it home that our theoretical knowledge of specific heats is still incomplete. Measuring very accurately,[6] they found that c_p is *structure sensitive* and varies appreciably with the mechanical treatment of the specimens. Another series of investigations [7] was devoted to testing Neumann's law (section 16) with the result that it was found satisfied, within the experimental accuracy of 1%, in mixed crystals

[1] Giauque and McDougall, Phys. Rev. **44**, p. 235, 1933.

[2] Ahlberg and Freed, Phys. Rev. **39**, p. 540, 1932.

[3] Mendelssohn, Ruhemann, and Simon, Zs. phys. Chem. (B) **15**, p. 121, 1931.

[4] F. Simon, Sitzungsber. Berlin, p. 477, 1926.

[5] F. Bloch, Zs. Physik **52**, p. 555, 1928; Leipziger Vorträge, p. 67, 1930; P. S. Epstein, Phys. Rev. **41**, p. 91, 1932.

[6] Jaeger, Rosenbohm, and Bottema, Proc. Amsterdam **35**, pp. 763, 772, 1932.

[7] Bottema and Jaeger, ibidem, **35**, pp. 352, 916, 929, 1932.

(Ag-Au). On the other hand, in homopolar intermetallic compounds (AuSn, PtSn) there were found appreciable deviations from Neumann's law which, moreover, increased with rising temperature (between 0° and 200° C).

124. Liquids. The liquid state of matter is the most complicated and has not yet been made amenable to theoretical treatment. There exists a number of elements and compounds having in the liquid state approximately the same molal heats which are characteristic of solids, according to the laws of Dulong and Petit and of Neumann (section 16), namely, about 6 cal/mol per atom (Table 47).

TABLE 47

SPECIFIC HEATS OF LIQUIDS

Liquid	c	n	c/n	Liquid	c	n	c/n
Hg	6.7	1	6.7	H_2O	18	3	6.0
N_2	13.2	2	6.6	S_2Cl_2	22.4	4	5.6
O_2	12.8	2	6.4	$SiCl_4$	34.4	5	6.9
AgBr	14.0	2	7.0	$TiCl_4$	36.8	5	7.4
TlCl	13.6	2	6.8				

This would indicate that the conditions are similar to those in solids in that one must take into account both the kinetic and the potential energy of the atoms. However, many liquids have atomic heats much larger than 6 cal.

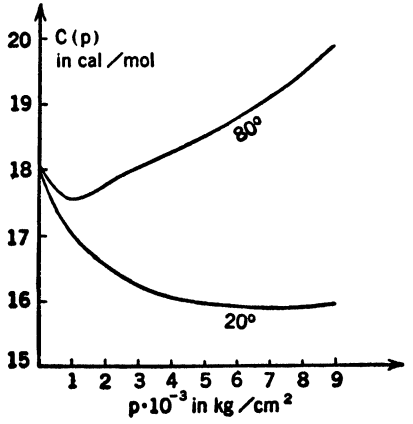

FIG. 59.—Specific heat of water as a function of pressure.

Because of its practical importance, much attention was devoted to the specific heat of water. Of particular interest is the dependence of c_p on pressure represented graphically in Fig. 59. These curves were not determined by direct measurement but inferred from the thermal expansion at different pressures[1] by means of the relation p (4.59), or $c_p = \int T(\partial^2 v/\partial T^2)_p \, dp$. We shall see that these data have an important bearing on the question of specific heats of aqueous solutions.

[1] Bridgman, Proc. Am. Acad. 48, p. 309, 1913; F. Zwicky, Phys. Zs. 27, p. 271, 1926.

As was shown by Zwicky, the specific heats of non-electrolytic solvents in water are additive: i.e. the total heat capacity of the solution can be expressed by the formula

$$C_p = N_0 c_{p0} + N_1 c_{p1} \tag{18.71}$$

where $c_{p0} = 18.01$ is the molal heat of water (at 15° C) and c_{p1} of the solute. It is interesting to note that the values of c_{p1} observed in the solution are pretty close to those observed in the solid state of the solute, as appears from Table 48.

TABLE 48

SPECIFIC HEATS OF SOLUTES

Substance	Dextrose $C_6H_{12}O_6$	Lactose $C_{12}H_{22}O_{11}$	Urea OCN_2H_4	Glycerin $C_3H_8O_3$	Tartaric acid $C_4H_6O_6$
c_{p1} from eq. (18.71)..	55.2	104.5	24.8	56.0	67
c_{p1} in solid state.....	51.7	98.5	19.3	53.0	62

When we turn to aqueous solutions of electrolytes, we meet with the unexpected fact that the heat capacity is not increased but *lowered by the solutes*. A qualitative explanation of this behavior was given by Tammann,[1] who pointed out that the effect is analogous to a rise of pressure to about 500 atm: the electrolyte must increase, in some way, the pressure under which the particles of water stand. Accurate modern measurements in solutions of alkali chlorides[2] showed that at low molalities (up to $m = 0.5$) the heat capacity is still well represented by the linear formula (18.71). However, the coefficients c_{p1} *here take negative values* of the order -40.

Taking up Tammann's suggestion, Zwicky (*loc. cit.*) developed it into a detailed theory. The field of the ions exercises large ponderomotive forces on the electric dipoles of the water molecules which actually produce a strong compression of the aqueous medium in their vicinity. Each ion is, therefore, surrounded by a little sphere within which the specific heat of the water is reduced by pressure. As long as the concentration is low, the spheres do not overlap and the reduction of the heat capacity is proportional to their number, i.e. to the molality. Hence the validity of the linear expression (18.71). The quantitative calculation of this effect gave the right order of magnitude.

[1] G. Tammann, Innere Kräfte und Eigenschaften der Lösungen, 1907.

[2] Richards and Rowe, J. Am. Chem. Soc. **43**, p. 770, 1921; **44**, p. 684, 1922.

CHAPTER XIX

EQUILIBRIUM INVOLVING RADIATION

125. Equivalence of mass and energy. We devoted Chapters XIII to XV to questions pertaining to the determination of the absolute value of the entropy S. It should not be forgotten, however, that there is another fundamental function, the internal energy U, whose absolute value is also indeterminate. As far as the first and second laws are concerned, S and U are on the same footing since only the differentials of these two functions are defined in thermodynamics (compare sections 13 and 22). Both contain, therefore, additive integration constants. That the indeterminacy of the energy constant was much less emphasized was due to historical and practical reasons. It was taken as a matter of course, because the thermochemical methods of measuring the differences of these constants in a reaction had already been developed before thermodynamics was established as a separate science.

It became possible to determine the absolute value of the energy after Einstein [1] had established the law of proportionality of mass and energy as an important result of his theory of relativity. The fact that the inertial mass of a particle depends on its kinetic energy was not an exclusive feature of relativity but was proved long before its advent. But only the theory of relativity gave a sharp definition of the concepts here involved, and abolished the difference between inertial and gravitational masses. Let M be the mass of a system, E its total energy, and c the velocity of light. Einstein's law is then expressed by the simple relation

$$E = Mc^2. \tag{19.01}$$

If we consider 1 mol of a substance at the temperature $T = 0$, its internal energy will be u_0, while its mass will be equal to its molecular (or atomic) weight μ. Einstein's law gives, therefore,

$$u_0 = \mu c^2. \tag{19.02}$$

[1] A. Einstein, Ann. Physik 18, p. 639, 1905.

Strictly speaking, the mass depends on the temperature since the energy changes with it. To be exact we should have specified that μ is the molecular weight at $T = 0$. Chemistry proper deals with differences Δu_0 (for instance in dissociation of molecules) so small that the attendant change of mass $\Delta\mu = \Delta u_0/c^2$ cannot be detected by the finest measurements. In this chapter, however, we shall treat processes in which an appreciable part of the energy of the reacting substances is converted into radiation. To the same extent their mass will undergo a loss: conservation of energy and conservation of mass hold only for matter and radiation together and not for the material part of the system separately. Compared with the huge changes of mass involved in these processes the difference between μ at $T = 0$ and $T = 300°$ abs is irrelevant and we shall understand under the symbol μ the molecular weight as tabulated by international agreement.

As an example we write out the explicit expression for the thermodynamic potential of a monatomic perfect gas

$$\varphi = RT(\log p - \tfrac{5}{2}\log T - j) + \mu c^2. \tag{19.03}$$

For some applications it will be more convenient to express the pressure in terms of z (the number of molecules or atoms per unit volume) by the relation (1.15), $p = zkT$,

$$\varphi = RT(\log z - \tfrac{3}{2}\log T - j + \log k) + \mu c.^2 \tag{19.04}$$

126. Energy and entropy of black radiation. The theory of radiation is so extensive a subject that it is best treated in separate books,[1] and it is not advisable to discuss it at length in a textbook devoted to thermodynamics. We limit ourselves to a brief review of some of its concepts and laws which shall be needed in the remaining part of this chapter.

Let us consider a closed system part of which is free of matter (vacuum) and filled only with radiation, while matter is present in other parts. Left to itself such a system reaches a state of equilibrium in which the temperature T is uniform throughout and the radiation in the evacuated part has quite definite properties. It is called *black radiation*, and its spectral composition is given by a universal law, independent of the nature of the material part of the system in equilibrium with it: the energy density $u_\nu d\nu$ (i.e. energy per unit volume) belonging to the interval of frequencies between ν and $\nu + d\nu$ is a universal function of ν and T only

$$u_\nu d\nu = F(\nu,T)d\nu. \tag{19.05}$$

[1] For instance, M. Planck, The Theory of Heat Radiation, 1914.

This implies, of course, that the total energy density

$$u = \int_0^\infty u_\nu d\nu = \int_0^\infty F(\nu,T)d\nu = u(T) \tag{19.06}$$

is a function of the temperature alone.

If black radiation is enclosed in an evacuated container, it exerts a pressure p on its walls and through it resists compression. Assuming the walls to be movable, the radiation does the work $p\,dV$ when the volume is increased by dV (compare section 7). If an element of heat dQ is imparted to the radiation, the first law of thermodynamics requires that it be converted, in part, into an increase of its energy U, in part, into work done by it

$$dQ = dU + p\,dV.$$

The second law can be also applied to radiation and includes the familiar expression (4.07) for the entropy differential

$$dS = (dU + p\,dV)/T. \tag{19.07}$$

In particular, when the volume of the system remains constant ($V = \text{const}$, $dV = 0$) the increment of the entropy is

$$dS = dU/T. \tag{19.08}$$

The same results hold, of course, if the vessel is not quite evacuated but contains, in addition to the radiation, gases in equilibrium with it, of so low a density that their refraction is negligible, so that the propagation of light is appreciably the same as in vacuo. This is the case we shall consider in the following sections. The restriction to low densities, though not absolutely necessary, greatly simplifies matters and saves lengthy discussions.

The general relation (19.08) which contains practically no restricting assumptions about the function U is all we shall need. As far as our applications are concerned, the rest of this section has a purely academic interest. The quantum theory of radiation leads, in its present form, to the result that empty space contains a certain constant energy density u_0 even at $T = 0$. It is usually thought that this is merely a formal defect and that this *zero point energy* (which is, by the way, infinite) has no physical reality. There were, however, those who argued that a part of it may have physical significance, that it may influence the absolute entropy constant of the radiation and through it the equilibrium with matter. We shall see in the next section that *the conditions of equilibrium are independent of the*

absolute entropy of radiation. Nevertheless the question how it is affected by u_0 is worth looking into. We shall write, therefore, for the energy density, $u + u_0$, meaning by u that part which is due to temperature radiation. The total radiation is then $U = (u + u_0)V$; as to pressure, it is known to be $p = u/3$, since it is certain from empirical and theoretical considerations that the zero point energy does not contribute to it. The entropy differential (19.08) takes the form

$$dS = \frac{V}{T}\frac{du}{dT}dT + \left(\frac{4}{3}u + u_0\right)\frac{dV}{T}. \tag{19.09}$$

The reciprocity relation (2.10) is easily integrated and gives

$$u = aT^4 - \tfrac{3}{4}u_0, \tag{19.10}$$

a being a constant. We see that the inclusion of a constant term u_0 (not exerting pressure) into the energy density leads to a contradiction. The result gives for $p = \frac{1}{3}u = \frac{1}{3}aT^4 - \frac{1}{4}u_0$, so that u_0 does, after all, produce a negative pressure. It follows that the zero point energy, whether it is in other ways real or not, must be left out in computing the entropy. We arrive thus at the usual form of the Stefan-Boltzmann law

$$u = aT^4, \tag{19.11}$$

and substituting this into (19.09)

$$S = \tfrac{4}{3}aT^3V + S_0.$$

S_0 is an integration constant and as such must be independent of V and T. It is obvious that it cannot be anything but $S_0 = 0$, otherwise we would have still a finite entropy when the volume is reduced to zero, i.e. when we have no system. The entropy density is, therefore,

$$s = \frac{S}{V} = \frac{4}{3}aT^3. \tag{19.12}$$

Comparing this with (19.11), we verify

$$ds = du/T. \tag{19.13}$$

This equation is compatible with the following interpretation forming an important part of the theory of black radiation. The entropy density s is considered as the sum of the densities $s_\nu d\nu$ belonging to the different frequency intervals

$$s = \int_0^\infty s_\nu d\nu,$$

where s_ν is defined by

$$ds_\nu = du_\nu/T. \tag{19.14}$$

In fact, the integration of this relation with respect to $d\nu$ (at constant T) gives eq. (19.13). The relation shows that the frequency intervals of the radiation can be regarded as statistically independent systems in equilibrium with one another at the temperature T (compare section 22). In the particular case of constant volume ($dV = 0$), we can write

$$\frac{dU_\nu}{dS_\nu} = \frac{dU}{dS} = \frac{1}{T}, \tag{19.15}$$

if we denote $U_\nu = Vu_\nu$, $S_\nu = Vs_\nu$.

127. General conditions of equilibrium. Let us envisage a system enclosed by rigid, perfectly reflecting, adiabatic walls and consisting of a sufficiently thin mixture of perfect gases (compare preceding section) and radiation. Let $N_1, N_2, \ldots N_\beta$ be the mol numbers of the gases; the total energy and total entropy of the system are then

$$U = \sum_{l=1}^{\beta} N_l u_l + U_R, \quad S = \sum_{l=1}^{\beta} N_l s_l + S_R,$$

if U_R, S_R stand for the energy and entropy of the radiation. The total volume of the system is expressed in terms of the molal volume v_l of each gas as

$$V = N_l v_l.$$

The conditions of equilibrium (compare section 31) are given by S having its maximum while U and V stay constant, in view of our assumptions about the walls. In variational form they are

$$\delta S = \delta U = \delta V = 0,$$

or

$$\sum_{l=1}^{\beta} (N_l \delta u_l + u_l \delta N_l) + \delta U_R = 0, \tag{19.16}$$

$$\sum_{l=1}^{\beta} (N_l \delta s_l + s_l \delta N_l) + \delta S_R = 0, \tag{19.17}$$

$$N_l \delta v_l + v_l \delta N_l = 0, \quad (l = 1, 2, \ldots \beta) \tag{19.18}$$

We can regard the first equation as the main condition, the others as subsidiary ones. The difference between this system and that of section 40 lies only in the presence of radiational terms. Apart from

this, the procedure is exactly the same as in treating the ordinary gas mixture. We first eliminate the variations of the internal energies by means of (4.15) and (19.13)

$$\delta u_l = T_l \delta s_l - p_l \delta v_l, \quad \delta U_R = T_R \delta S_R,$$

whence (19.16) takes the form

$$\sum_l (N_l T_l \delta s_l - N_l p_l \delta v_l + u_l \delta N_l) + T_R \delta S_R = 0. \tag{19.19}$$

Now we apply the method of Lagrangean multipliers (section 38): we multiply the first subsidiary condition (19.17) by λ_0 and the others (19.18) by λ_l, $(l = 1, 2, \ldots \beta)$, and add them to the main condition (19.19)

$$\sum_l \{N_l(T_l + \lambda_0)\delta s_l + N_l(-p_l + \lambda_l)\delta v_l + (u_l + \lambda_0 s_l + \lambda_l v_l)\delta N_l\} + (T_R + \lambda_0)\delta S_R = 0. \tag{19.20}$$

As was explained in section 38, the variations δs_l, δS_R, δv_l can now be considered as independent, whence their coefficients must vanish

$$-\lambda_0 = T_l = T_R = T$$

(i.e. the temperature is uniform) and

$$\lambda_l = p_l.$$

The last equation supplies only the physical interpretation of the multipliers λ_l. Recalling the definition (5.33) of the molal thermodynamic potential $\overline{\varphi}_l = u_l - Ts_l + p_l v_l$,[1] we can write what remains of (19.20) in the form

$$\sum_{l=1}^{\beta} \overline{\varphi}_l \delta N_l = 0,$$

which is identical with (6.41) derived without considering radiation. If the reaction taking place in the mixture is expressed by the equation

$$\nu_1 G_1 + \nu_2 G_2 + \ldots + \nu_\beta G_\beta = 0, \tag{19.21}$$

the condition of equilibrium is

$$\sum_{l=1}^{\beta} \nu_l \overline{\varphi}_l = 0. \tag{19.22}$$

[1] As in (8.08) we use the notation $\overline{\varphi}_l$ (and not φ_l) to indicate that this function is calculated as if the other gases were not present, i.e. in terms of the *partial* pressure.

Though formally identical with (6.49), these conditions have a wider scope of applications. In deriving them we explicitly admitted that the energy and mass of the material part of the system need not remain constant but may be converted, wholly or in part, into radiation. We are, therefore, free to apply them also to such reactions (19.21) in which substances disappear altogether under emission of radiation (*annihilation of matter*) or in which one kind of atoms disappears and another is created (*permutation of elements*). We may also mention that, because of eq. (19.15), we would have obtained the same result writing in (19.16), (19.17), δU_ν, δS_ν instead of δU_R, δS_R, where ν is the frequency of the photons emitted in the reaction. In other words, the reacting substances set themselves in direct equilibrium with the frequency interval corresponding to their emission and through it, indirectly, with the rest of the radiation.

