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THE STRENGTHS OF CHEMICAL BONDS

THE STRENGTHS OF CHEMICAL BONDS

By

T. L. COTTRELL

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PREFACE

It is the opinion of the author that much of the theoretical work at present carried out on problems of molecular structure and reactivity has been hampered by the widely varying reliability of the available experimental information on these questions. Therefore, when he was asked whether he thought that a book on the strengths of chemical bonds would command much interest, he considered whether there was any existing account of the whole range of experimental evidence on the subject. Although there were two works covering diatomic molecules in some detail, and some review articles on polyatomic molecules, there did not appear to be any recent complete book on the whole subject. The present book is therefore an attempt to give an account of the methods and results of the experimental investigation of the strengths of chemical bonds. It is hoped that it will be of assistance to anyone looking for values of bond strengths, or interested in the reliability of particular values or of particular methods. It is intended to be written at a level which will commend itself to the honours year undergraduate interested in these matters, and to form an introduction to the subject for anyone about to start research in it.

The author is of course solely responsible for any errors which may, and probably will, be found in this book, but it is his pleasant duty to acknowledge the help of those who have made his task easier than it might otherwise have been. He is indebted to several friends who read much of the manuscript, in particular to Dr. C. A. McDowell and Dr. R. E. and Mrs. E. E. Richards who read Chapter 5 carefully and critically, to Dr. L. H. Long and Mr. G. Pilcher who performed the same service for Chapters 6 and 7 respectively, and to Dr. L. E. Sutton, F.R.S., Dr. F. D. Miles, Dr. G. A. Harrow, Dr. R. A. Hamilton, Dr. R. A. W. Hill, Mr. G. M. Duff and Mr. N. Ream who have all assisted him by discussing points of difficulty and reading parts of the manuscript.

He must also thank his employers, Messrs. Imperial Chemical Industries Ltd., Nobel Division, for permission to undertake this work, and express his gratitude for the excellent library facilities which have been at his disposal.

T. L. C.

Imperial Chemical Industries Ltd.,
Nobel Division, Research Department,
Stevenston, Ayrshire.

January 1954.

1

INTRODUCTION

1.1. THE CONCEPT OF THE CHEMICAL BOND

WITHIN the accepted formulation of the subject matter of chemistry we can recognize varying degrees of abstraction in the concepts by which we systematize our knowledge of matter in bulk. The chemist is chiefly concerned with that behaviour of matter which is classified in terms of the chemical elements and their compounds. Most of this area of knowledge is conveniently interpreted in terms of molecules, which are usually well defined entities with properties which can be assigned to them with little conceptual trouble. This is most nearly true for gases, where the forces between the molecules are very much smaller than the forces binding the atoms together in molecules. Thus, in a gas at low pressure, we can assign some properties to molecules with fair certainty. In liquids, although the forces between molecules are important, the molecule itself is still the most significant entity for chemists. Even in many solids, the identity of the molecule is clearly preserved. However, for discussion of some solids the concept of the molecule is not so convenient. In ionic crystals, for example, the ions are the important chemical and structural units, and the 'molecular formula' does not express more than the atomic ratios of the elements present. Also for some cross-linked high polymeric substances the concept of the molecule is artificial because the whole block of material is one vast molecule.

The place of the chemical bond in this hierarchy of concepts must now be examined. It is a characteristic of a molecule which we abstract for further consideration. Where the molecule is well defined, its constituent bonds stand one remove further from experiment. We cannot study an isolated chemical bond. Whereas we can alter continuously the environment of a molecule in the gas phase simply by varying the temperature and pressure, and can extrapolate measurements so that they refer to isolated molecules, we can only change the environment of a bond discontinuously by studying it in different molecules. Where the molecule is not well defined, the bond may be more directly related to observation than is the molecule. This is so for some solid high polymers, where

certain chemical bonds and groupings can be recognized although the molecule itself is not sufficiently defined. It has also been suggested that the idea of the chemical bond is valuable in the discussion of the properties of solid metals, although it is not possible to talk of molecules in this connection[236a, 383]. However, it is usually true that the chemical bond is a higher abstraction than the molecule, and its properties less clearly definable.

What is meant by a chemical bond? Briefly, it corresponds to the line between the atoms in the graphic formulae used by the chemist. It exists in order to account for the facts of chemistry. Knowledge of the various chemical reactions which compounds can and cannot undergo, generalized to give the classical theory of valency, requires some notation to show that, for example, a hydrogen atom or a chlorine atom must be concerned exclusively with one other atom, or that a carbon atom cannot combine with more than four hydrogen or chlorine atoms.