Using the expression (19.04) for the thermodynamic potential of monatomic gases, we obtain from (19.22)

$$\sum_i \nu_i \log z_i = \log I + \tfrac{3}{2}\,\nu \log T - \Delta\mu \cdot c^2/RT, \tag{19.23}$$

where $\nu = \nu_1 + \nu_2 + \ldots + \nu_\beta$; the change of mass in the reaction is

$$\Delta\mu = \sum_i \nu_i \mu_i,$$

and

$$\log I = \sum_i \nu_i j_i - \nu \log k. \tag{19.24}$$

According to section 120, the chemical constant of a monatomic gas is $j_{10} = 4.417 + \frac{3}{2}\log_{10}\mu + \log g$, where g must include also the nuclear statistical weight, and $\log_{10} k = -15.8630$. Therefore,

$$\left.\begin{aligned} \sum_i \nu_i \log z_i &= \log K_s, \\ \log_{10} K_s &= 20.280\nu + \sum_i \nu_i \left(\tfrac{3}{2}\log_{10}\mu_i + \log_{10} g_i\right) \\ &\quad + \tfrac{3}{2}\nu \log_{10} T - \frac{4.695 \times 10^{12}\Delta\mu}{T}. \end{aligned}\right\} \tag{19.25}$$

128. Negative and positive electrons. Equilibrium of matter and radiation as a problem of thermodynamics was first treated by O. Stern.[1] He envisaged a state of affairs in which atoms disappear, being converted into radiant energy, and others suddenly appear in the field of radiation, absorbing the amount of energy equivalent to

[1] O. Stern, Zs. Elektrochemie 31, p. 448, 1925.

their mass. As science progressed processes of this sort were regarded as less and less speculative. With the discovery of the positive electron (positron) by C. D. Anderson [1] the creation and annihilation of electron pairs became an established fact. The tracks of the two electrons (one positive, one negative) produced by a cosmic ray or γ-ray can be observed in the Wilson chamber. There is also direct evidence that they recombine, emitting their whole energy in the form of two photons.

If we characterize the electron and positron by the subscripts e and p, eq. (19.21) of the reaction becomes

$$G_e + G_p = 0, \tag{19.26}$$

whence $\nu_e = \nu_p = 1$, $\nu = 2$, and [2]

$$z_p z_e = K. \tag{19.27}$$

For the electron of either sign $\frac{3}{2} \log \mu + \log g = -4.59$ (compare section 113), $\Delta\mu = 2\mu = 1.096 \times 10^{-3}$

$$\log_{10} K = 31.38 + 3 \log_{10} T - \frac{5.146 \times 10^9}{T}. \tag{19.28}$$

In the empty space, in the absence of all other types of matter, positive and negative electrons would exist in equal numbers, $z_p = z_e$, so that the density of positive electrons would be

$$z_p = K^{1/2}. \tag{19.29}$$

This number is exceedingly small at ordinary temperatures and becomes appreciable only when the temperature approaches 10^8 degrees. In fact, for $T = 8 \times 10^7$ deg, we find $z_p = 2.5 \times 10^{-5}$ cm^{-3}, or 1 positron per 40000 cm^3. From then on the rise is rapid: for $T = 2 \times 10^8$, we already have $z_p = 1.9 \times 10^{15}$ cm^{-3}.

Of course, temperatures of this order do not prevail in interstellar space. The only place where they may possibly exist is the interior of stars. Here the conditions are different from those in empty space, in that there is a large excess of free negative electrons, which depress the density of the positrons in the way explained in section 53. Let us denote by z_0 the density of the free electrons which are in the star from the start, being stripped by ionization off the atoms of the stellar material. In addition to this, there are the positive-negative pairs

[1] C. D. Anderson, Science **76**, p. 238, 1932.

[2] Since there is no danger of misapprehension, we drop the subscript s of K in the remainder of this chapter.

created by the reaction (19.26). The strong electric attraction will assure that the stellar matter remain electrically neutral. If the density of positrons is z_p, the total density of negatives will be $z_e = z_p + z_0$, the excess negative charge being neutralized by the atomic ions. Equation (19.27) gives, therefore,

$$z_p(z_p + z_0) = K,$$

or

$$z_p = [(K + z_0^2/4)^{1/2} - z_0/2]. \tag{19.30}$$

To fix our ideas, let us assume $z_0 = 5 \times 10^{21}$ cm^{-3}, which is, presumably, of the right order of magnitude for stars of the G and K types. Table 49 gives the density of positrons z_p for a large range of temperatures which may or may not exist in the stars. The last column lists the heat function stored up in the pairs per 1 cm^3. From about 5×10^8 degrees on, z_p and χ become independent of z_0 and would be the same for all values of this density smaller than 5×20^{21}. At the same time the kinetic energy of the electrons becomes more important than the intrinsic.

TABLE 49

EQUILIBRIUM OF NEGATIVE AND POSITIVE ELECTRONS

T	K	z_p	$\chi\left(\frac{\text{cal}}{\text{cm}^3}\right)$
8×10^7	6.0×10^{-10}	1.2×10^{-31}	4.5×10^{-45}
9	1.2×10^{-2}	2.4×10^{-24}	9.3×10^{-38}
1×10^8	8.5×10^3	1.7×10^{-18}	6.1×10^{-32}
2	9.1×10^{29}	1.8×10^8	7.3×10^{-6}
3	5.0×10^{38}	1.0×10^{17}	4.2×10^3
5	6.2×10^{46}	7.9×10^{22}	3.5×10^9
1×10^9	1.7×10^{53}	4.1×10^{26}	2.2×10^{13}
1×10^{10}	7.4×10^{60}	2.7×10^{30}	5.5×10^{17}

At first sight, one is inclined to doubt if the assumption made in section 127 is fulfilled, namely, if the index of refraction of the radiation is approximately 1 in matter as dense as that. However, a check shows that such is indeed the case because the wave length which must be here considered is that emitted in the reaction, and it is extremely short (1.2×10^{-10} cm) even at low temperatures.

129. Neutrons and protons. The neutron has a mass slightly larger than the proton. There is, therefore, the possibility of its being

converted into a proton under ejection of a negative electron and perhaps of a quantum of radiation. In fact, there is much reason to believe than an intranuclear process of this type plays a role in the emission of radioactive β-rays. Equation (19.21) takes here the form

$$G_n - G_{H+} - G_e = 0,$$

whence $\nu_n = 1$, $\nu_{H+} = \nu_e = -1$, $\nu = -1$ if we characterize the neutron and proton by the subscripts n and H^+. The equation of equilibrium (19.23) is then

$$z_n/z_{H+} = z_e K.$$

The atomic weights of the neutron and proton are[1] $\mu_n = 1.0090$, $\mu_{H+} = 1.0076$, $\Delta\mu = 0.0009$, the (nuclear) statistical weights $g_n = g_{H+} = 2$, whence

$$\log_{10} K = -15.688 - \frac{3}{2}\log_{10} T - \frac{4.2 \times 10^9}{T}. \qquad (19.31)$$

The process of dissociation is here exothermic, and, therefore, the conditions are peculiarly inverted. The presence of excess electrons does not depress the degree of dissociation but favors it. The equilibrium constant does not rise monotonically with temperature but only rises to a maximum (at $T = 6.5 \times 10^9$) and then drops again. This maximum value of K is equal to

$$K = 7 \times 10^{-32}.$$

Of course, the last decimal figure in the atomic weights μ_n and μ_{H+} is not quite certain and the heat of reaction is affected with a considerable probable error. But even if $\Delta\mu$ were only half as large (0.00045) the maximum value of K would be but little increased, namely $K = 2 \times 10^{-30}$. As the density of electrons z_e in ordinary stars (not white dwarfs) is only of the order of magnitude 10^{21} (referred to in the preceding section), we conclude that the ratio of free neutrons to protons in them must be negligible.

This conclusion would not be safe with respect to white dwarfs. The density in them is so enormously high that the electrons may form a completely degenerate gas even at temperatures as high as 10^8 degrees. The thermodynamic potential of these electrons is then (17.35), $\varphi_e = f\Omega_i + \mu_e c^2$, and the equation of equilibrium, $\varphi_n - \varphi_{H+} - \varphi_e = 0$, gives simply

$$\log_{10}\frac{z_n}{z_{H+}} = -\frac{4.2 \times 10^9}{T}, \qquad (19.32)$$

[1] Bonner and Brubaker, Phys. Rev. 50, p. 308, 1936.

since $f\Omega_i$ is negligible compared with $\Delta\mu$. The molal volume of the electrons in the white dwarfs may be as low as $v = 3 \times 10^{-5}$ cm^3, whence, by the formula (17.29), $\Theta = 0.7 \times 10^{-8}\, T$. Therefore, the electrons may be regarded as degenerate at temperatures of the order 10^8 but not of the order 10^9. In other words, the temperature within the white dwarfs hardly rises higher than 10^9 degrees. We are, therefore, justified in concluding that free neutrons do not play any important role in stars, including the white dwarfs.

130. Hydrogen and deuterium. As early as 1815 the English chemist, William Prout, formulated the hypothesis that the atoms of heavier elements are formed by the association of hydrogen atoms. This view is confirmed by modern science and found its expression in the very name "proton," which is derived from the Greek "$\pi\rho\tilde{\omega}\tau os$" meaning " first " or " primary". A scientific theory of nuclear structure became possible after the discovery of the neutron: every nucleus is supposed to consist of neutrons and protons.[1] There is a considerable body of experimental facts to support this theory. In the so-called experiments on permutation of matter it is observed how fast-moving particles knock protons and neutrons from or into atoms, converting them into other elements. Inasmuch as a neutron can be formed by the association of a proton and an electron (preceding section), we can also say that any nucleus may be produced out of a suitable number of protons and electrons, although the electrons do not retain in it their individuality but merge with the protons, forming neutrons.

The simplest examples of the building up of heavier elements is the *formation of deuterium and helium*, which we shall discuss in this and the next section. There is direct experimental evidence for these processes. When a fast-moving deuteron hits a target, phenomena are observed which offer evidence of its being split sometimes into a proton and a neutron. On the other hand, we have seen in the preceding section that a neutron dissociates into a proton and an electron. It must be possible, therefore, for two protons and one electron to unite, forming a deuteron

$$2G_{H+} + G_e - G_{D+} = 0,$$

$\nu_{H+} = 2$, $\nu_e = -\nu_{D+} = 1$, $\nu = 2$ and

$$z_{H+} = (Kz_{D+}/z_e)^{1/3}.$$

[1] W. Heisenberg, Zs. Phys. 77, p. 1932; 78, p. 156, 1933.

The atomic weight of the deuteron [1] is $\mu_{D+} = 2.0142$, the statistical weight [2] is $g_{D+} = 3$. Hence $\Delta\mu = 0.0015$,

$$\log_{10} K = 35.63 + 3 \log_{10} T - \frac{7.04 \times 10^9}{T}. \qquad (19.33)$$

Numerically:

TABLE 50

DEUTERON-PROTON EQUILIBRIUM

T	K	$K^{1/2}$
10^8	1.6×10^{-11}	4×10^{-6}
2×10^8	2×10^{25}	4×10^{12}
4×10^8	7×10^{43}	8×10^{21}

It is clear from this equation that in the state of equilibrium there should be very little hydrogen below 10^8 degrees. The density of H_+ cannot be larger than $K^{1/2}$ since z_{D+}/z_e is certain to be smaller than 1.

At low temperatures the conditions are somewhat different because one cannot treat the gases as completely ionized but must regard them as atomic or even as molecular. For atomic hydrogen and atomic deuterium the equation would be

$$2G_H - G_D = 0,$$

$$\nu_H = 2, \quad \nu_D = -1, \quad \nu = 1.$$

$$z_H = (Kz_D)^{1/2} \quad \text{or} \quad z_D = z_H{}^2 K,$$

$$\log_{10} K = 20.260 + \frac{3}{2} \log_{10} T - \frac{7.04 \times 10^9}{T}. \qquad (19.34)$$

Again we see that in the state of equilibrium there should be an enormous excess of deuterium. There is little doubt that positive and negative electrons, in our universe, are really in equilibrium in the sense of section 127. The recombination of pairs progresses with great rapidity, and under ordinary conditions there are no more of them than calculated from our equations. Also, there is no direct evidence that the free neutrons are more numerous than would be expected theoretically. But when it comes to the formation of deuterium from hydrogen and to the analogous processes considered in the next two sections, we must conclude that the world is very far from

[1] Bonner and Brubaker (footnote on p. 339).

[2] At the high temperatures here in question there may exist and be stable another modification of the deuteron (with zero nuclear spin). The joint statistical weight would then be $g_{D+} = 4$ and the constant 35.50.

equilibrium, indeed. It appears that the protons, unless they are in some unusual state of activation, are unable to combine and form heavier nuclei.

131. Hydrogen and helium. The case of formation of helium by the association of four hydrogen atoms is of historical interest because it was the first example of permutation of elements to which the theory of thermodynamical equilibrium was applied.[1] The helium nucleus or α-particle can be formed of four protons and two electrons:

$$4G_{H+} + 2G_e - G_\alpha = 0,$$

whence $\nu_{H+} = 4$, $\nu_e = 2$, $\nu_\alpha = -1$, $\nu = 5$, and

$$z_{H+}{}^4 \, z_e{}^2/z_\alpha = K \quad \text{or} \quad z_{H+} = (Kz_\alpha/z_e)^{1/4} z_e{}^{-1/2}.$$

The atomic weight of helium is $\mu_{He} = 4.0040$, and of the α-particle $\mu_\alpha = 4.0029$, the statistical weight in both cases $g_{He} = g_\alpha = 1$. This gives $\Delta\mu = 0.0284$, and

$$\log_{10} K = 92.44 + 7.5 \log_{10} T - \frac{1.333 \times 10^{11}}{T}. \qquad (19.35)$$

Numerically:

TABLE 51

HELIUM-HYDROGEN EQUILIBRIUM

T	K	$K^{1/4}$
7×10^8	2×10^{-32}	1.2×10^{-8}
8×10^8	4×10^{-8}	1.4×10^{-2}
10^9	4×10^{26}	4.6×10^6
5×10^9	3×10^{138}	4.3×10^{34}

Seeing that $z_\alpha < z_e$ and that, in ordinary stars, $z_\alpha{}^{1/4}$ is considerable (up to 10^5), hydrogen should be practically absent at temperatures below 10^9. At low temperature, the gases must be taken as atomic because they are no longer ionized

$$4G_H - G_{He} = 0,$$

$$z_H = (Kz_{He})^{1/4} \quad \text{or} \quad z_{He} = z_H{}^4 K.$$

It is hardly necessary to calculate K in this case, because it is immediately obvious that the positive terms in its expression are diminished while the negative remain the same as in (19.35) so that $\log_{10} K$ has an enormously large negative value. If equilibrium prevailed, with respect to this reaction, no appreciable amount of hydrogen could exist outside the stellar cores.

[1] R. C. Tolman, J. Am. Chem. Soc. **44**, p. 1902, 1922.

The formation of deuterium and helium are merely the beginning of the process of association of protons into heavier elements. The further combination of α-particles, protons, and electrons into stable nuclei is also exothermic, taking place under a reduction of mass (mass defect). The heavier atoms are, thermodynamically, still more probable than helium. Although the nuclei with the largest mass defects are the most abundant, it does not seem that their abundance relatively to helium and to one another is in quantitative agreement with the thermodynamical expectations. It is not certain that the present data on atomic weights are sufficiently accurate to decide this question. Be this as it may, it is quite certain that equilibrium does not exist with respect to hydrogen, as has already been emphasized at the end of the preceding section.

132. Annihilation of hydrogen. The only experimentally established case of annihilation of matter is the mutual destruction of a positive and a negative electron. The annihilation of protons, hydrogen atoms, or heavier atoms has not as yet been directly observed. However, in the present state of theoretical knowledge no valid reason can be advanced why such a particle could not completely disappear, converting its energy into radiation. The equations for the annihilation of a neutron, on one hand, and of a proton-electron system, on the other, are very little different, and we shall consider the latter because of the greater abundance of protons. The reaction is given by

$$G_{H+} + G_e = 0,$$

$\nu_{H+} = \nu_e = 1$, $\nu = 2$, $\Delta\mu = 1.0081$, whence and from (19.25),

$$\left.\begin{aligned} z_{H+} &= K/z_e, \\ \log_{10} K &= 36.275 + 3\log_{10} T - \frac{4.73 \times 10^{12}}{T}. \end{aligned}\right\} \qquad (19.36)$$

Numerically:

TABLE 52

T	K
5×10^{10}	2×10^{-27}
7×10^{10}	2×10^{1}
8×10^{10}	7×10^{9}
10^{11}	1×10^{22}

If this process is possible, the universe is extremely far from the state of equilibrium: no matter should exist at temperatures below 7×10^{10} degrees.

The view was expressed that there may exist also negative protons, unobserved, so far, because of their scarcity. If this is true, there is

the possibility of the creation and mutual annihilation of positive-negative proton pairs. The reaction is the same as in the case of positive-negative electron pairs only the heat is much larger ($\Delta\mu = 2.015$). It follows

$$\left.\begin{aligned} z_{H^+} z_{H^-} &= K, \\ \log_{10} K &= 39.948 + 3 \log_{10} T - \frac{9.48 \times 10^{12}}{T}. \end{aligned}\right\} \qquad (19.37)$$

This means that temperatures of the order of 10^{12} degrees are necessary to create such pairs. Expressed in electron-volts, the energy of such a pair is 1.88×10^9 e.-v.

How exceedingly small the numbers in (19.36) and (19.37) are, appears from the following fact. A few years ago the astronomers calculated the size of the universe as 10^{87} cm^3 (in the meantime it has become doubtful whether the universe is finite). The reciprocal of this is still very large compared with K at $T = 10^{10}$ or at lower temperatures. It follows that there could not be a single proton, either isolated or as a positive-negative pair, in the whole of the universe. The last atom of matter should have been converted into radiation if equilibrium prevailed.

133. Influence of gravitational fields. The interest of the processes discussed in this chapter lies in their applications to problems of cosmology. However, in treating them we have not taken into consideration the gravitational fields existing in and around the stars. It will be well to say a few words of explanation why the effects of the gravitational fields can be neglected on account of their smallness. We have treated the problem of equilibrium of heavy gases in a gravitational field in section 108 and have seen there that the only correction which the equations need is a term

$$-(\Omega_g/RT)\sum_j \nu_j \mu_j = -\,\Omega_g \Delta\mu/RT$$

added to the equilibrium constant $\log K$. This constant, as given by eq. (19.23), already contains the term $-\,\Delta\mu \cdot c^2/RT$, which, combined with the correction for gravitation, becomes

$$-(1 + \Omega_g/c^2)\Delta\mu \cdot c^2/RT.$$

In other words, the heat of reaction or the energy available in the process is changed in the proportion $(1 + \Omega_g/c^2)$ owing to gravitational forces:

$$\Delta\mu' = (1 + \Omega_g/c^2)\Delta\mu. \qquad (19.38)$$

The gravitational potential Ω_g vanishes at a great distance from a star and is negative in its vicinity, having its minimum at the surface. The factor is, therefore, smaller than 1, meaning that the heat of reaction is decreased. But even the largest known gravitational potentials, those of the white dwarfs, are materially smaller (in absolute value) than $0.002 \times c^2$, whereas within the accuracy of the preceding chapter a correction of 0.2% is negligible.

Equation (19.38) is, of course, quite general and applies to any molecular or atomic process in which energy is converted into radiation. According to the quantum theory, the frequency ν of the emitted radiation is connected with the available energy per atom or molecule $\Delta E = c^2 \Delta\mu/n_A$ by the relation $\Delta E = h\nu$, whence

$$\nu' = (1 + \Omega_g/c^2)\nu. \tag{19.39}$$

The gravitational field changes the frequency of radiation emitted in an elementary process, decreasing it (gravitational red shift), a phenomenon predicted by Einstein and since confirmed experimentally.

We have based these remarks on the Newtonian theory of gravitation. On general grounds we are justified in saying that the conditions cannot be materially different in the general relativity of Einstein as long as Ω_g/c^2 is small. In fact, chemical equilibrium was investigated from the standpoint of the general relativity by Tolman,[1] who found the same relations as in the absence of any gravitational fields. Einstein's formula of the gravitational red shift

$$\nu' = [(1 + 2\Omega_g/c^2)^{1/2} - 1]\,\nu$$

is, in practice ($\Omega_g/c^2 \ll 1$), identical with (19.39).

[1] R. C. Tolman, Proc. Nat. Acad. Sci. 17, p. 159, 1931.

CHAPTER XX

MAGNETIC AND ELECTRIC PHENOMENA

134. Langevin's theory of magnetization. The systems treated in the preceding chapters were completely described by the thermodynamical variables p, V, T, apart from data about their composition. Even in the case of charged gases, discussed in sections 106–115, the electric potential was regarded as only a part of the energy constant and not as an additional parameter of the system. It is instructive to consider also variables of a non-mechanical nature, and we are going to do so in this chapter, beginning with the theory of *magnetics* or substances capable of magnetization. It will be sufficient to treat the case of isotropic substances because the generalization is obvious and would only encumber our expressions without adding anything essential to them. Suppose that a system of this sort is placed in a homogeneous magnetic field whose strength is H *in the absence of the system* (i.e. before the system is brought in). Let M denote the component of the total magnetic moment (or total magnetization) *in the direction of the field.*

We know from the theory of electromagnetism that the work which the field does, in raising the magnetization from M to $M + dM$, is $DW' = -HdM$. In accordance with the convention of section 7, we count the work done by outer forces against the system as negative. The total element of work (2.02), including the mechanical and magnetic parts, is then

$$DW = pdV - HdM$$

and eq. (3.04) of the first law has the form

$$DQ = dU + DW = dU + pdV - HdM. \tag{20.01}$$

The state of the magnetized system depends on the two thermal parameters T, V we used all along and, in addition, on the magnetic parameter M. In order to have a complete description of the system, we must know the three functions

$$U = U(T, V, M), \qquad p = p(T, V, M), \tag{20.02}$$

$$H = H(T, V, M) \tag{20.03}$$

In the sense of section 10, we may call these three relations *the caloric, the thermal, and the magnetic* equations of state. Of course, it is arbitrary which of the six parameters we regard as independent. For most of the applications it will be convenient to describe the system in terms of T, p, H, but occasionally we shall use also T, p, M.

The first application of the second law of thermodynamics to such a system was due to Langevin.[1] As he pointed out, in the expression (4.07) of the entropy differential, $dS = DQ/T$, the magnetic work gives rise to the additional term

$$dS' = \frac{DW'}{T} = -\frac{II}{T}dM, \tag{20.04}$$

and he postulated that dS' be an exact differential. This is possible only when the factor H/T is a function of M (compare section 8) and, vice versa, M is a function of H/T,

$$M = f\left(\frac{II}{T}\right). \tag{20.05}$$

This is the form of the magnetic equation of state (20.03), according to Langevin. It is quite obvious that this law is not general, a case in point being the behavior of *diamagnetic substances* whose magnetization is known to be independent of temperature:

$$M = -AH, \tag{20.06}$$

where A is a constant.[2] What is, then, the special assumption made in this theory and leading to the formula (20.05)? It lies in the separate treatment of the magnetic part of the entropy (20.04) as an exact differential, independently of the remaining part

$$(dU + p\,dV)/T. \tag{20.07}$$

This implies, of course, that the expression (20.07) is also an exact differential which cannot depend on the variable M (or H) since its differential is absent in it. Consequently the functions U and p must be also independent of M. Instead of (20.02),

$$U = U(T, V), \qquad p = p(T, V). \tag{20.08}$$

We met with a similar case in the theory of perfect gases. In the expression (4.16) of dS the two terms are separately exact differentials,

[1] P. Langevin, Ann. Chim. Physique 5, p. 70, 1905.

[2] We speak here of the ordinary or *atomic diamagnetism.* There exist a few substances (as bismuth, antimony, etc.) with so-called *crystal diamagnetism* which has a temperature coefficient.

and this is due to the internal energy depending only on the thermal variable T. By analogy we shall call a substance whose equations of state follow the simple laws (20.05), (20.08) a *perfect magnetic.*

Langevin initiated also the statistical theory of magnetization and gave an explicit expression of the law (20.05) for paramagnetic materials. As corrected to take into account the restrictions of the quantum theory, it can be written

$$\left.\begin{aligned} M &= Zjg\beta_0 F(jg\beta_0 H/kT), \\ F(a) &= \left(1+\frac{1}{2j}\right)\coth\left(a+\frac{a}{2j}\right)-\frac{1}{2j}\coth\frac{a}{2j} \end{aligned}\right\} \tag{20.09}$$

and is sometimes called the *Langevin-Brillouin* formula. Z represents here the total number of atoms, and the product $jg\beta_0$ the total magnetic moment of one atom. The factors have the following meaning:

β_0 the Bohr magneton

$$\beta_0 = \frac{eh}{4\pi M_e c} = (0.9174 \pm 0.0013) \times 10^{-20} \text{ erg gauss}^{-1}, \tag{20.10}$$

g the Lande factor

$$g = \frac{3}{2} + \frac{s(s+1)-l(l+1)}{2j(j+1)}, \tag{20.11}$$

j is the quantum number of the total angular momentum of the atom, compounded of the resultant spin momentum s and the resultant angular momentum l. At 20° C the numerical value of β_0/kT is 2.28×10^{-7}: since jg is rarely larger than 7, the argument of the function F is small (< 0.050) at room temperature, even for fields of the order of 30 000 gauss. Under these circumstances all terms of the expansion of $F(a)$ into a power series are negligible, excepting the first linear term, and the magnetization is well represented by Curie's law

$$M = \frac{CH}{T}, \tag{20.12}$$

where C is a constant. For large values of the argument, the function F asymptotically approaches the value 1 (magnetic saturation), but its indications appear only at very low temperatures.

The formula (20.09) was derived for gases and solutions of salts in which the atoms or ions can freely rotate. Even for these substances its validity is not general, being often impaired by doublet or multiplet structure of the energy levels. Only when the width of

these multiplets is very small or very large compared with kT is the formula applicable. It is remarkable, however, that it represents with great accuracy the magnetization of solid paramagnetic salts of rare earths, especially those in which the paramagnetic atoms are not very close together but separated by non-magnetic atoms (as, for instance, in hydrates). The classical example, in this respect, is hydrated gadolinium sulfate investigated in Leiden.[1] The magnetic moment of this substance was measured down to 1°3 K and found to obey strictly the law (20.09) with $j = \frac{7}{2}$ and $g = 2$. At the lowest temperature and highest field the saturation was far advanced, the magnetization being 95% of the possible maximum.

Exercise 106. Calculate the entropy term S' from (20.04) for substances whose magnetic moments are expressed by (20.09). Show that

$$S' = kZ\left\{\log\left[\sinh\left(a + \frac{a}{2j}\right)\Big/\sinh\frac{a}{2j}\right] - aF(a)\right\} + \text{const.}$$

Exercise 107. In his original formula Langevin assumed that the orientations of the molecular magnetic moments are not restricted by quantum conditions. This formula can be obtained from (20.09) by the following transition to the limit: let j go to ∞, while β_0 goes to zero in such a way that $jg\beta_0 = \beta$ remains constant where β represents the molecular magnetic moment). Show that the result is

$$M = Z\beta\, f(\beta H/kT), \quad f(a) = \coth a - 1/a.$$

135. Magnetothermal and magnetocaloric relations.—It will be well to derive a few relations which will elucidate still further the thermodynamical status of perfect magnetics and diamagnetics. We start from the generalized thermodynamic potential

$$\Phi = U - TS + pV - HM, \tag{20.13}$$

whose differential is, according to (20.01) and (4.07),

$$d\Phi = -SdT + Vdp - MdH. \tag{20.14}$$

Hence

$$S = -\left(\frac{\partial\Phi}{\partial T}\right)_{p,H}, \quad V = \left(\frac{\partial\Phi}{\partial p}\right)_{T,H}, \quad M = -\left(\frac{\partial\Phi}{\partial H}\right)_{T,p}. \tag{20.15}$$

Substituting this into (20.13)

$$U = \Phi - T\left(\frac{\partial\Phi}{\partial T}\right)_{p,H} - p\left(\frac{\partial\Phi}{\partial p}\right)_{T,H} - H\left(\frac{\partial\Phi}{\partial H}\right)_{p,T} \tag{20.16}$$

[1] H. R. Woltjer and H. Kamerlingh Onnes, Leiden Comm. 167 *b*, *c*.

The three partials (20.15) give reciprocity relations when differentiated a second time. Thus we obtain from the second and third

$$\left(\frac{\partial V}{\partial H}\right)_{p,T} = -\left(\frac{\partial M}{\partial p}\right)_{T,H}. \tag{20.17}$$

This is a relation between measurable quantities. The left side is the change of volume due to the field, its relative value (divided by V) is called *volume magnetostriction* or Barrett effect. The right side represents the change of the total magnetic moment due to pressure. Such an effect was foreseen and first measured by *Nagaoka and Honda* [1] and is named after them. Although accurate modern measurements of both effects are available, they were not carried out under comparable conditions and are not suitable for a quantitative test of the relation (20.17). It should be noted that in *perfect magnetics* the volume does not depend on the magnetic parameters (preceding section). The experimental existence of magnetostriction in ferromagnetic materials shows, therefore, that these substances do not strictly follow Langevin's law (20.05). However, the effect is very small and the deviation, presumably, not large.

Exercise 108. In a particular specimen of iron (at $t = 20°$ C, $H = 1$ gauss) the partial $(\partial M/\partial p)_{T,H}$ was found to be -3×10^{-3} gauss per unit volume and per 1 atm. Calculate the volume magnetostriction from formula (20.17). (Use absolute units).

The other two reciprocity relations following from (20.15) are

$$\left(\frac{\partial S}{\partial p}\right)_{T,H} = -\left(\frac{\partial V}{\partial T}\right)_{p,H}, \quad \left(\frac{\partial S}{\partial H}\right)_{T,p} = \left(\frac{\partial M}{\partial T}\right)_{p,H}. \tag{20.18}$$

We shall use them for transforming eq. (20.16) as follows. We differentiate (20.13) partially with respect to p, and with respect to H, and take into account the relations (20.17) and (20.18):

$$\left(\frac{\partial U}{\partial p}\right)_{T,H} = -T\left(\frac{\partial V}{\partial T}\right)_{p,H} - p\left(\frac{\partial V}{\partial p}\right)_{H,T} - H\left(\frac{\partial V}{\partial H}\right)_{T,p}, \tag{20.19}$$

$$\left(\frac{\partial U}{\partial H}\right)_{T,p} = T\left(\frac{\partial M}{\partial T}\right)_{p,H} + p\left(\frac{\partial M}{\partial p}\right)_{T,H} + H\left(\frac{\partial M}{\partial H}\right)_{T,p}. \tag{20.20}$$

In the case of perfect magnetics we have $(\partial U/\partial H)_{T,p} = (\partial V/\partial H)_{T,p} = 0$, and from (20.17) and (20.20)

$$T\left(\frac{\partial M}{\partial T}\right)_{H} = -H\left(\frac{\partial M}{\partial H}\right)_{T}.$$

[1] Nagaoka and Honda, Phil. Mag. **46**, p. 261, 1898; see also S. R. Williams, Int. Crit. Tables VI, p. 439, 1929.

This is only another proof of Langevin's result because the general integral of this equation is the expression (20.05). On the other hand, the law (20.06) of diamagnetism gives $(\partial U/\partial H)_{T,p} = -AH = M$, so that the internal energy contains a magnetic term whose differential is

$$dU' = (\partial U/\partial H)_{T,p}\, dH = MdH = HdM. \tag{20.21}$$

A look at the structure of the element of heat (20.01) shows that the additional term in dU just cancels the work of the magnetic field $DW' = -HdM$, so that DQ is independent of magnetic parameters. We see from this that *diamagnetic and perfect magnetic substances are complete opposites* with respect to the caloric action of putting them into a magnetic field. In diamagnetics, the (positive) work against the field is done at the expense of the internal energy without any contribution from external heat sources. It is a process at the same time adiabatic and isothermal: the loss is sustained, as it were, by the constant of the internal energy and does not affect the temperature of the body or its equilibrium with the environment. On the contrary, the (negative) work of magnetizing perfect magnetics is completely supplied by outer sources, when conducted isothermally. When the process is adiabatic it leads to a rise of temperature in the substance.

In the interest of the following section we shall say here a few words about the heat capacity of magnetics. In treating simple systems, we distinguished in section 14 the specific heats at constant volume c_v and at constant pressure c_p. Similarly, we have to speak here about the following two heat capacities. The *heat capacity at constant magnetization* (and, say, constant pressure) is the heat that must be imparted to the magnetic when its temperature is raised by 1 degree and, at the same time, the magnetic field is changed in such a way as to keep its magnetization constant: $C_{pM} = \lim(\Delta Q/\Delta T)_{pM}$. According to the expression (20.01), no part of this heat is used for magnetic work. On the other hand, the *heat capacity at constant field strength* $C_{pH} = \lim\,(\Delta Q/\Delta T)_{pH}$ refers to a process accompanied by a change of M and involving magnetic work. In view of the relation $\Delta Q = T\Delta S$, we can also write

$$C_{pM} = T\left(\frac{\partial S}{\partial T}\right)_{p,M}, \quad C_{pH} = T\left(\frac{\partial S}{\partial T}\right)_{p,H}. \tag{20.22}$$

The relation between these quantities analogous to (4.27) is found, in the simplest way, by considering S a function of T and M, while M, in its turn, depends on T and H, i.e. $S = S[T, M(T, H)]$. (We need

not bother about the pressure p, since it is assumed to be always constant.) The rules of partial differentiation give us

$$\left(\frac{\partial S}{\partial T}\right)_{H,p} = \left(\frac{\partial S}{\partial T}\right)_{p,M} + \left(\frac{\partial S}{\partial M}\right)_{p,T} \cdot \left(\frac{\partial M}{\partial T}\right)_{p,H} \cdot$$

In the partial $(\partial S/\partial M)_{p,T}$ the variables p and T are considered as constant so that M is a function of H only: therefore,

$$(\partial S/\partial M)_{p,T} = (\partial S/\partial H)_{p,T} \cdot (\partial H/\partial M)_{p,T} \cdot$$

Substituting this and making use of eq. (20.18), we find the desired relation

$$C_{pH} - C_{pM} = T\left(\frac{\partial M}{\partial T}\right)^2_{p,H} \cdot \left(\frac{\partial H}{\partial M}\right)_{p,T} \cdot \tag{20.23}$$

136. Cooling by adiabatic demagnetization. Adiabatic demagnetization of a paramagnetic substance is analogous to the adiabatic expansion of a simple system. In either case, the work against external forces is done at the expense of the internal energy of the system and leads, in general, to a decrease of its temperature. The use of this " magnetocaloric effect " for the production of very low temperatures was proposed independently by Giauque [1] and Debye.[2] The usual method of lowering the boiling pressure of liquid helium does not permit in practice [3] to reach temperatures below 0°.7 K. Work with the magnetocaloric method has been under way in recent years, at Berkeley (California) under the direction of Giauque,[4] and at Leiden (Holland), under the direction of deHaas.[5] It has been very successful in bringing the range of accessible temperatures considerably nearer to the absolute zero point.

The equation of the adiabatic $dS = dQ/T = 0$ is, according to (20.01),

$$dS = (dU + pdV - HdM)/T = 0, \tag{20.24}$$

when S is expressed as a function of T, p, H, also

$$\left(\frac{\partial S}{\partial T}\right)_{p,H} dT + \left(\frac{\partial S}{\partial p}\right)_{H,T} dp + \left(\frac{\partial S}{\partial H}\right)_{T,p} dH = 0.$$

[1] W. F. Giauque, J. Am. Chem. Soc. **49**, pp. 1864, 1870, 1927.

[2] P. Debye, Ann. Physik **81**, p. 1154, 1926.

[3] Keesom, Proc. Amsterdam **35**, 136, 1932.

[4] W. F. Giauque and C. W. Clarke, J. Am. Chem. Soc. **54**, p. 3135, 1932; W. F. Giauque and D. P. McDougall, Phys. Rev. **43**, p. 768; **44**, p. 235, 1933.

[5] W. J. deHaas, E. C. Wiersma, and H. A. Kramers, Physica **13**, p. 171; **1**, p. 1, 1933; W. J. deHaas and E. C. Wiersma, Physica **1**, p. 1107, 1933.

Substituting from (20.22) and (20.18),

$$C_{PH}\frac{dT}{T}-\left(\frac{\partial V}{\partial T}\right)_{p,H}dp+\left(\frac{\partial M}{\partial T}\right)_{p,H}dH=0. \tag{20.25}$$

The procedure consists in precooling the specimen in vacuo, in a strong magnetic field, and then turning off the field.

With $p = 0$, eq. (20.25) gives for the rate of the adiabatic cooling

$$\frac{dT}{dH}=T\left(\frac{\partial M}{\partial T}\right)_{p,H}\Big/C_{pH}, \tag{20.26}$$

or from (12.23)

$$\frac{dT}{dH}=\frac{T\left(\frac{\partial M}{\partial T}\right)_{p,H}}{C_{pM}+T\left(\frac{\partial M}{\partial T}\right)^2_{p,H}\left(\frac{\partial H}{\partial M}\right)_{p,T}}. \tag{20.27}$$

As was pointed out in the preceding section, the heat capacity C_{pM} does not contain any magnetic work. Therefore, it should not be materially different from the ordinary capacity C_p as measured in the absence of a magnetic field. Of particular interest are the perfect magnetics: from the kinetic point of view, they are the substances in which every atom is free to adjust itself in the field without being hindered by its neighbors. Other things being equal, they should show the highest magnetization and the highest caloric action. For this reason, both Giauque and Debye suggested the use of gadolinium sulfate as a testing substance because it was known to follow the law (20.09) down to the lowest temperatures. If we denote $x = H/T$, this law implies

$$\left(\frac{\partial M}{\partial T}\right)_{p,H}=-\frac{x}{T}\frac{dM}{dx},\qquad \left(\frac{\partial M}{\partial H}\right)_{p,T}=\frac{1}{T}\frac{dM}{dx},$$

so that (20.27) becomes

$$\frac{dT}{dH}=-\frac{x(dM/dx)}{C_{pM}+x^2(dM/dx)}. \tag{20.28}$$

Of course, in the case of perfect magnetics there is no need to use a differential formula because the two terms (with $p = 0$), in the formula (20.24), are separately integrable. At zero pressure there is no difference between c_p and c_v, and the energy differential is $dU = C_v dT$. Hence

$$\int\frac{C_v dT}{T}-\int x\frac{dM}{dx}dx=\text{const.} \tag{20.29}$$

If the specific heat follows the third power law (18.70), the first integral is equal to $6.45 \times 10^9 (T/\Theta)^3$ erg/deg mol. Suppose we start the demagnetization at the temperature T_0 and the field H_0. When the field is reduced to $H = 0$, the temperature has the value

$$T = \left[T_0^3 - 1.55 \times 10^{-10} \Theta^3 \int_0^{x_0} x \frac{dm}{dx} dx \right]^{1/3}, \qquad (20.30)$$

where $x_0 = H_0/T_0$ and m is the molal magnetic moment.