It is worth remembering that in spite of the great success of the scheme of graphic formulae, many chemists regarded it originally as a part of a purely formal system of notation. The success of the scheme in explaining chemical reactions, however, led chemists to try to discuss the physical properties of compounds in the same terms. Relationships were sought between boiling point, refractive index, surface tension and the like, and the number and nature of the bonds in the molecule. Although some success was obtained, this was carried out without any theory of why the properties concerned might be expected to be amenable to such treatment.

A more sophisticated approach was made possible by the disclosure of molecular structure in more intimate detail by the advent of powerful physical methods. The interpretation of x-ray diffraction and electron diffraction by solids and gases, and of the rotational and vibrational spectra of molecules, revealed that the formulae of the chemist were valid in a much more detailed way than he had expected. The spatial disposition of the atoms in molecules could be represented by just the same formulae as had been used to represent their chemical behaviour. This means that the representation of the molecule as a system of atoms linked by bonds could describe the physical structure of molecules. It does not mean that the discoveries concerning the geometry of the molecule, by itself, require the postulation of the chemical bond. The knowledge, for example, that the structure of the methane molecule is that of a regular tetrahedron, with the carbon atom at the centre and the hydrogen atoms at the vertices, does not provide any reason for drawing lines between the carbon atom and the hydrogen atoms

but not between the hydrogen atoms themselves. It is necessary to know some chemistry to realize that the carbon atom stands in a relationship to the hydrogen atoms which is a special one, and not merely that determined by symmetry, in which the hydrogen atoms do not stand to one another. The existence of this relationship has to be postulated to explain the chemistry of the substance; it is said that there is a chemical bond between carbon and hydrogen in methane.

Treatment of molecules in terms of bonds implies the existence of properties which can be associated with these bonds, such as their length or their strength. It is the purpose of this book to describe the experimental approach to the study of bond strengths. However, before we do so, it is important briefly to discuss the results of another important contribution of physics to chemistry, the clarification of molecular energy relationships.

1.2. MOLECULAR ENERGIES (AND UNITS) *

Although thermodynamics and thermochemistry were well established studies by the end of the nineteenth century, and a large body of information about the energies involved in chemical changes had been built up, many important details of molecular energies were not understood until the advent of quantum theory. In particular the notion, essential to the understanding of spectra, of the existence of discrete energy states has been of immense importance. It is worth remembering, when we are despondent about the failure of theoretical chemistry to calculate exactly the energy involved in some particular electronic transition, that the whole nature of spectra was completely obscure until the application of quantum theory. In this section we shall summarize the ways in which energy may appear in molecules.

At normal temperatures molecular energy in gases can be divided into three components which are effectively independent: translational, rotational, and vibrational. Energy is distributed among these components according to the laws of statistical mechanics. Translational energy is the average energy of motion through space of the molecule as a whole, in which there are three degrees of freedom. Because the quanta are very small indeed, this energy may be regarded as classically distributed; in which case the translational energy per molecule is $(3/2)kT$, where k is Boltzmann's

* *Units.* Following usual thermochemical practice, the unit of energy is the kcal, defined by 1 kcal $= 4{\cdot}1840 \times 10^3$ abs. joules. It is common practice among spectroscopists to quote energies in electron volts (eV). 1 eV $= 23{\cdot}063$ kcal[217]. Both units will be used[217, 529].

constant and T is the absolute temperature, or $(3/2)RT$ per mole, where R is the gas constant. This is about 0·9 kcal per mole at room temperature. For linear molecules there are two degrees of rotational freedom possible (for non-linear molecules there are three) and the quanta involved are also small, so that at ordinary temperature this energy is classically distributed and is RT per mole for linear molecules and $(3/2)RT$ per mole for non-linear molecules. Linear molecules have only two rotational degrees of freedom because they are axially symmetrical, and rotation about the axis of symmetry involves no distinguishable change of position; similarly atoms, which are spherically symmetrical, have no rotational degrees of freedom*. The number of vibrational degrees of freedom depends on the number of atoms, n, in the molecule, being $3n-5$ for linear molecules and $3n-6$ for non-linear molecules, because the total number of degrees of freedom is $3n$. For at least some of the vibrational degrees of freedom in most molecules, the vibrational quantum, $h\nu$, where h is Planck's constant and ν the vibration frequency, is large compared with kT, so that vibrational energy is not distributed classically. It was, incidentally, just this fact which led to the quantum theory. For example, at a vibration frequency of 1,000 cm^{-1}†, towards the lower end of the usually observed range of vibration frequencies in molecules, $h\nu/kT$ at 300° K is 4·8, and the vibrational quantum is 2·86 kcal $mole^{-1}$. At the absolute zero, molecules retain a half-quantum of vibrational energy for each vibrational degree of freedom, known as the zero-point energy. For polyatomic molecules this can be quite large; for example, for methane it is 27·1 kcal $mole^{-1}$, whereas at room temperature the total heat content of methane, relative to the molecule in the ground vibrational state at 0° K, is only 2·3 kcal $mole^{-1}$.