It was found, however, that the specific heat of gadolinium sulfate does not follow the third power law but exhibits an anomaly due to multiplet structure of the lowest energy level (compare section 117). The curve reproduced on p. 327 was obtained by Giauque and McDougall by measuring the magnetocaloric effect dT/dH and by calculating C_{pM} from a formula equivalent to (20.27). Although they reached a temperature of 0°.287 K, this substance is not particularly suitable for magnetocaloric cooling. At the time of the writing, the greatest success was obtained by deHaas with a mixture of two alums, $K_2SO_4Cr_2(SO_4)_3 \cdot 24H_2O + 14.4K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$. Demagnetizing from 24 075 gauss to 1 gauss, he reached 0°.0044 K. In all this work the measurements themselves were used to establish the scale of absolute temperatures by the method explained in section 29. However, the last figure (0°.0044 K) rests, in part, on an extrapolation and has only approximate validity.

Exercise 109. Consider a substance satisfying eq. (20.30) whose magnetization obeys the law (20.09), with $j = \frac{1}{2}$, $g = 2$. Start with $T_0 = 3°$ K and $H = 25\,000$ gauss and demagnetize to $H = 0$. What will be the final temperature if $\Theta = 200$?

137. Supraconductivity and thermodynamics. It was discovered by Kamerlingh Onnes that the electric resistance of certain metals suddenly drops to practically nothing when they are cooled below temperatures called their *transition points*. We give the transition points of the principal supraconductive substances in Table 53.

The transition point is displaced when the system is put into a magnetic field H. As the magnetic field is increased, the transition point moves continuously to lower temperatures, and at a certain strength of it (*threshold value*) the supraconductive state ceases to exist altogether. From the point of view of electromagnetism, the immediate effect of switching on a field consists in setting up currents in the supraconductor, in conformity with Faraday's law of induction. But the conductivity of these substances is so large that the currents continue to flow, without apparent loss, as long as the state of supra-

TABLE 53

SUPRACONDUCTIVE TRANSITION POINTS

Elements		Elements		Intermetallic compounds		Intermetallic compounds	
Mg	0°.70 K	V	4°.3 K	Au_2Bi	1°.84 K	ZrB	2°.82 K
Zn	0.78	Nb	9.2	CuS	1.6	TaSi	4.2
Cd	0.6 (ca)	Ta	4.4	VN	1.3	PbS	4.1
Hg	4.22	La	4.7	WC	2.8		
Al	1.14			W_2C	2.05	Alloys	
Ga	1.05	Intermetallic compounds		MoC	7.7		
Tl	2.37			Mo_2C	2.4		
Ti	1.75			TiN	1.4	Pb–Sn–Bi	8.5
Th	1.5	Bi_6Tl_3	6.5	TiC	1.1	Pb–As	8.4
Sn	3.71	Sb_2Tl_7	5.5	TaC	9.2	Pb–As–Bi	9.0
Pb	7.2	Na_2Pb_5	7.2	NbC	10.1	Pb–Bi–Sb	8.9
In	3.37	Hg_5Tl_7	3.8				

conductivity is maintained: they are therefore called *persistent currents*. Another result also follows from the theory of electromagnetism: when the magnetic field is switched on, after the supraconductive state is established, neither the field nor the currents can penetrate to any appreciable depth of the metal. The persistent currents flow at the surface and produce a magnetic field which exactly compensates within the metal the external field. Experimental work has shown that the same conditions prevail when the metal is cooled below the transition point in an already existing magnetic field. The lines of magnetic induction are pushed out of the metal, as it becomes supraconductive, until the induction in the interior vanishes. This result was first announced by Meissner and Ochsenfeld[1] and has been confirmed since by many investigators. Although there is still some doubt whether it holds rigorously, it describes the phenomena with an accuracy sufficient for thermodynamical purposes. In short, a supraconductor behaves in a magnetic field like a substance of the permeability $\mu = 0$. Since μ is connected with the susceptibility κ by the relation $\mu = 1 + 4\pi\kappa$, the supraconductors can be formally described as diamagnetics with the susceptibility $\kappa = -1/4\pi$.

Let us consider a long stretched (needle-shaped) supraconductive body placed with its axis in the direction of the magnetic field. According to the electromagnetic theory, the outer magnetic field produced by a body of this shape is negligible. Its (negative) magnetic energy

[1] W. Meissner and R. Ochsenfeld, Die Naturwissenschaften 21, p. 787, 1933.

is due to the absence of any field in the interior and is equal to $-H^2/8\pi$, per unit volume, or to

$$u_H = -\frac{vH^2}{8\pi} \tag{20.31}$$

per mol. The magnetization (per unit volume) is an expression of the type (20.06) characteristic of diamagnetics. We can apply, therefore, to supraconductors the results established in the preceding section for diamagnetic substances: the internal energy contains u_H as an additive term, while the entropy is independent of the magnetic parameters. Consequently the thermodynamic potential ($\varphi = u - Ts + pv$) has, in the case of supraconductive materials, the form

$$\varphi = \varphi_0 - \frac{vH^2}{8\pi}, \tag{20.32}$$

where φ_0 is the potential in the absence of a field. At the very low temperatures we are here considering, the pressure effects are negligible: there is no observable change of specific volume, so that it is permissible to ignore the pressure as a variable and to regard $\varphi_0(T)$ as a function of temperature only, and v as a constant. The normal (non-supraconductive) modification of the metal is, as a rule, non-magnetic, so that its thermodynamic potential does not contain any magnetic term but is, simply, $\varphi_n(T)$. The equation of equilibrium between the two phases becomes, therefore, $\Delta\Phi = \varphi_n - \varphi = 0$ or

$$\Delta\Phi = \varphi_n(T) - \varphi_0(T) + \frac{vH^2}{8\pi} = 0. \tag{20.33}$$

Of course, it is not a priori certain that the supraconductive state is in true equilibrium and that the second law can be applied to it. The hypothesis that it represents a phase in the thermodynamical sense was first made by Langevin.[1] It was corroborated by the great sharpness of the transition point in good crystalline specimens. The experimental test of the equation (20.33) is also reassuring: its consequences hold with good accuracy. This relation gives the dependence of the transition point on the strength of field H and can be tested in several ways. The first and second partials of $\Delta\Phi$ with respect to T are, according to (5.37) and (7.22),

$$-\Delta\Phi_T = s_n - s = \frac{l}{T}, \quad -\Delta\Phi_{TT} = \frac{c_n - c}{T} = \frac{\Delta c}{T}. \tag{20.34}$$

[1] P. Langevin, Rapports du 1er Conseil Solvay, p. 301, 1911.

The differentiation of (20.33) gives the equation $-(l/T)dT + (vH/4\pi)dH = 0$ or

$$\frac{l}{T} = \frac{vH}{4\pi}\frac{dH}{dT}, \tag{20.35}$$

analogous to the Clausius-Clapeyron equation. It was tested by Keesom and Kok [1] and found to be in agreement with experiments. Of great interest is the observation of these authors that the latent heat decreased as the field diminished and could not be measured at all in the case of field free transitions (i.e. $dH/dT \neq \infty$ for $H = 0$). If this observation is confirmed, it would mean that the equilibrium, in the case $H = 0$, is of the second order (section 49). Let us consider this case: we denote the transition point in the absence of a field by T_0 and express $\Delta\Phi$, for $T = T_0 + dT$, $H = dH$, to terms of the second order. From (20.34)

$$-\Delta\Phi = \frac{1}{2}\left(\frac{\Delta c_0}{T_0}\right)(dT)^2 - \frac{v}{8\pi}(dH)^2 = 0$$

or

$$\frac{\Delta c_0}{T_0} = \frac{v}{4\pi}\left(\frac{dH}{dT}\right)^2. \tag{20.36}$$

This equation was obtained by Rutgers[2] and in a different way by Gorter and Casimir.[3] All these authors regarded the equilibrium in question as one of the second order. The equation (20.36) was confirmed with remarkable accuracy by the beautiful measurements of Keesom and Kok on tin and thallium.[4]

TABLE 54

	T_0 K	v cm³ mol⁻¹	dH/dT gauss deg⁻¹	Δc_0 (calc) cal deg⁻¹ mol⁻¹	Δc_0 (obs)
Tin.....	3.71	14.2	151.2	0.00229	0.0024
Thallium.....	2.36	16.9	137.4	0.00144	0.00148

Nevertheless we do not agree with Rutgers, Gorton, and Casimir.

[1] W. H. Keesom and J. A. Kok, Physica 1, pp. 503, 595, 1934.
[2] Appendix to Ehrenfest's paper, note on p. 128.
[3] C. J. Gorter and H. Casimir, Physica 1, p. 306, 1934.
[4] W. H. Keesom and J. A. Kok, Physica 1, p. 175, 1933.

The equilibrium cannot be of the second order since an unsurmountable difficulty is introduced by the double sign of

$$\frac{dH}{dT} = \pm \left(\frac{4\pi}{v} \frac{\Delta c_0}{T_0} \right)^{1/2}.$$

Represented graphically (Fig. 60), the transformation is of the general type of Fig. 18 on p. 132. With any plausible choice of the functions $\varphi_0(T)$, $\varphi_n(T)$, the analysis shows that the lines representing the equilibrium continue beyond the point T_0. Therefore, both regions labeled (1) in Fig. 60 correspond to the supraconductive state so that cooling along the line $H = 0$ does not involve any transition. We maintain, therefore, that the equilibrium in question is, in reality,

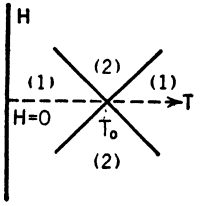

FIG. 60

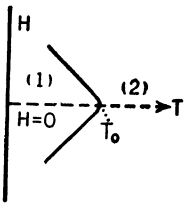

FIG. 61

Supraconductive transition point in its dependence on magnetic field.

of the first order, there being a small but finite latent heat. According to the general discussion of section 49, this would imply a transition curve of the shape given in Fig. 61. That Rutgers' formula is satisfied with such a remarkable accuracy is due to the following coincidence. Equation (20.35) holds for the whole curve and can be differentiated along it. Since $l/T = \Delta s$, its differential is $(\Delta c/T)dT$, and we find

$$\frac{\Delta c}{T} = \frac{v}{4\pi} H \frac{d^2H}{dT^2} + \frac{v}{4\pi} \left(\frac{dH}{dT} \right)^2. \tag{20.37}$$

Where the line of Fig. 61 is straight ($d^2H/dT^2 = 0$), the slope is given exactly by Rutgers' expression, whether the equilibrium in T_0 is of the first or of the second order.[1]

There were attempts to make other aspects of supraconductivity amenable to a thermodynamical treatment. However, they failed to

[1] In a later paper (Phys. Zs. 35, p. 963, 1934) Gorter and Casimir admit that the supraconductive state would be thermodynamically stable above the transition point "if it existed." They postulate, therefore, that it cannot exist. This seems an adhoc hypothesis, and the difficulty is much better disposed of by the simple assumption made in the text, that the equilibrium is of the first order.

give a complete picture of the phenomena for which they were intended. Limitations of space do not permit us to enter into their discussion.

138. Electrostatic phenomena. *Dielectrics* or substances capable of electric polarization P form, in many respects, an analogue to the magnetics treated in section 134. The work which must be done on a dielectric body in order to increase its total electric moment (or polarization), in the direction of the field E, from P to $P+dP$, is

$$DW'_e = -E\,dP,$$

so that the complete element of work becomes

$$DW = pdV - E\,dP, \tag{20.38}$$

in analogy with the magnetic expression of section 134. There are two types of dielectric polarization which, from a thermodynamical point of view, correspond closely to the types of magnetization in atomic diamagnetics and in perfect magnetics.

(A) *The Lorentz type of polarization.* If the molecules of a substance have no electric moments in their normal state, the application of an electric field creates such moments in them by displacing the electrons from their normal position. The expression for this sort of polarization (taking account of the field of the electric moments) is

$$P = AE', \tag{20.39}$$

where A is a constant and $E' = E + \frac{4\pi}{3}P$ is the *effective* field strength. The phenomenon is mainly intramolecular, and A is independent of temperature. This has the thermodynamical implications discussed in connection with diamagnetism.

(B) *Dipole polarization.* It was pointed out by Debye [1] that some dielectric substances may possess permanent molecular dipoles. He suggested, therefore, taking over Langevin's formula (developed for magnetic dipoles) in order to account for empirically observed changes of electric polarization with temperature. The case of polarization is simpler in two respects. In the first place, the electric dipoles have no tendency to orient themselves in discrete quantized directions. The original Langevin formula derived on lines of classical statistics holds for them: this means that one has to take in eq. (20.09) $j = \infty$ and $jg\beta_0 = \beta_e = \text{const.}$[2] In the second place, the conditions in dielec-

[1] P. Debye, Phys. Zs. **13**, p. 97, 1912.

[2] The transition to the limit is the same as in exercise 107. When the argument a is small, there holds the expansion $\coth a = 1/a + \frac{1}{3}a$; therefore, the function of exercise 107 becomes $f(a) = \frac{1}{3}a$, leading to formula (20.40).

trics hardly ever approach saturation so that the term of first order in E'/T represents an excellent approximation

$$P = \frac{Z\beta_e^2 E'}{3kT}, \tag{20.40}$$

where β_e is the electric dipole of a molecule and Z the total number of molecules. Of course, one should expect this expression to hold only in substances where the dipoles can freely rotate, i.e. in gases and liquids. In analogy with the *perfect magnetics* of section 134 they may be called *perfect dielectrics.*

In general the dipole dielectrics possess also an appreciable polarization of the Lorentz type so that very few of them are, even approximately, perfect. The dielectric constant D (which is accessible to direct measurement) is connected with the polarization by the relation $(D-1)/(D+2) = \frac{4}{3}\pi P/VE'$ and has the general expression

$$\frac{D-1}{D+2} = \frac{4\pi}{3}\frac{A}{V} + \frac{4\pi}{9} z \frac{\beta_e^2}{kT}, \tag{20.41}$$

with $z = Z/V$. By plotting D against $1/T$ one can separate out the part due to dipoles and determine the moment. This proved a very helpful method for investigating the properties of many organic molecules.[1]

The electric analogue to magnetostriction is the phenomenon of electrostriction. Because of the close parallelism of the thermodynamical properties of dielectrics and magnetics we can directly take over eq. (20.17), writing

$$\left(\frac{\partial V}{\partial E}\right)_{p,T} = -\left(\frac{\partial P}{\partial p}\right)_{T,E}.$$

We see that electrostriction (represented by the left side) is associated with another effect called *piezoelectricity*, which consists in the dependence of the polarization P on pressure. Our formula refers to the *volume effect*, but piezoelectricity is mostly observed in crystals, where it is particularly strong in certain crystallographic directions. In turmaline the piezoelectric effect (increase of a component of the polarization per unit volume and per unit increase of a strain component) is 5.78×10^{-8} in e.-s. cgs units, in quartz -6.9×10^{-8}, but it is particularly large in Rochelle salt, where it reaches 8100×10^{-8}. An electromagnetic wave, acting upon a plate cut from a piezoelectric crystal, periodically changes its size, because of the electrostriction

[1] See P. Debye, Polare Molekeln, Leipzig, 1929.

associated with piezoelectricity, and sets up in it elastic oscillations. The amplitude is particularly large when the frequency of the wave is in resonance with the characteristic period of the elastic oscillations in the plate. Such *piezoelectric resonators* have received important technical applications in the last decades. According to eqs. (20.02), the deeper reason for the existence of piezoelectricity is the dependence of the pressure (or strain) on the polarization P. It is to be expected that the internal energy and entropy should then also depend on P and H. From (20.18) we can, therefore, conclude that piezoelectric substances are at the same time *pyroelectric*, i.e. their electric moment is influenced by a change of temperature.[1]

It is here the place to make a few supplementary remarks about the theory of strong electrolytes (section 115) and to explain why we could not calculate the internal energy U directly but had to take the indirect way over the work function Ψ. The reason is that the electric or magnetic energy of a system cannot always be regarded as a part of its internal energy. We have seen that such simple conditions obtain only in the case of atomic diamagnetism or of polarization of the Lorentz type, *when the electromagnetic work does not depend on the thermal parameters*. The opposite extreme are the perfect magnetics and dielectrics in which U remains completely unaffected by the electromagnetic energy of the system. The strong electrolytes occupy an intermediate position. The addition U_e to the internal energy due to the ionic interaction should be calculated from the expression (17.64) of the work function Ψ_e by means of the relation $\Psi_e = U_e - TS_e$ or

$$U_e = \Psi_e - T\left(\frac{\partial \Psi_e}{\partial T}\right)_V .$$

The difficulty is, however, that Ψ_e depends on T not only explicitly but also implicitly through the dielectric constant D. In a similar way, the thermodynamic potential Φ_e is connected with Ψ_e by the formula $\Phi_e = \Psi_e + p_e V$, or

$$\Phi_e = \Psi_e - V\left(\frac{\partial \Psi_e}{\partial V}\right)_T ,$$

and here again the dependence of D on the volume is not sufficiently well known for a quantitative evaluation.

139. Thermoelectric phenomena. In section 109 we introduced the concept of the potential difference built up by thermoelectric action

[1] For a discussion of these phenomena see: Geiger and Scheel, Handbuch der Physik, Vol. XIII. Berlin 1928.

across a junction of two conductors. The discovery of the e.m.f. (electromotive force) of thermoelectricity was made by Seebeck in 1822. It was supplemented in 1834 by observations of Peltier's on a peculiar heat development due to electric currents flowing through thermoelectric junctions. Let J denote the current flowing from conductor (1) to conductor (2): in order to maintain the junction at constant temperature, it is necessary to impart to it, in unit time, the heat

$$Q_{12} = \Pi_{12} J, \tag{20.42}$$

where Π_{12} is the so-called *Peltier coefficient*, depending on the nature of the conductors and on the temperature of the junction. Π_{12} is positive (i.e. heat must be imparted to the system) when the current J has the same direction as that produced by the thermoelectric action of the junction. The sign of the Peltier coefficient is reversed when the current flows in the opposite direction ($\Pi_{21} = -\Pi_{12}$). This fact gives the experimental possibility of separating it from Joule's heat, which does not depend on the direction of the current. From the theoretical point of view, the same fact is taken as an indication that the development of Peltier heat is a reversible process, amenable to thermodynamical treatment.

The final step was the discovery (1854) by William Thomson, later Lord Kelvin, of the following phenomenon: when the current J flows through a wire of homogeneous material and cross-section, but of non-uniform temperature, heat must be supplied in order to maintain the temperature gradient. To an element of the wire with the temperature rise dT, there must be imparted in unit time the heat

$$dQ = \sigma dT J. \tag{20.43}$$

σ is called the *Thomson coefficient*, and it is positive when the current flows in the direction of rising temperature. The Thomson effect is reversible, in the sense that dQ changes its sign when the direction of the current is reversed.

The thermodynamical theory of thermoelectricity is due to Lord Kelvin. Let us consider the circuit of Fig. 62, consisting of two wires (1) and (2) whose junctions are kept at the respective temperatures T and T'. When the current J is sent through the (closed) circuit, the total heat which must be imparted to it in unit time to keep the conditions stationary is, according to (20.42) and (20.43),

$$Q = [\Pi_{12} - \Pi'_{12} + \int_T^{T'} (\sigma_2 - \sigma_1) dT] J. \tag{20.44}$$

From the point of view of the first law of thermodynamics, Q is the energy which maintains the circulation of the current. In the theory of electricity this energy has the expression

$$Q = EJ, \tag{20.45}$$

where E is the e.m.f. (electromotive force) of the circuit, J being the electric charge flowing through any cross-section in unit time. Equation (20.44) indicates how this energy is spent. There is a profound analogy between the conduction electrons streaming across a thermojunction and a gas forced through a cotton plug in the Joule-Thomson process (section 15): the energy which the electron gas gains or loses is equal to the difference of its heat functions in the two conductors, $Q = \Delta\mathbf{X}$. The same is true for the Thomson effect (20.43): $dQ = d\mathbf{X}$. If the molal heat function is denoted by χ and the molal electron charge by $f = -F = -n_A e$, eqs. (20.42) and (20.43) can be written

$$\Pi_{12} = \frac{(\chi_2 - \chi_1)}{f}, \quad \sigma = \frac{1}{f}\frac{d\chi}{dT}. \tag{20.46}$$

Combining (20.44) and (20.45), we can write

$$E = \Pi_{12} - \Pi'_{12} + \int_T^{T'} (\sigma_2 - \sigma_1) dT, \tag{20.47}$$

as the expression of the first law of thermodynamics. In particular, when the temperature difference of the junctions is infinitesimal, $T - T' = dT$

$$\frac{dE}{dT} = \frac{d\Pi_{12}}{dT} + \sigma_1 - \sigma_2. \tag{20.48}$$

Further relations can be obtained from the second law, assuming that the heat items of eq. (20.44) are imparted to the system in a reversible way and that the thermoelectric effect satisfies the entropy principle separately. Let us follow a portion of the electron gas, responsible for the current, in its motion around the circuit back to the initial position. The process is *cyclic* in that the final state is identical with the initial and the total entropy change in it must be zero: $\Sigma\Delta S = \Sigma\Delta Q/T$. The items of heat ΔQ imparted to the electron gas are the same as in eq. (20.44). We find, therefore,

$$\frac{\Pi_{12}}{T} - \frac{\Pi'_{12}}{T'} + \int_T^{T'} \frac{\sigma_2 - \sigma_1}{T} dT = 0, \tag{20.49}$$

or taking again $T - T' = dT$,

$$\frac{d(\Pi_{12}/T)}{dT} = \frac{\sigma_2 - \sigma_1}{T}.$$

The ratio Π_{12}/T is called the *thermoelectric power* of the pair of conductors. There follows from (20.48)

$$\left.\begin{aligned} \frac{dE}{dT} &= \frac{\Pi_{12}}{T}, \\ \sigma_2 - \sigma_1 &= T\frac{d}{dT}\left(\frac{\Pi_{12}}{T}\right) = T\frac{d^2E}{dT^2}. \end{aligned}\right\} \tag{20.50}$$

Finally, the third law of thermodynamics has also a bearing on thermoelectricity. Since Π_{12}/T represents the change of entropy which the electrons (or other carriers) undergo in passing across the junction, Nernst's postulate (13.07) gives directly

$$\lim_{T=0} (\Pi/T) = 0. \tag{20.51}$$

Hence the integrated form of (20.50) becomes

$$\Pi_{12} = T\int_0^T \frac{\sigma_2 - \sigma_1}{T}\, dT. \tag{20.52}$$

This equation implies, of course, that the integral must be convergent, so that $\lim_{T=0}(\sigma_2 - \sigma_1) = 0$. But not only the difference must vanish (in the limit $T = 0$), but also σ_1 and σ_2 individually. In fact, we see from (20.46) that σ has the physical meaning of the *specific heat* of the carriers: eq. (13.15) requires, therefore,

$$\lim_{T=0} \sigma = 0. \tag{20.53}$$

The *empirical representation* of the thermoelectric e.m.f. is usually given by the equation

$$E = [at + 10^{-2}\ \tfrac{1}{2}bt^2 + 10^{-5}\ \tfrac{1}{3}ct^3] \times 10^{-6} \text{ volt}, \tag{20.54}$$

supposing that one of the junctions is at 0° C, the other at t° C. A few data are given in Table 55.

From (20.54) we find (neglecting c)

$$a = (\Pi/T)_{t=0}, \qquad \sigma_2 - \sigma_1 = bT.$$

It is interesting to note that the coefficients a and b in some cases have opposite signs. Because of the parabolic character of the formula (20.54), as the temperature is increased the e.m.f. rises to a

maximum, then declines again, and finally reverses its sign. For instance, in the case of Cd–Pb the reversal takes place at about 300° C.

TABLE 55

THERMOELECTRIC E.M.F.

(1)	(2)	Range in °C		a	b	c
		From	To			
Ag	Pb	0	200	3.34	0.85	
Al	Pb	0	200	0.50	0.17	
Au	Pb	0	200	2.90	0.93	
Bi	Pb	0	100	−74.4	3.2	
Cd	Pb	0	200	2.62	−1.79	
Cu	Pb	0	100	2.76	1.22	
Fe	Pb	−230	100	16.65	−2.97	−26.75
Ni	Pb	0	200	−19.07	−3.02	
Pt	Pb	0	100	− 1.79	−3.46	12.6
Sb	Pb	0	100	35.6	14.5	
W	Pb	0	100	1.59	3.4	
Zn	Pb	0	250	3.18	0.11	

Very large thermoelectric e.m.f.'s are observed in circuits composed of semi-conductors (Table 56).

TABLE 56

THERMOELECTRIC E.M.F. IN SEMI-CONDUCTORS

(1)	(2)	Range in °C		a	b
		From	To		
Bi_2O_3	Pb	500	800	1 946	−186
Co_3O_4	Pb	200	1200	629	− 22.1
Cr_2O_3	Pb	950	1285	− 704	43.2
CuO	Pb	170	850	− 1 029	171
PbO	Pb	250	390	−48 300	11 720
Si	Pb	−200	350	− 408	− 47
ZnO	Pb	355	1350	− 735	25.9

As to the Thomson coefficients, their temperature dependence can be represented by the empirical formula

$$\sigma = [\alpha + 10^{-2}\beta t + 10^{-5}\gamma t^2] \times 10^{-6} \text{ volt deg}^{-1}. \qquad (20.55)$$

It is apparent from Table 57 that the Thomson effect is positive in some metals and negative in others.

TABLE 57

THOMSON EFFECT

Metal	Range in °C		α	β	γ
	From	To			
Ag	−123	127	−1.17	−0.50	
Al	− 13	119	−0.04	+0.475	
Au	−100	103	−1.49	−0.44	
Bi	+ 25	32	+6.76	+2.8	
Cu	− 60	127	−1.42	−0.74	
Fe	− 51	115	+4.00	+8.4	
Pb	−153	117	+0.61	+0.221	−0.38
Pt	− 72	128	+9.10	−0.475	+4.75
Zn	−173	40	−2.74	−1.15	

Only the order of magnitude of the constants in Tables 55, 56, and 57 is significant: the thermoelectric power is highly sensitive to the purity and mechanical treatment of the substances and shows considerable variation in different samples of the same material. Nevertheless, it is possible to test the thermodynamical relation (20.50) by carrying out on the same sample the measurement of the e.m.f. and the calorimetric determinations of Π and σ. The agreement is very good, as appears from the examples in Table 58.

TABLE 58

TEST OF THERMODYNAMICAL RELATIONS

Metals	$\frac{\Pi}{T}$	$\frac{dE}{dT}$	Reference	$\frac{\sigma_2 - \sigma_1}{T}$	$\frac{d^2E}{dT^2}$	Reference
	In 10^{-6} volt			In 10^{-8} volt		
Cu—Pt	3.66	3.67	(1)	3.0	3.6	(2)
Cu—Fe	−10.16	−10.15	(1)	2.0	2.7	(2)
Cu—nickeline	18.90	18.88	(1)	6.01	6.28	(2)
Cu—German silver	25.25	25.22	(1)	3.92	3.79	(2)

[1] Borelius, Ann. Physik 56, p. 388, 1918.
[2] Berg, Ann. Physik 32, p. 477, 1910.

Recent measurements of the Thomson coefficient at very low temtemperatures [1] showed that σ vanishes in supraconductors and conforms to eq. (20.53) in non-supraconductive metals.

Let us now find the connection between the Peltier coefficient Π_{12} (or the thermoelectric power Π_{12}/T) and the difference of potentials $\Omega_1 - \Omega_2$ which we calculated in sections 109 and 112 from the electron theory of thermoelectricity. We must bear in mind, however, that in its present form this theory cannot yet account for the detailed phenomena and gives correctly only the order of magnitude of the thermoelectric power. The results of Chapter XVII refer to *open* chains, but, if we take the case of a closed circuit (Fig. 62) with a very large resistance, the current will be very weak and potentials compensating the thermoelectric forces will be built up, practically, to the same extent as in the open circuit. Starting from eq. (20.46), we can apply to the heat function the expressions it has in equilibrium. We begin with the case when *the electron gas is non-degenerate* obeying eqs. (17.01) and (17.02) of the classical perfect gas. The heat function has then the expression $\chi = c_p T + u_0 + f\Omega$, so that we obtain, taking into consideration (17.13),

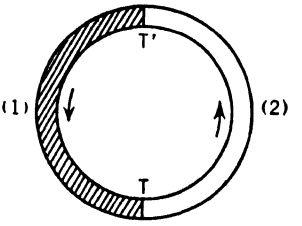

FIG. 62.—Thermoelectric couple.

$$\Pi_{12} = \Omega_2 - \Omega_1 = \frac{kT}{e} \log \frac{z_2}{z_1}. \tag{20.56}$$

It was mentioned in section 109 that this expression applies only to semi-conductors. As $k/e = 86 \times 10^{-6}$ volt deg^{-1}, this would imply that log (z_2/z_1) for some of the substances of the Table 56 is of the order of magnitude 20, whence z_2/z_1 would be about 5×10^8. While it is within reason that a semi-conductor should have an electronic density 10^8 times smaller than that of lead, the signs of a in Table 56 offer a greater difficulty. They seem to indicate that in some of the semi-conductors the carriers of the electric current have a positive charge. As we shall see in the next section this difficulty is not quite so baffling as it was a few years ago.

Turning to the case of the *degenerate electron gas*, we shall make use of the equation $\varphi_2 = \varphi_1$, from which the results of the section 112 were obtained. In view of the relation $\varphi = \chi - Ts$, we can write

[1] Borelius, Keesom, and Johansson, Comm. Leiden, 196a; Borelius, Keesom, Johansson, and Linde, ibidem, 217a, b, c.

$f\Pi_{12} = \chi_2 - \chi_1 = T(s_2 - s_1)$. Hence with the help of eq. (17.33) we obtain the formula due to Sommerfeld

$$\Pi_{12} = \frac{\pi^2}{2}\left(\frac{kT}{e}\right)^2\left[\frac{1}{\Omega_{i2}} - \frac{1}{\Omega_{i1}}\right],$$

or

$$\frac{\Pi_{12}}{T} = 3.67 \times 10^{-8}\, T\left(\frac{1}{\Omega_{i2}} - \frac{1}{\Omega_{i1}}\right) \text{volt deg}^{-1}. \qquad (20.57)$$

For the combination lead-silver the formula (with the data of Table 55) gives $\Pi_{12}/T = 0.86 \times 10^{-8}$ volt deg^{-1}, which is of the right order of magnitude. However, the electron theory, in its present form, is incomplete as it does not account for the phenomena quantitatively.

According to eq. (20.50), the e.m.f. is obtained from the thermoelectric power by the relation

$$E = \int_{T'}^{T} \frac{\Pi_{12}}{T}\, dT.$$

Intimately connected with thermoelectricity are the so-called *galvanomagnetic and thermomagnetic effects* describing the influence of a magnetic field on the phenomenon of electric conduction. The scope of this book does not permit us to enter into their discussion, and we refer the reader interested in the subject to its analysis in a paper by Professor Bridgman.[1]

140. Semi-conductors. The difference between metallic conductors and semi-conductors is not only quantitative but also qualitative. The *conductivity of metals* (in the range about 0° C) has numerical values between 10^{15} and 10^{17} abs e-s and is inversely proportional to the absolute temperature

$$\lambda \propto 1/T,$$

so that it has a negative temperature coefficient. On the other hand, in *semi-conductors* λ is only of the order 10^4 to 10^{13} and its temperature dependence can be best represented by the law[2]

$$\lambda = \lambda_0 \exp(-\alpha/T) \qquad (20.58)$$

with a positive temperature coefficient.

Recent work on the quantum theory of electrons in metals[3] has

[1] P. W. Bridgman, Phys. Rev. **24**, p. 644, 1924.
[2] W. Voigt, Krystallphysik, 1910; E. Engelhard, Ann. Physik **17**, p. 501, 1933.
[3] A. H. Wilson, Proc. Roy. Soc. **133**, p. 458; **134**, p. 277, 1931.

greatly contributed to our understanding of the peculiarities of semiconductors. As a part of the argumentation can be given a thermodynamical guise,[1] we shall outline here its main ideas, even though the experimental data for testing the results are extremely meager.

While treating electron clouds in metals in Chapter VII, we assumed that the electrons are free, actually implying in these words two different assumptions. In the first place, the free electron does not belong to any particular atom; it is shared by all atoms and can travel from one end of the conductor to the other. In the second place, we assumed that the energy levels of the free electrons can be calculated, as if the atoms were absent and as if the electron gas were contained in an empty box. It is of particular importance that the energy levels in our calculation were distributed practically continuously: any small energy increment could raise a few of the electrons to a higher level. We shall show now that electrons, which are free in the first sense, need not necessarily be free in the second, and that in this case they do not contribute to the conductivity, they are not *conduction electrons*.

To fix our ideas let us consider two elements, the one divalent, the other monovalent. The free *divalent atom* has two valency electrons which, in their normal or s-states, have the same energy and differ only by the orientation of their spins. There are no other states of the same, or nearly the same, energy available: just as many s-states as electrons. The next higher electron levels belong to the first excited or p-state and have a considerably larger energy. It is different with the *monovalent atom*; its single valency electron can assume a new quantum state without change of energy, simply reversing its spin: there are twice as many s-states as electrons. When Z atoms are brought together to form a crystal lattice, we know from general mechanical principles the following two facts. (1) The number of quantum states remains the same. The Z atoms had in their free condition $2Z$ s-states; therefore, the number of s-states in the crystal is also $2Z$. (2) While the s-states of the free atoms had all the same energy level, this level is split up in the crystal owing to the forces of interaction between the atoms. In general it is replaced by $2Z$ slightly different levels lying close together. In short, to the s-states of the free atoms there corresponds in the crystal an s-band of closely crowded levels (Fig. 63*a*).

The distribution of electrons over the states of the band is very different in the cases of monovalent and divalent elements. In

[1] R. H. Fowler, Phys. Zs. Sovjetunion 3, p. 507, 1933.

monovalent elements there are only half as many electrons as quantum states. Because of the exclusion principle, there can be only one electron in each level so that, at $T = 0$, the electrons would fill the lower half of the band. At finite temperatures, they can spread out into the upper half. These are the conditions of freedom, in the second sense mentioned above, which formed the basis of the electron theory of section 111. It is immaterial that the band has an upper limit because the electron gas is under ordinary conditions largely degenerate and the overflow above the lower half is but small. On the other hand, in *divalent elements*, there are in the *s*-band exactly as many levels as electrons. Supposing that the excited states (forming

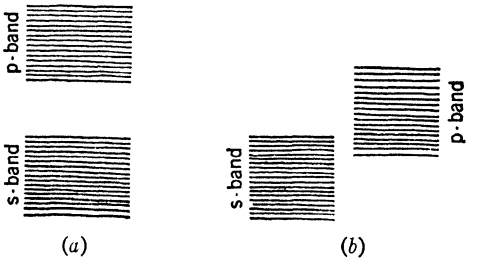

FIG. 63.—Position of *s*- and *p*-bands in (*a*) insulators, (*b*) metallic conductors.

the *p*-band) lie so high that they are unattainable at ordinary temperatures, each state is occupied by an electron: the electrons are restricted to their positions in the band, they are "bound electrons" in the second sense.[1]

What bearing have these facts on the problem of electric conduction? From the point of view of the quantum theory, the mechanism by which an electromotive force produces a current is *redistributing the electrons over the quantum states.* According to the above analysis, such a redistribution is possible in the case of a monovalent element because it possesses plenty of unoccupied levels of accessible energy. A monovalent element is, therefore, always a conductor (provided its electrons are "free in the first sense"). On the other hand, a divalent crystal may be either an insulator or a conductor, even when its electrons are shared by the whole system. When the *p*-band of excited levels lies so high as to be inaccessible (Fig. 63*a*) the electrons completely fill the *s*-band, they are "bound electrons" and their redistribution is impossible: the crystal is then an insulator. On the con-

[1] Interchanges of electrons need not be considered since they do not lead to a new state of the system.

trary, when the p-band lies low and partially overlaps with the s-band (Fig. 63b), it can take the overflow of electrons so that they can be redistributed: the crystal is a metallic conductor.

In this way, the quantum theory gives us a simple explanation of why some substances are metals, others dielectrics. It has, moreover, the great advantage that the several kinds of semi-conductors can be easily fitted into the picture.