These thermal energy quantities are statistical averages, characteristic properties of an assembly of molecules. The thermal energy itself is not essentially relevant to what we might describe as the chemical energy of the molecule, and is chiefly important because much of our information about molecules is derived from assemblies which possess it. We have now to consider what this 'chemical energy' is.

* This result, though glibly stated, is by no means self-evident because it is obviously possible to give rotational energy to a spherically symmetrical billiard ball. The reason behind the statement is that the measured properties of gases of molecules and atoms agree with those calculated on these assumptions.

† It is a common practice in spectroscopy to express frequencies, and energies, as reciprocal wavelengths. The corresponding cyclic frequency is obtained by multiplying by c, the velocity of light, and the energy by multiplying by h.

1.2. MOLECULAR ENERGIES (AND UNITS)

Chemical changes usually take place with the liberation or absorption of energy. This energy change is obviously related to chemical energy, which we may consider to be the energy associated with compounds by virtue of the particular state of chemical combination of the elements they contain. If chemical energy changes are defined simply as those energy changes which accompany chemical reaction they must include changes in thermal energy. For example, we may consider a dilute gas consisting of hydrogen molecules and oxygen molecules. It will remain as such indefinitely and it possesses well-defined thermodynamic properties, the values of which depend on the temperature. We may imagine this mixture reacting isothermally at constant volume with the evolution of heat to give a gas made up of water molecules. Now only part of the heat evolved can be directly associated with the chemical change from hydrogen molecules and oxygen molecules to water molecules, because some of it must be associated with a change in average thermal energy which has taken place by reduction in the number of molecules present. Although the total number of mechanical degrees of freedom has not altered, the number of translational degrees of freedom in the system has decreased, and the number of vibrational degrees increased. As a consequence, the total thermal energy at room temperature will have decreased, and this energy change will have been part of the observed overall change in energy. In brief, part of the energy change is not specifically due to the properties of single atoms and molecules.

The change in chemical energy per molecule might be regarded as a change in the potential energy of the atoms composing the molecules. We may elaborate this way of looking at chemical energy. For chemical purposes atoms can be regarded as consisting of electrons and nuclei; the difference in mass between these is so great that usually it is a very good approximation to consider separately the motion of the nuclei and the motions of the electrons relative to the nuclei. Let us consider the simple case of the union of two atoms to form a single molecule. We might in principle calculate the energy of the system nuclei-plus-electrons for a fixed internuclear distance. This energy is essentially the electronic energy. We might then repeat the calculation of the energy of the system for another internuclear distance, and so on, to construct the energy of the system of electrons-plus-nuclei as a function of internuclear distance. We could then regard this energy function as the potential governing the motion of the nuclei and calculate their motion on this basis.

We can now discuss qualitatively what happens when two atoms come together to form a molecule. When they are very far apart there is no interaction between them, but as they move together the total energy of the system nuclei-plus-electrons decreases to a minimum. This is a minimum of potential for the nuclei. As they come still closer together the energy increases again rapidly. Thus a plot of energy against internuclear distance must resemble *Figure 1.2.1*, curve (*a*).

The depth of the energy minimum is the characteristic change in energy, per molecule, which occurs when two atoms combine. It

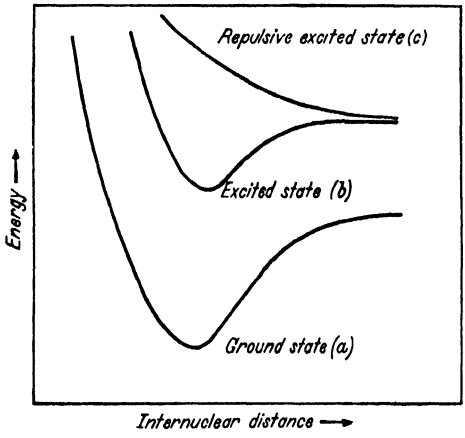


Figure 1.2.1. Plot of energy of the system nuclei + electrons for various internuclear distances in a diatomic molecule (schematic).

is not an average, thermal, quantity, but a direct property of the molecule concerned. For polyatomic molecules the situation is similar, though here the equilibrium configuration is represented by a minimum on an energy hypersurface. In the system of four hydrogen atoms and two oxygen atoms, for example, there is more than one minimum; there is one corresponding to the formation of two hydrogen molecules and one of oxygen, and another and lower corresponding to the formation of two water molecules.