(A) *Intrinsic semi-conductors.* Suppose that the p-band of excited states lies neither very high nor so low as to overlap with the s-band, but has an intermediate position (Fig. 64a). We call $\Delta\epsilon$ the energy difference between the lowest p-levels and the highest s-levels. We consider the case that, at $T = 0$, the s-band is completely filled with electrons (as in the preceding example of divalent elements). At higher temperatures, there is the possibility of an electron spontaneously leaving the s-band and rising to one of the p-levels. We assume that $\Delta\epsilon$ is small enough for the probability of such a rise being appreciable at room temperature, so that the number of electrons belonging to the p-band is z_- per unit volume of the crystal. These z_- electrons are free carriers of conductivity because there are plenty of unoccupied states in the vicinity of their energy levels. Because of their removal, there appears in the s-band an equal number ($z_+ = z_-$) of unoccupied levels or "holes." It was pointed out by Peierls [1] that the formulas of the quantum theory can be given the following interpretation. *The "holes" behave in every way as if they were free carriers* similar to the electrons but having the opposite (positive) charge. In this way we arrive at the following model of an intrinsic semi-conductor: it contains two clouds of conductive carriers, the cloud of free negative electrons (G_-) and the cloud of "free (positive) holes" (G_+). The "bound electrons" (G_B) of the s-band can be left out of consideration as far as conduction phenomena are concerned.

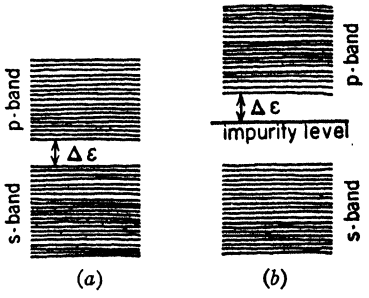

FIG. 64.—Position of s- and p-bands in (a) intrinsic, (b) impurity semi-conductors.

A free electron of the p-band may, of course, drop into a vacancy ("hole") of the s-band and so become a bound electron. This process can go also in the opposite direction and can be described in the sym-

[1] R. Peierls, Zs. Physik 53, p. 255, 1929. Compare also: Bronstein, Phys. Zs. Sovjetunion 2, p. 28, 1932.

bols of a chemical reaction as $G_- + G_+ - G_B = 0$. The equation of equilibrium is, therefore, according to (17.09),

$$\varphi_- + \varphi_+ - \varphi_B = 0.$$

The concentrations of free electrons and of free holes are very small so that both clouds can be regarded as non-degenerate in the sense of Chapter XVI. We shall assume, as a first approximation, that they obey the equations of classical perfect gases. On the other hand, the bound electrons are completely degenerate, and their thermodynamic potential is reduced to a constant (section 111), namely the mean energy level from which the transitions take place. If we measure all energies from this level we can ignore φ_B altogether and have the same conditions as in the case of equilibrium of positive and negative electrons. Therefore, we can apply eqs. (19.28) and (19.29) of section 128 with the only difference that here the heat of reaction is $\Delta\varepsilon$ [1]

$$z_- = 4.9 \times 10^{15} T^{3/2} \exp(-11\,600\Delta\varepsilon/2T) \qquad (20.59)$$

(if $\Delta\varepsilon$ is expressed in electron-volts), a reasonable result as we shall see below.[2] Since the electrons and "holes" are treated as classical perfect gases, the electric conductivity can be computed by means of the Drude-Lorentz formula which was derived precisely under this assumption: $\lambda = \frac{4}{3}e^2(2\pi M_e kT)^{-1/2} lz$. The mean free path l is known to be inversely proportional to the temperature, $l = l_{20} \cdot 293/T$ (l_{20} being the value at 20° C). Substituting the numerical values of M_e and k, we can write, therefore,

$$\lambda = 1.01 \times 10^5 T^{-3/2} l_{20}\, z. \qquad (20.60)$$

Using the expression (20.59), and seeing that there are two kinds of carriers, we obtain

$$\lambda = 1.0 \times 10^{21}\, l_{20} \exp(-5800\Delta\varepsilon/T). \qquad (20.61)$$

As l_{20} is of the order 10^{-6} cm, the expression is of a reasonable order of magnitude when $\Delta\varepsilon$ is of the order 0.1 e-v.

(B) *Impurity semi-conductors.* There exist substances which are insulators in their pure states but semi-conductors when impure. Often as small an admixture of foreign atoms as 1 in 10^5, or even less,

[1] Already J. Koenigsberger (Jahrb. Radioaktiv. 4, p. 158, 1907) suggested an exponential dependence of z on $1/T$.

[2] A. H. Wilson (loc. cit.) does not treat the electrons as a perfect gas. His formula for z is a little more general, differing from ours by a factor k/β, where β measures the tightness of binding of the electrons and is a characteristic constant of the material.

is sufficient to produce an appreciable conductivity. Cuprous oxide (Cu_2O), the only semi-conductor investigated with modern accuracy, belongs to this class. The impurity on which the conduction of Cu_2O depends is free oxygen: it has been shown[1] that the conductivity of this material is lowered by glowing in vacuo and increased by heating in an oxygen atmosphere. The interpretation in terms of our model is as follows: conduction electrons in the p-band are supplied by the impurity atoms. The distance between the p- and s-bands is so large that in the pure substance the p-band would be empty. On the other hand, each impurity atom possesses an electron which can be more easily separated because its energy level is only little ($\Delta\varepsilon$) below the lowest levels of the p-band (Fig. 64*b*). We denote by z_- the number of conduction electrons in the p-band, by z_{i+} the number of ionized, and by z_i of neutral, impurity atoms. In analogy with the preceding case, the equation of reaction can be written $G_- + G_{i+} - G_i = 0$, and the equation of equilibrium $\varphi_- + \varphi_{i+} - \varphi_i = 0$. We regard again the conduction electrons as a classical perfect gas and use for it the expression (19.04). As to $\varphi_i = u - Ts + pv$ of the impurity atoms, they must be considered as stuck in the crystal lattice and having a negligible thermokinetic motion:[2] therefore, $u = u_0$, $pv = 0$, while their only entropy is the entropy of mixing given by eqs. (15.03) of section 98 or (11.39) of section 80, so that $s_{i+} - s_i = -R \log (z_{+i}/z_i)$. Substituting the numerical values of the chemical constant and of k,

$$\log_{10}(z_- z_{i+}/z_i) = 15.69 + \tfrac{3}{2}\log_{10} T - 5040\Delta\varepsilon/T,$$

or

$$z_- = 7.00 \times 10^7 \sqrt{z_i} T^{3/4} \exp(-5800\Delta\varepsilon/T). \qquad (20.62)$$

Vogt[3] and Engelhardt measured the coefficient of the exponential (i.e. $7.00 \times 10^7 \sqrt{z_i} T^{3/4}$ in our theory) and obtained values between 1.5×10^{17} and 9.4×10^{19} in different samples. This would give for z_i numbers from 1×10^{16} to 4×10^{20}, or from 4×10^{-7} to 2×10^{-2} impurity atoms per molecule of Cu_2O. The measured $\Delta\varepsilon$ was about 0.65 e–v. The conductivity, as obtained from (20.60), is

$$\lambda = 7.0 \times 10^{12}\, z_i^{1/2} T^{-3/4} l_{20} \exp(-5800\Delta\varepsilon/T). \qquad (20.63)$$

(C) *Light-sensitive semi-conductors.* There exist substances whose conductivity increases many times when they are exposed to light,

[1] R. Engelhardt, *loc. cit.*

[2] A more rigorous statement is that the impurity atoms have the same thermokinetic motion whether they are ionized or not, so that the *differences* in u and pv drop out of the equation.

[3] W. Vogt., Ann. Physik 7, p. 183, 1930.

the best-known example being selenium. This case also fits readily into the model of Fig. 63*a*. Here the *p*-band lies so high that the number of its electrons is negligible in the dark. However, when light of sufficiently high frequency is absorbed by the crystal, it raises electrons into the *p*-band by photoelectric action. The return into the *s*-band requires a radiative transition and may be a very slow process, thus assuring an appreciable density of conduction electrons.

One of the most important aspects of the theory outlined above is that it provides a new type of positive carriers of electric conduction: the "free holes" of the *s*-band. We have considered under (B) impurities which supply free electrons. There may exist other impurities which have an affinity for electrons and are able to bind them, thus producing "holes". In this way some conductors may have an excess of negative, others of positive, carriers. More important still, in the more accurate theory the electrons and "holes" are not regarded as entirely free. The binding of the two kinds of carriers is different, and, for this reason, there is an asymmetry in their actions, even if they are present in equal numbers. It was always emphasized by E. H. Hall that the peculiarities of the effect bearing his name could not be explained without an assumption of this sort. The same hypothesis would be helpful in accounting for the great variations in the sign of the thermoelectric e.m.f. and of the Thomson coefficient.

CHAPTER XXI

THE DIRECTION OF THERMODYNAMICAL PROCESSES

141. General remarks. General rules predicting the direction in which a process is influenced by outer forces are very desirable from a practical point of view. They may offer a quick orientation in the workings of new experimental arrangements and so facilitate their theoretical and practical understanding. This applies to thermodynamics even more than to other parts of physical science because the thermodynamical treatment is more abstract and formal and less accessible to visualization. The attempts to establish such rules, with respect to thermodynamical processes, were all influenced, directly or indirectly, by the famous *principle of electrodynamics* enunciated in 1833 by Lenz[1]: "When a force acting on a primary electric current induces a secondary current, the direction of this secondary current is such that its electrodynamical action opposes the acting force."

An analogous *principle of thermodynamics* was formulated by LeChatelier[2] in 1884 and in an extended form by Braun[3] in 1887. Their procedure was essentially inductive (although Braun included a few formulas in his paper): they reviewed a large number of examples which they tried to state in a form roughly analogous to Lenz's principle. They claimed that all these examples could be regarded as special cases of a general rule which they proceeded to formulate. However, this formulation was so vague that it was impossible to apply the rule without ambiguity. This fact was first pointed out by Raveau[4] and Ehrenfest[5] and has been generally accepted since. It will serve no purpose to mention here the form they gave to their principle, but it is well to reproduce two of the examples from which it was derived.

[1] H. F. Lenz, St. Petersburg Acad. of Sci. 29, XI, 1933; reprinted: Ann. Phys. u. Chem. 31, p. 483, 1934.

[2] H. LeChatelier, Comptes Rendus 99, p. 788, 1884.

[3] F. Braun, Zs. phys. Chem. 1, p. 269, 1887; Ann. Physik 33, p. 337, 1888.

[4] M. C. Raveau, J. Phys. 8, p. 572, 1909.

[5] P. Ehrenfest, J. Russ. Phys. Soc. 41, p. 347, 1909; Zs. phys. Chemie, 77, p. 227, 1911.

(A) *Influence of pressure on solubility.* Substances whose solubility increases with pressure dissolve (at constant temperature) with volume contraction; those which have the opposite pressure dependence dissolve with volume dilatation. This fact (although not new) was rediscovered by Braun a little earlier and was the starting point of his considerations.

(B) *Influence of temperature on compressibility.* Suppose that we compress a gas, increasing the pressure under which it stands by the small amount Δp. We can do this in two different ways: (1) keeping the temperature constant (T = const) with the help of a heat bath; (2) "leaving the gas to itself" (i.e. adiabatically, S = const). The compressibility is smaller in the second case

$$\left|\frac{\partial v}{\partial p}\right|_S < \left|\frac{\partial v}{\partial p}\right|_T. \tag{21.01}$$

We selected the two examples so as to show the heterogeneity of the cases considered by LeChatelier and Braun. The first involves only *three* parameters of the system: pressure, volume, and concentration of the saturated solution. In the second we have an interplay of *four* parameters: pressure, volume, temperature and entropy. The closer analysis will show that the two cases are also quite different in their mathematical characteristics. In fact, Braun himself discussed the two types represented by them separately but claimed, in the end, that they are reducible to the same principle. Without maintaining that all possible examples belong to the types (A) or (B), we assert that *the principle of LeChatelier-Braun must be resolved into at least two different and unconnected rules* which we shall analyze in the next two sections.

142. Displacement of equilibrium involving transformation of matter. It will be noticed that example (A) of the preceding section is only a special case of the first of the two laws stated at the end of section 59. These laws, in their turn, are consequences of eqs. (6.51) and (6.53) derived from the fundamental conditions of equilibrium, as stated in section 40, namely:

$$\delta U = 0, \tag{21.02}$$

with the subsidiary conditions

$$\delta S = 0, \qquad \delta V = 0. \tag{21.03}$$

The gist of the argument which led in Chapter VI to the explicit equilibrium conditions is as follows. The variables S and V possess

the *additive property*. In a heterogeneous system the total entropy and the total volume are sums of the contributions of the several phases

$$S = \sum_j S^{(j)}, \qquad V = \sum_j V^{(j)}. \tag{21.04}$$

As was shown in section 40, this property together with the conditions (21.02) and (21.03) immediately leads to the uniformity of the parameters T and p, conjugate to S and V

$$\left.\begin{aligned} T^{(1)} &= T^{(2)} = \ldots = T, \\ p^{(1)} &= p^{(2)} = \ldots = p. \end{aligned}\right\} \tag{21.05}$$

The generalization for systems depending on other variables than S and V is obvious. For instance, in Chapter XX we discussed magnetization and electrostatic polarization. We considered systems placed in homogeneous magnetic or electric fields of the strength H or E (i.e. being homogeneous and having this strength when the system is not there). The element of work was denoted by $-HdM$, $-EdP$, where M and P are the magnetic and electric moments of the system in the direction of the fields. When the system consists of several phases, the equations analogous to (21.05)

$$H^{(j)} = H, \qquad E^{(j)} = E,$$

are a matter of course since all the phases are placed in the same homogeneous field. Moreover, the moments have the additive property

$$M = \sum_j M^{(j)}, \qquad P = \sum_j P^{(j)}.$$

Finally, it is known from the electromagnetic theory that in equilibrium

$$\delta M = 0, \qquad \delta P = 0.$$

The set of equations governing the properties of these variables is formally identical with that applying to the parameters S, V.

Passing to the general case we assume a heterogeneous system which has the following properties:

(1) Each phase (j) is described by the variables

$$X_0^{(j)}, X_1^{(j)}, \ldots X_n^{(j)},$$

which *have the additive property*

$$\sum_j X_i^{(j)} = X_i. \tag{21.06}$$

In particular let $X_0^{(j)}$ stand for the entropy $S^{(j)}$.

(2) The differential of the internal energy has the form

$$dU^{(j)} = \sum_{l=0}^{n} y_l^{(j)} dX_l^{(j)}. \tag{21.07}$$

We call the coefficient $y_l^{(j)}$ the *generalized force* conjugate to the additive variable $X_l^{(j)}$. The temperature $T^{(j)} = y_0^{(j)}$ is classed as a generalized force;[1] the pressure p must be counted as a negative force ($p = -y_1^{(j)}$).

(3) The equilibrium of the system is determined by

$$\delta U = 0,$$

with the subsidiary conditions

$$\delta X_l = 0, \quad (l = 0, 1, \ldots n). \tag{21.08}$$

(4) The chemical composition and mass of each phase are determined by the mol numbers $N_k^{(j)}$ of its components ($k = 1, 2, \ldots \beta$). The variations $\delta N_k^{(j)}$ are given by the reactions possible in the system (section 42): $\delta N_k^{(j)} \propto \nu_k^{(j)}$,

$$\sum_j \sum_k \nu_k^{(j)} G_k^{(j)} = 0. \tag{21.09}$$

The explicit equilibrium conditions can be obtained exactly in the same way as in section 40 where a less general case was treated. The procedure need not be repeated here but only indicated in its bare outline. The problem is broken up in two partial ones: first, changes of composition and mass are excluded ($\delta N_k^{(j)} = 0$). The variation of the internal energy has then the form

$$\delta U = \sum_j \sum_l y_l^{(j)} \delta X_l^{(j)} = 0, \tag{21.10}$$

with the subsidiary conditions (21.08). This gives immediately (as in section 40)

$$y_l^{(j)} = y_l, \qquad (l = 0,1, \ldots n). \tag{21.11}$$

The generalized forces are uniform throughout the system. To treat the second partial problem, we introduce the generalized thermodynamic potential

$$\Phi^{(j)} = U^{(j)} - \sum_l y_l^{(j)} X_l^{(j)}, \tag{21.12}$$

[1] As compared with (2.02) the coefficients y are defined with the opposite sign.

whose differential is, according to (21.07),

$$d\Phi^{(j)} = -\sum_i X_i^{(j)} dy_i^{(j)}, \tag{21.13}$$

so that it must be regarded as a function of the variables

$$\Phi^{(j)} = \Phi^{(j)}(y_0^{(j)}, \ldots y_n^{(j)}; N_1^{(j)}, \ldots N_\beta^{(j)}).$$

We denote the *partial thermodynamic potentials*, as before,

$$\overline{\varphi}_k^{(j)} = \frac{\partial \Phi^{(j)}}{\partial N_k^{(j)}}. \tag{21.14}$$

When the generalized forces y_i are kept constant, the conditions (21.02) and (21.08) can be replaced by

$$\delta\Phi = 0.$$

for the same reasons which were adduced in section 36.

We consider only variations in which $y_i = \text{const}$; the condition $\delta\Phi = 0$ is then valid and can be written in the form

$$\Delta\Phi \equiv \sum_j \sum_k \nu_k^{(j)} \overline{\varphi}_k^{(j)} = 0. \tag{21.15}$$

The partials of $\Delta\Phi$ with respect to the generalized forces are, according to (21.13),

$$\frac{\partial \Delta\Phi}{\partial y_i} = \Delta X_i, \tag{21.16}$$

where

$$\Delta X_i = \sum_j \sum_k \nu_k^{(j)} \frac{\partial X_i}{\partial N_k^{(j)}}$$

is the change of the variable X_i (for the whole system) in the transformation or reaction (21.09)

Apart from the generalized definition of $\Phi^{(j)}$ the condition (21.15) is precisely the same as (6.50) of section 42. The consequences derived in Chapters VII to XI are based on this condition and remain true. In particular, applying the generalized form of the thermodynamic potential to the expressions (9.13) or (11.15) of the equilibrium constant, we find from (21.16)

$$\frac{\partial \log K}{\partial y_i} = \frac{\Delta X_i}{RT}. \tag{21.17}$$

The increase of the generalized force y_i produces a displacement of equilibrium attended by a process (transformation or chemical reaction) *in which the change of the conjugate variable ΔX_i is positive.*

In addition to example (A) of Braun's (preceding section), we shall illustrate this principle by considering the influence of a magnetic field on the equilibrium: $y_l = H$, $X_l = M$,

$$\frac{\partial \log K}{\partial H} = \frac{\Delta M}{RT}. \tag{21.18}$$

The increase of the magnetic strength of field produces a displacement of equilibrium in which the magnetic moment of the system (in the direction of the field) is increased. The more paramagnetic phases and components increase their mass at the expense of the less paramagnetic. Since supraconductors are classed as diamagnetics, this includes also the equilibrium between metals in the normal and the supraconductive states: a magnetic field makes the normal phase increase at the expense of the supraconductive. These phenomena are manifestations of the same causes which make an inhomogeneous magnetic field suck in paramagnetic and push out diamagnetic bodies. In a similar way, an electric field favors stronger dielectrics at the expense of weaker ones.

143. The restricted LeChatelier–Braun principle. (Influence of secondary forces.) Example (B) of section 141 is a true analogue of Lenz's principle: when the temperature is allowed to change, it opposes the acting force of compression. This is in keeping with the expression (21.07) in which the temperature is treated as a generalized force. Another example of the same sort is the longitudinal compression of of a solid elastic bar with uniform cross-section. It can be compressed by a longitudinal force p_1 in two ways: (1) keeping the forces (of pressure) on the lateral surfaces constant (p_2 = const); (2) keeping the lateral dimensions constant (l_2 = const) and preventing a bulging out of the cross-section. If the length of the bar is denoted by l_1, it is known from the theory of elasticity that

$$\left|\frac{\partial l_1}{\partial p_1}\right|_{l_2} < \left|\frac{\partial l_1}{\partial p_1}\right|_{p_2}. \tag{21.19}$$

Here, too, the secondary (lateral) force, if permitted to change, opposes the acting (longitudinal) force. As it is sometimes said, *the secondary forces help the system to resist the acting force.*

The analytical connection of the examples of this type with the foundations of thermodynamics was cleared up by Ehrenfest.[1] We shall call the rules pertaining to class (B) *the restricted LeChatelier-*

[1] See footnote on p. 375.

Braun principle. Ehrenfest himself refrained from formulating the principle,[1] but the enunciation given below is based on his analysis.

Unlike our treatment in section 142, we may restrict our considerations to *homogeneous* systems described by the parameters $X_0, X_1, \ldots X_n$ so that the differential of the internal energy has the expression

$$dU = y_0 dX_0 + y_1 dX_1 + \ldots + y_n dX_n, \tag{21.20}$$

defining the generalized forces $y_0, y_1, \ldots y_n$. As dU is an exact differential, the following reciprocity relations hold:

$$\frac{\partial y_l}{\partial X_i} = \frac{\partial y_i}{\partial X_l}. \tag{21.21}$$

In addition to them, we shall assume the validity of the inequalities

$$\frac{\partial y_l}{\partial X_l} \geqq 0, \tag{21.22}$$

which are often called *conditions of stability.* If the variables X are those of section 142, the first of these conditions is $\partial T/\partial S \geqq 0$, which expresses the fact that the temperature rises when heat is imparted to the system. As to the condition relating to the volume ($X_1 = V$), it must be borne in mind that $y_1 = -p$, so that $\partial p/\partial V \leqq 0$. In fact the sign generally given to the hydrostatic pressure is an anomaly among the generalized forces. In hydrodynamics and elasticity the tension, and not the pressure, is taken as positive. The inequality $\partial p/\partial V \leqq 0$ was discussed at length in section 5, where it was shown to be a necessary condition of stability. The same applies in all cases where the generalized force y_l can be envisaged as different in the system and in the environment. If the condition (21.22) were not fulfilled, the difference would tend to increase and a stable equilibrium between system and environment would be impossible. However, this argument does not apply to cases like magnetization and polarization (sections 134 and 138) where the generalized forces are defined as H and E, as they would be in the absence of the system. Here the validity of the conditions (21.22) is simply a coincidence, as far as thermodynamics is concerned. As a matter of fact, diamagnetic bodies form an exception to the rule: for them $\partial H/\partial M < 0$, if M is the magnetization in the direction of the field.[2] Fortunately, the principle we

[1] The reason for this was that he did not segregate class (A) into a separate principle and was looking for a single rule embracing all cases. Planck (Ann. Physik 19, p. 759, 1934) also failed to draw the distinction.

[2] It would not help to define $y_l = -M$ because this would reverse the sign of $y_l dX_l$ in eq. (21.20).

are going to formulate need not be amended because of diamagnetics (see below). Sometimes it is said that the inequalities (21.22) hold because the internal energy U has its minimum in equilibrium. But such a conclusion may not be drawn when the minimum is contingent upon subsidiary conditions of the type (21.03). In this case, the equations of stability (21.22) are not, in general, invariant with respect to transformations of coordinates.

All we shall need for the proof of the principle are the relations (21.20), (21.21), and (21.22). It is immaterial whether the parameters X_l have the additive property or not; therefore, *we drop the requirement of additivity.* We are now ready for the enunciation.

(I) *Suppose that the system is described by the variables* $X_0, \ldots X_n$ *and the generalized forces* $y_0, \ldots y_n$ *for which eqs.* (21.20) *and* (21.21) *and the inequalities* (21.22) *are satisfied.*

(II) *We keep all the variables* X *constant except two,* X_l *and* X_i, *and we give a primary increment* δy_l *to the force* y_l *which acts directly on its conjugate variable* X_l. *We let this increment change* X_l *in two different ways*:

(*a*) *keeping the (secondary) force* y_i *constant* ($y_i = \text{const}$);

(*b*) *keeping the variable* X_i *constant* ($X_i = \text{const}$) *and allowing the force* y_i *to change.*

(III) *We assert that the primary increment* δy_l *is less effective in case* (*b*)

$$\left(\frac{\partial X_l}{\partial y_l}\right)_{X_i} \leqq \left(\frac{\partial X_l}{\partial y_l}\right)_{y_i}. \tag{21.23}$$

In other words, the secondary force y_i, *if permitted to act, opposes the primary force* y_l.

The proof is simple: the generalized forces y_l and y_i, as all the coefficients of the expression (21.20), are functions of the variables X. But since only X_l and X_i are allowed to change, we need to bring in evidence only these two parameters

$$y_l = y_l(X_l, X_i), \quad y_i = y_i(X_l, X_i). \tag{21.24}$$

We can resolve the second equation with respect to X_i

$$X_i = X_i(X_l, y_i). \tag{21.25}$$

Now $\partial y_l/\partial X_l$ is the reciprocal of $\partial X_l/\partial y_l$, so that the condition (21.23) can be also written

$$\left(\frac{\partial y_l}{\partial X_l}\right)_{y_i} \leqq \left(\frac{\partial y_l}{\partial X_l}\right)_{X_i}. \tag{21.26}$$

According to the rules of partial differentiation

$$\left(\frac{\partial y_l}{\partial X_l}\right)_{y_i} = \left(\frac{\partial y_l}{\partial X_l}\right)_{X_i} + \left(\frac{\partial y_l}{\partial X_i}\right)_{X_l} \cdot \left(\frac{\partial X_i}{\partial X_l}\right)_{y_i},$$

i.e. y_l in (21.24) must be differentiated in so far as it contains X_l explicitly and in so far as it contains it through the medium of X_i. From the second eq. (21.24) we find, as in section 3,

$$\left(\frac{\partial X_i}{\partial X_l}\right)_{y_i} = -\left(\frac{\partial X_i}{\partial y_i}\right)_{X_l} \cdot \left(\frac{\partial y_i}{\partial X_l}\right)_{X_i}.$$

We substitute this, taking into account (21.21)

$$\left(\frac{\partial y_l}{\partial X_l}\right)_{y_i} = \left(\frac{\partial y_l}{\partial X_l}\right)_{X_i} - \left(\frac{\partial y_l}{\partial X_i}\right)^2_{X_l} \cdot \left(\frac{\partial X_i}{\partial y_i}\right)_{X_l}. \tag{21.27}$$

This finishes the proof of the inequalities (21.26) and (21.23) since all three partials $(\partial y_l/\partial X_l)_{y_i}$, $(\partial y_l/\partial X_l)_{X_i}$, $(\partial X_i/\partial y_i)_{X_l}$ are positive because of (21.22).

It will be seen that diamagnetic bodies do not contradict the principle although they do not satisfy the conditions (21.22). In fact, for them $X_l = M$, $y_l = H$ and $(\partial M/\partial X_i) = 0$, since the magnetic moment depends only on H, as was pointed out in section 134. For diamagnetics the second term on the right side of (21.27) vanishes and they fulfill the limiting case of (21.23) corresponding to the sign of equality. It is conceivable, of course, that applications may arise in which the stability conditions (21.23) are not satisfied any more than in diamagnetics but which are not so innocuous and break through the law (21.23). It is obvious how the principle can be extended to take care of such contingencies: one must write the inequality (21.23) for the *absolute values* of the partials and must make the sense ($<$ or $>$) depend on whether $(\partial y_l/\partial X_l)$ and $(\partial y_i/\partial X_i)$ have the same or opposite signs.

144. Intensive and extensive quantities. The principle of LeChatelier-Braun is sometimes brought in connection with the division of physical variables into " Quantitaeten " and " Intensitaeten " proposed by the defunct school of energeticists.[1] This nomenclature is still used by German and Dutch writers and has some relationship to the English terms: *extensive* and *intensive quantities*. As the reader is likely to come across both designations in his

[1] Main proponents: Mach, Ostwald, Helm. Compare G. Helm, Energetik. Leipzig 1898.

study of foreign and domestic literature, it will be well to explain here, briefly, their similarities and dissimilarities.

As defined by Tolman,[1] *extensive* quantities are those which have the additive property, for instance, the variables $X_0, \ldots X_n$ of section 142. Every quantity which is not additive is called by him *intensive.* The division is intended to be exhaustive so that every variable must fall into one of these two classes. It is possible, and often convenient, to use as parameters describing the system not the variables X but simple functions of them (like the reciprocals $1/X$ or the squares X^2) which are not additive. In this case, the system would be described only by intensive variables. It must be said, however, that Tolman's definitions are not universally accepted and that some authors use the term *intensive* in the same sense in which we have used the words *specific quantity* in section 39 (i.e. a homogeneous function of the degree zero in the mol numbers).

On the other hand, the classification into *Quantitaeten* and *Intensitaeten* is not meant to be exhaustive. They are exceptional or preferred variables, and a parameter chosen at random need not belong to either of the two groups. Ostwald and Helm give no sharp definition, saying only that the element of work (section 7) can be represented as a sum of terms, each the product of a "Quantitaet" and an "Intensitaet". It is safe to say that the additive variables X of section 142 (i.e. the extensive quantities) belong to the "Quantitaeten" and the generalized forces y, conjugate to them, to the "Intensitaeten". But it is vague what other parameters (if any) may be classed in these groups. The only practicable suggestion seems to be that of Mesdames Ehrenfest-Afanassiewa and De Haas-Lorentz,[2] who propose to restrict these terms to such variables and conjugate generalized forces which leave invariant eqs. (21.20) and (21.22) of the preceding section.

[1] R. C. Tolman, Phys. Rev. 9, p. 234, 1917.

[2] T. Ehrenfest-Afanassiewa and G. L. DeHaas-Lorentz, Physica 2, p. 743, 1935.

CHAPTER XXII

LIMITATIONS OF THERMODYNAMICS[1]

145. The statistical point of view. The statistical interpretation of the entropy concept was treated in section 30. It was stated there that the entropy of a thermodynamical system can be brought in connection with its probability P by means of Boltzmann's principle (4.67)

$$S = k \log P. \tag{22.01}$$

While we emphasized in section 30 the parallelism between the thermodynamical and the statistical points of view, we shall dwell now on the discrepancies between them which have produced in the last decades a profound change in the outlook of science upon the theory of heat and, especially, upon the second law.

The identification of entropy and probability involves the following difficulty. According to the second law, the entropy of an adiabatically isolated system can never decrease: $\Delta S \geqq 0$. If we leave such a system to itself, its entropy will either increase monotonically or remain stationary. On the other hand, the probability P shows a different behavior. Owing to the interplay of atomic and molecular movements and forces, the system undergoes, continuously, small but erratic changes. In general they occur in the direction of more probable states. However, this is only an average effect: it lies in the nature of the concept of probability that the less probable states are not totally excluded but only less frequent in their occurrence. Therefore, the probability of a system will, occasionally, decrease. In fact, it was rigorously proved by Poincaré[2] that a finite system, subject to the Hamiltonian equations of dynamics, returns again and again to any state through which it once has passed.

When Boltzmann's principle as expressed in eq. (22.01) was first advanced, scientific thought divided itself into two schools. One school

[1] With the kind permission of Yale University Press parts of this chapter were patterned after the exposition by P. S. Epstein, Commentary on the Scientific Writings of J. W. Gibbs, Article *O*, Section 16.

[2] H. Poincaré, Acta Mathematica **13**, p. 1, 1890.

regarded the lack of conformity between thermodynamics and the kinetic theory as a serious objection against the statistical interpretation. The other contended that the principle of the increase of entropy had itself only a statistical validity and was true only in the time average. As Gibbs put it as early as 1876: "The impossibility of an uncompensated decrease of the entropy seems reduced to an improbability." The views of the two schools were brought to a focus in a very interesting polemic between Zermelo [1] and Boltzmann.[2] The wide attention which this discussion received stimulated new work on the subject, and, before long, the controversy was definitely settled in favor of the statistical point of view through the investigations of Von Smoluchowski [3] and of Einstein.[4] These authors showed that deviations from the entropy principle do, actually, occur and can be observed provided the system is sufficiently small. They accomplished this by turning eq. (22.01) into a heuristic method for the treatment of problems lying outside the scope of classical thermodynamics. Let l be one of the parameters describing the state of the system, and let l_0 be its value in the normal state of maximum entropy S. We ask the following question: what is the probability of this parameter assuming a value between $l_0 + \Delta l$ and $l_0 + \Delta l + dl$? Let the entropy, corresponding to $l_0 + \Delta l$, be $S_0 + \Delta S$, where ΔS is, necessarily, negative, S_0 being the possible maximum. Inverting the relation (22.01) between entropy and probability, we find that P must be proportional to $\exp[(S_0 + \Delta S)/k]$. On the other hand, the probability must be also proportional to the interval dl. Therefore, we can write for it

$$P_l\, dl = Ce^{\Delta S/k}\, dl. \tag{22.02}$$

The factor C may depend on the normal values of all the parameters of the system.[5] It is determined by the condition

$$\int P_l\, dl = 1, \tag{22.03}$$

which expresses the fact that the value of l will lie, certainly, in one of the intervals dl.

[1] E. Zermelo, Ann. Physik **57**, p. 485, 1896; **59**, p. 743, 1897.

[2] L. Boltzmann, Ann. Physik **57**, p. 773, 1896; **60**, p. 392, 1897.

[3] M. Von Smoluchowski, Boltzmann-Festschrift, p. 626. Leipzig 1904; Ann. Physik **21**, p. 756, 1906; **25**, p. 205, 1908.

[4] A. Einstein, Ann. Physik **17**, p. 549, 1905; **19**, p. 373, 1906; **33**, p. 1275, 1910.

[5] Strictly speaking, the parameter l must be selected in a definite way to make C depend only on the normal values l_0 and not on the l themselves. We cannot enter here into the rules of selection as they represent a problem of statistical mechanics.

146. Brownian movements. Classical thermodynamics cannot account for the fact that small particles dispersed in a liquid or gas form a permanent suspension, that is to say, float in the medium and are in a state of irregular agitation called Brownian movement. From the point of view of that theory the particle is merely a part of the boundary of the liquid, and its position is determined not by thermodynamical but by dynamical laws. These laws tell us that the position of equilibrium for the particle is its motionless state at the bottom of the vessel. Let us suppose the vessel to be of heat-insulating material so that our thermodynamical system (liquid or gas) is adiabatically isolated. In this case, the dynamical equilibrium of the particle corresponds also to the maximum of entropy of the liquid (or gas). In fact, it would require the energy expenditure $\varepsilon = M'gx$ to raise the particle from the bottom to the height x, g being the acceleration of the gravity field and M' the effective mass of the particle (its true mass minus the mass of the displaced medium). This energy can be supplied only by the liquid (or gas) which undergoes a corresponding loss of internal energy $\Delta U = -\varepsilon$. In general the entropy is expressed by $\Delta S = (\Delta U + \Delta W)/T$; in our particular case, the volume of the liquid remains unchanged when the particle is raised and no work is done by the system ($\Delta W = 0$). Therefore, $\Delta S = -\varepsilon/T$: this entropy change is negative, and the strict point of view on the second law would deny the possibility of the particle being permanently afloat.

On the other hand, the statistical point of view admits the existence of small entropy fluctuations. The probability of the floating particle's being found at a height between x and $x + dx$ is given directly by the formula (22.02)

$$P_x\,dx = Ce^{-\frac{\varepsilon}{kT}}dx = Ce^{-\frac{M'gx}{kT}}dx. \tag{22.04}$$

It is equally easy to find the probability for the particle being in motion. Suppose the components of its velocity c lie between the limits c_x and $c_x + dc_x$, c_y and $c_y + dc_y$, c_z and $c_z + dc_z$ while its kinetic energy is $Mc^2/2$. We conclude, as in the preceding case, that this energy is supplied by the liquid which experiences the changes $\Delta U = -Mc^2/2$, $\Delta S = -Mc^2/2T$. The formula (22.02) gives for the probability of this state of the particle

$$Pdc_xdc_ydc_z = C' \exp(-Mc^2/2kT)dc_xdc_ydc_z. \tag{22.05}$$

If the suspension consists of a large number of identical particles, each having the mass M, the formulas (22.04) and (22.05) determine their numbers z at the height x and in the velocity interval $dc_xdc_ydc_z$.

The first equation can be written

$$z = z_0 \exp(-M'gx/kT), \tag{22.06}$$

where z is the number of particles (referred to unit volume) at the height x, and z_0 at the bottom ($x = 0$). It is identical with the barometric law of Laplace, which was deduced in section 107 in a generalized form starting from the law of perfect gases. We see now that the particles of a suspension also obey the barometric law, and this implies that their osmotic pressure is that of perfect gases: $pv = RT$ or $p = zkT$ (section 66). The simplest way of showing this is to invert the usual form of the derivation of Laplace's formula. At the height x the pressure is higher than at $x + dx$ by the amount dp because of the weight of the particles in the layer dx. This weight is $-dp = zM'gdx$ per unit area. On the other hand, we find from (20.06) $x = -kT \times \log(z/z_0)/M'g$ and $dx = -kTdz/zM'g$, whence $p = zkT$.

The formula (22.05) represents Maxwell's velocity distribution and is equivalent to the caloric equation of state $u = \frac{3}{2}RT + u_0$. This follows immediately from calculating the total kinetic energy of all particles by integrating $\frac{1}{2}M\int\int\int c^2 P dc_x dc_y dc_z$ and keeping in mind that $\int\int\int P dc_x dc_y dc_z = 1$. Of course, the particles have also rotational kinetic energy which is not included in our calculation of u. It is easy to show that its amount is RT per mol, but the above examples will suffice.

Extensive experimental work on suspensions was done by Perrin [1] and Svedberg.[2] These authors tested the barometric formula (20.06) directly, and Maxwell's distribution law (20.05) indirectly, and found both in excellent agreement with experiments.

Brownian movements affect not only particles in a suspension but indeed every movable object. For instance, a delicate torsion balance continuously undergoes small deflections from its zero position. If the directing force is α and the angle of deflection ϑ, the potential energy of the balance becomes $\varepsilon_\vartheta = \frac{1}{2}\alpha\vartheta^2$. As in the case just treated, this energy is taken from the surrounding medium (air) whose internal energy and entropy experience the changes $\Delta U = -\frac{1}{2}\alpha\vartheta^2$, $\Delta S = -\frac{1}{2}\alpha\vartheta^2/T$. Again we find from (20.02) as the probability of a deflection between ϑ and $\vartheta + d\vartheta$

$$P_\vartheta d\vartheta = C \exp(-\tfrac{1}{2}\alpha\vartheta^2/kT)\, d\vartheta. \tag{20.07}$$

[1] J. Perrin, Brownian Movement and Molecular Reality. London 1910.
[2] The Svedberg, Die Existenz der Moleküle. Leipzig 1912.

The mean potential energy of the balance is, therefore,

$$\bar{\varepsilon} = \int_{-\infty}^{+\infty} \varepsilon_\vartheta P_\vartheta d\vartheta.$$

Determining the coefficient from the condition (22.03) we find

$$2\bar{\varepsilon} = \overline{\alpha\vartheta^2} = kT, \tag{20.08}$$

corresponding to equipartition of energy (section 30). Observation on a torsion balance were carried out by Kappler.[1] He found that the distribution of the deflections is accurately represented by the Gaussian curve (20.07). Substituting into (20.08) the measured mean $\overline{\alpha\vartheta^2}$, he obtained an experimental value for k and derived from it (because of $n_A = R/k$) the result $n_A = (6.06 \pm 0.06) \times 10^{-23}$ mol^{-1} for the Avogadro number.

147. Theory of fluctuations. According to classical thermodynamics, any substance is in equilibrium quite uniform and not subject to spontaneous changes. The statistical view on the second law, on the contrary, permits us to put the question as to local deviations from uniformity. Let us focus our attention on a small part of the system, a group of adjacent molecules, and let us calculate the probability that the parameter l has in it an abnormal value. We denote by M_1, M_2 the masses of the small part and of the remaining large part of the system ($M_2 \gg M_1$), by s_0, l_0 the normal specific values of the entropy and of the parameter l. We consider the case, however, when these quantities have in the two parts the slightly abnormal values $s_0 + \Delta s_1$, $l_0 + \Delta l_1$, and $s_0 + \Delta s_2$, $l + \Delta l_2$. The total deviation of entropy is, therefore, $\Delta S = M_1\Delta s_1 + M_2\Delta s_2$, or expanding into a Taylor series with respect to Δl_1, Δl_2 (which we assume to be very small quantities)

$$\Delta S = \frac{\partial s_0}{\partial l_0}(M_1\Delta l_1 + M_2\Delta l_2) + \frac{1}{2}\frac{\partial^2 s_0}{\partial l_0^2}[M_1(\Delta l_1)^2 + M_2(\Delta l_2)^2] + \ldots$$

Since the entropy has its maximum in the normal state, the first term must vanish: $M_1\Delta l_1 + M_2\Delta l_2 = 0$ or $\Delta l_2 = -(M_1/M_2)\Delta l_1$. In the second term $M_2(\Delta l_2)^2 = M_1(\Delta l_1)^2 M_1/M_2$ becomes then negligible, whence

$$\Delta S = \frac{1}{2} M_1(\Delta l_1)^2 \frac{\partial^2 s_0}{\partial l_0^2}. \tag{22.09}$$

The entropy deviation in the small part of the system is expressed

[1] E. Kappler, Ann. Physik 11, p. 233, 1931; 15, p. 545, 1932.

in terms of its own properties. We may, therefore, drop the subscript (1) treating it as if it were alone. Equation (22.02) takes the form

$$P_l\, dl = C \exp\left[\frac{M(\Delta l)^2}{2k}\frac{\partial^2 s}{\partial l^2}\right] dl.$$

The mean quadratic deviation of the parameter l (in the small part of the system) is by definition

$$\overline{(\Delta l)^2} = C\int_{-\infty}^{+\infty} (\Delta l)^2 P_l dl,$$

while C is to be determined from (22.03). It must be remembered that $\partial s^2/\partial l^2$ is necessarily negative: S being a maximum, the deviation can have only the negative sign. Therefore, the integration is easily carried out giving

$$\overline{(\Delta l)^2} = -\frac{k}{M\partial^2 s/\partial l^2}. \tag{22.10}$$

148. Density fluctuations and light scattering. We shall apply this formula to compute the magnitude of the spontaneous density fluctuations in a gas. Let us take as the parameter the molal volume in the small selected portion of the gas: $l = v$. Considering the fluctuations of one parameter only implies that the others drop out in the averaging process, being on the average constant. The question arises, therefore, which other parameter we have to regard as constant in taking the partial of s with respect to v. The answer is simple in this particular case because we know from section 31 that a subsidiary condition of equilibrium is $\delta U = 0$. Unless we want to calculate the fluctuations of the internal energy itself, we must always consider changes at u = const. We have, therefore, for the relative fluctuation

$$\overline{\left(\frac{\Delta v}{v}\right)^2} = \overline{\left(\frac{\Delta \rho}{\rho}\right)^2} = -\frac{k}{Mv^2(\partial^2 s/\partial v^2)_u}, \tag{22.11}$$

where $\rho \propto 1/v$ is the density, whence $\Delta\rho \propto -\Delta v/v^2$. From (4.15), $(\partial s/\partial v)_u = p/T$, the result of the second differentiation at u = const is little different from that at $T = 0$. We may write with a good approximation $(\partial^2 s/\partial v^2)_u = (\partial p/\partial v)_T/T$, or denoting the compressibility $\beta = -(\partial v/\partial p)_T/v$,

$$\overline{\left(\frac{\Delta \rho}{\rho}\right)^2} = \frac{kT\beta}{V}. \tag{22.12}$$

In the case of the ideal gas, $\beta = 1/p$, $V = kZT/p$, Z being the total number of molecules in the considered small portion of the gas. We obtain, therefore,

$$\overline{\left(\frac{\Delta\rho}{\rho}\right)^2} = \frac{1}{Z}, \tag{22.13}$$

as found already by Bernoulli for the fluctuations of independent units (molecules). This formula shows us that the mean relative deviation of the density from its normal value is very small for a large mass of gas but becomes appreciable when the mass decreases. Measuring the density of 1 cm of air ($Z = 2.7 \times 10^{19}$) we are not likely to find any deviation from the norm, as it is in the mean only 2×10^{-10}. However, the deviation is measurable in an air-filled cube whose edge is of the order of a wave length of light (5×10^{-5} cm) because here $Z = 3.6 \times 10^{6}$ whence $1/Z^{1/2} = 0.53 \times 10^{-3}$. There exist, therefore, in the gas numerous condensed and rarefied regions of this size and smaller. This inhomogeneity must produce a scattering action on light passing through the gas, and the amount of scattering to be expected on the basis of the formula (22.12) was computed by Von Smoluchowski [1] and by Einstein.[2]

A simple way of deriving this formula is as follows.[3] The theory of optics gives the following expression for the intensity of light scattered by a small dielectric particle under the angle ϑ from the direction of the incident plane wave (whose intensity is J) and at the distance r from the particle

$$\frac{\Delta J_\vartheta}{J} = \frac{\pi^2 V^2 (\Delta D)^2}{2\lambda_0^4} \cdot \frac{1 + \cos^2\vartheta}{r^2} \tag{22.14}$$

(Rayleigh scattering). ΔD is the difference between the dielectric constants of the particle and of the surrounding medium. It is supposed that ΔD is small; under this assumption the scattered intensity depends only on the volume V of the particle and not on its shape. λ_0 is the wave length of the incident light, as it would be *in vacuo*. The formula applies only to particles whose dimensions are small compared with the wave length. We can regard the spontaneous inhomogeneities of a gas as particles of this sort. Its whole bulk consists of such inhomogeneities lying side by side, but if we focus our attention on one of them, we can say that the *average* dielectric constant of its environ-

[1] See footnote on p. 386.

[2] See last paper in footnote on p. 386.

[3] P. S. Epstein, Enzyklopädie der math. Wiss. V 3, p. 519, Leipzig, 1915.

ment has the normal value D while its own dielectric constant deviates from it by ΔD. This deviation is connected with the density fluctuation (22.12) by the well-known formula $(D-1)/(D+2)\rho = \text{const}$, whence

$$\Delta D = \frac{\Delta\rho}{\rho} \cdot \frac{(D-1)(D+2)}{3}. \tag{22.15}$$

We now put the question as to the scattering of a mass of gas of the volume V_{tot}. The inhomogeneities are distributed in it quite irregularly, and there are no phase relations between the amounts of light scattered by them. The total scattering is, therefore, simply the sum of these amounts. According to our previous analysis the inhomogeneities of small volume greatly dominate, so that there is no objection to applying the formula (22.14): The summation of the expressions for all the homogeneities in V_{tot} will lead to $V^2(\Delta D)^2$ being replaced by

$$\Sigma V^2(\Delta D^2) = \overline{V(\Delta D)^2} \cdot \Sigma V = \overline{V(\Delta D)^2} \cdot V_{tot}.$$

Substituting from (22.15) and (22.12)

$$\Sigma V^2(\Delta D)^2 = \frac{1}{9} kT\beta(D-1)^2(D+2)^2.$$

Using the abbreviation

$$\alpha = \frac{8\pi^3}{27\lambda_0^4} kT\beta(D-1)^2(D+2)^2, \tag{22.16}$$

the scattering by a unit volume of gas becomes

$$\frac{\Delta J_\vartheta}{J} = -\frac{3\alpha}{16\pi} \cdot \frac{1+\cos^2\vartheta}{r^2}, \tag{22.17}$$

or integrated over all space directions

$$\frac{\Delta J}{J} = -\alpha. \tag{22.18}$$

α has, therefore, the meaning of the *coefficient of extinction* through scattering.

In the particular case of permanent gases D is very little different from 1, β is practically $1/p$, and $kT\beta = 1/z$, where z is the number of molecules per unit volume:

$$\alpha = \frac{8\pi^3}{3z\lambda_0^4}(D-1)^2. \tag{22.19}$$

The last three formulas were first given by Lord Rayleigh [1] in his theory of atmospheric scattering. He explained the blue color of the sky as a consequence of the factor $1/\lambda_0^4$: light of short wave length is scattered more strongly so that the sunlight which indirectly reaches our eyes, after being scattered in the upper layers of the atmosphere, has its intensity maximum in the blue. Numerous measurements confirmed the dependence on the wave length and on the angle ϑ given by these formulas.[2] The direct observations of the coefficient of extinction give $8\pi^3(D-1)^2/3z = 1.00 \times 10^{-24}\,\mathrm{cm}^{-1}$, reduced to 1 atm and 0° C, the calculated value being $1.04 \times 10^{-24}\,\mathrm{cm}^{-1}$. The more general formula (22.16) shows that light scattering must be particularly strong when the gas is in the vicinity of the critical state because the compressibility β is then very large. This explains the phenomenon of the so-called *opalescence in the critical state.* It has been investigated quantitatively by Keesom [3] and found in agreement with the theory.

In conclusion, we repeat that the entropy principle cannot account for Brownian movements or density fluctuations. The existence of these phenomena is conclusive proof that an uncompensated decrease of the entropy is not impossible but only highly improbable. This fact does not impair the value of thermodynamics as a method of analyzing physical reality: in systems of appreciable size the change of a deviation from the second law is so extremely small as to be entirely negligible.

[1] Lord Rayleigh, Phil. Mag. **41**, pp. 107, 274, 447, 1871; **12**, p. 81, 1881; **44**, p. 28, 1897; **47**, p. 375, 1899.

[2] H. Dember, Ber. Saxon Acad. **64**, p. 289, 1912; F. E. Fowle, Astrophys. J. Obs. Smithsonian Inst. III, Washington 1914; E. Kron, Ann. Physik **45**, p. 377, 1914.

[3] W. H. Keesom, Ann. Physik **35**, p. 591, 1911.

APPENDIX I

COMPARATIVE TABLE OF NOTATIONS

There are in use four major and numerous minor systems of thermodynamical notations. The major systems are as follows: (1) the Gibbs notations; (2) the system developed by the physicists Clausius, Helmholtz, and Planck (C.-H.-P.); (3) the notations adopted by the larger part of the American chemists, especially Lewis and Randall (L.-R.); (4) the system used in technical thermodynamics.

We believe that this lack of unity is neither strange nor particularly regrettable. Thermodynamics is primarily a method for deriving relations between measured quantities. Various branches of science make use of it, each applies it to its own distinctive material, and in each the problem of harmonizing the notations and avoiding duplications and ambiguities is entirely different. It would be extremely difficult, if not impossible, to devise a system satisfying all these complicated requirements. On the other hand, the inconvenicnce to the reader caused by the lack of unity is slight, as the relation of the different systems of notations can be set down in a simple comparative table.

As to the intrinsic merits of the different systems there is not much to choose between them. A systematic principle was first introduced in the C.-H.-P. system in the form of a rule with respect to additive or extensive quantities (sections 39 and 144): the *total* quantities (i.e. those referred to the whole system or, at least, to a phase) are denoted by capital, the molal and specific quantities by lower-case letters. L.-R. modify this by using for molal quantities a special size of type, an expedient which seems less convenient in classroom teaching.

We seriously considered adopting the L.-R. system, which has a large following among the chemists of this country. But their choice of the notations E and H for the internal energy and heat function (enthalpy) is too repugnant to the physicist who has to treat electric and magnetic applications of thermodynamics and is accustomed to denote by E and H the electromagnetic field strengths. Worse still, according to the above rule the molal energy and enthalpy would have to be denoted by e and h, letters which are already badly overtaxed. We have, therefore, chosen to use the C.-H.-P. system with the following slight corrections. (1) The letter F for the work function $(U-TS)$ seemed undesirable as it is used by L.-R. for the function $U-TS+pV$; therefore, we substituted for it Ψ, the choice of Gibbs. (2) The use of n_h for the mol number (i.e. number of mols of the component h in a system) and of N_0 for Avogadro's number is inconsistent with the above rule since the first quantity is total and the second molal. We write, therefore N_h and n_A.

In the following table we list the more important notations, omitting those which are identical in all systems.

Quantity	E.		C.-H.-P.		Gibbs	L.-R.
	Total	Molal	Total	Molal		
Internal energy	U	u	U	u	ϵ	E
Heat function (enthalpy)	$\mathbf{X}$	χ	$\mathbf{X}$	χ	χ	H
Entropy	S	s	S	s	η	S
Work function $(U-TS)$	Ψ	ψ	F	f	ψ	A
Thermodynamic potential $(U-TS+pV)$	Φ	φ	$-T\Phi$	$-T\varphi$	ζ	F
Partial molal thermodynamic potential	....	$\overline{\varphi}_h$	....	$-T\varphi_h$	μ_h	$\overline{\mathrm{F}}_h$
Mol number	N_h	....	n_h	....	n_h	n_h
Molality	....	m_h	....	....	....	m_h
Avogadro's number	....	n_A	....	N_0	....	N
Mol fraction	x_h		x_h, c_h		....	N_h

APPENDIX II

CONSTANTS AND CONVERSION FACTORS[1]

TABLE OF CONVERSION FACTORS

		$\log_{10}$
1 norm. atmosphere	$1.013\,249 \times 10^{6}$ dyne cm^{-2}	6.005 717
1 (15°) g-calorie	4.1852 joule	0.621 720
"	4.1852×10^{7} erg	7.621 720
"	426.78 g m	2.630 199
"	1.00 095 (20°) g-calorie	0.000 412
"	0.99 976 (mean) g-calorie	$\bar{1}$.999 896
1 e-v. (electron-volt)	2.0017×10^{-12} erg	$\overline{12}$.30 140
n_A e-v.	1.2139×10^{12} erg mol^{-1}	12.08 419
"	29 003 cal mol^{-1}	4.46 245

[1] Partially based on the critical compilations by R. T. Birge, Phys. Rev. Supplement **1**, p. 1, 1929; Phys. Rev. **40**, p. 207, 1932.

TABLE OF FUNDAMENTAL CONSTANTS

Symbol	Quantity	Units	Value	Uncertainty in %	$\log_{10}$
v_0	Molal volume of perfect gas at 0° C and 1 (norm) atm	$cm^3\ mol^{-1}$	22 414.1	0.004%	4.35 052
R	Gas constant	$erg\ deg^{-1}\ mol^{-1}$	8.3136×10^{7}	0.011	7.91 978
	"	$atm\ cm^3\ deg^{-1}\ mol^{-1}$	82.049	0.011	1.91 408
	"	$cal\ deg^{-1}\ mol^{-1}$	1.9864	0.011	$\bar{0}$.29 807
k	Boltzmann's constant	$erg\ deg^{-1}$	1.3709×10^{-16}	0.1	$\overline{16}$.13 701
n_A	Avogadro's number	mol^{-1}	6.064×10^{23}	0.1	$\overline{23}$.78 279
e	Electronic charge	abs. e–s	4.770×10^{-10}	0.1	$\overline{10}$.67 852
F	Faraday's constant	abs. e–s	2.8927×10^{14}	0.007	14.46 130
	"	abs. e–m	9648.9	0.007	3.98 448
k/e		volt deg^{-1}	0.8622×10^{-4}	0.1	$\bar{5}$.93 560
e/k		$volt^{-1}\ deg$	1.1572×10^{4}	0.1	4.06 340
M_e	Mass of electron	g	0.9056×10^{-27}	0.12	$\overline{28}$.95 693
μ_e	Atomic weight of electron	$g\ mol^{-1}$	5.492×10^{-4}	0.15	$\bar{4}$.73 972
e/M_e	Electronic ratio	abs. e–s	5.267×10^{17}	0.04	17.72 159
	"	abs. e–m	1.757×10^{7}	0.04	7.24 477
h	Planck's constant	erg sec	6.547×10^{-27}	0.12	$\overline{27}$.81 604
β_0	Bohr's magneton	$erg\ gauss^{-1}$	0.9174×10^{-20}	0.14	$\overline{21}$.96 256
c	Velocity of light	$cm\ sec^{-1}$	2.99774×10^{10}	0.004	10.47 679
g	Normal acceleration of gravity	$cm\ sec^{-2}$	980.665	.....	2.99 152

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