The vibrational energy of the nuclei is that which they possess by virtue of their oscillation about the point of minimum potential. This energy is quantized, and since near the minimum the potential well is approximately parabolic, the lower vibrational energy levels approximate to those of the harmonic oscillator. As a consequence of the uncertainty principle, the lowest allowed energy value cannot

be the potential minimum, and the nuclei accordingly possess vibrational zero-point energy in the ground state.

In the foregoing we have assumed that the energy of the system nuclei-plus-electrons is a single-valued function of the configuration of the nuclei; this is not so. This electronic energy is itself quantized, and we have so far been dealing with the lowest electronic energy state. A higher, or excited, electronic energy state may produce a similar potential well at a higher energy level, but not all excited states produce a potential well; for some, the energy increases monotonically as the nuclei approach, so that the nuclei repel one another at all distances. This is shown in *Figure 1.2.1.* A repulsive state may derive from the same level of the separated atoms as does an attractive state, depending upon whether the electron spins are the same or opposite.

For most molecules, the different electronic states are separated by much more than kT at all temperatures normally accessible to experiment, and thus electronic excitation does not normally occur purely as a result of thermal agitation. However, for some molecules, such as nitric oxide, there are excited electronic states lying sufficiently near the ground state for them to be excited thermally. For systems of several atoms, electronic states could be imagined as forming hypersurfaces analogous to the lines in *Figure 1.2.1*, electronic transitions taking place to higher surfaces if the system is supplied with the appropriate energy. Most chemical changes take place on the same electronic energy surface throughout. Such changes are commonly but objectionably termed 'adiabatic'*. Transition to upper excited states takes place chiefly under the influence of ultra-violet light, and the ultra-violet spectroscopy of molecules is concerned with such transitions. Much information of great importance about the ground states of molecules can be obtained in this way, as described in Chapter 5.

We may summarize the rough magnitudes of the types of energy quantity involved as follows, remembering that they are only indications, and that for several molecules significant differences may be found. We may neglect the quantization of translational energy, as the quanta are minute. Rotational energy has small quanta, about 0·003 kcal mole^{-1} usually classically distributed, but amenable to spectroscopic investigation in the 'microwave region' (*ca.* 1 cm)†. Vibrational energy levels are more widely spaced, and can be examined spectroscopically in the infra-red region; the quanta are about 3 kcal mole^{-1}‡. The depth of the minimum in

* Fowler and Guggenheim[157] suggest 'quasi-static'.

† For a review, see Whiffen[565].

‡ *See* Herzberg[216].

the energy curve in *Figure 1.2.1* corresponds to much larger energies, say from 30 to 200 kcal mole^{-1}. This must be so if molecules are to retain their identity over a large range of temperature. Electronic transitions can be investigated spectroscopically in the ultra-violet region, and the energies are in the range from this to hundreds of kcal mole^{-1}.

1.3. THE STRENGTH OF CHEMICAL BONDS

The discussion in Section 1.1. suggests three ways of regarding the structural formula of a molecule:

1. As a summary of the chemical reactivity.
2. As a summary of some of the physical properties of the substance.
3. As a representation of the geometry of the molecule.

There are various possible interpretations of bond strength, conforming to these different aspects of structural formulae. Corresponding to 1 is the view of bond strength as determining how much energy is required to break it; the bond dissociation energy is a measure of bond strength in this view. Corresponding to 2 is the view of bond strength as a bond energy term, characteristic of each bond, which, when summed over all the bonds in the molecule gives its heat of formation from atoms. Such a method was the earliest to be adopted. Corresponding to 3, the bond strength may be related to molecular physics and molecular geometry in two ways. First the bond energy terms deduced from the bulk heats of formation or the bond dissociation energies may be related to bond lengths and to various theoretically calculated parameters defining bond properties. Secondly, our knowledge of molecular vibrations may be used to derive force constants to characterize the strength of a bond, in the way in which the force constant of a spring measures its stiffness.

The idea of 'bond dissociation energy' as a measure of bond strength is straightforward. The strength of the bond measured by the energy required to break it is clear enough, provided we can specify sufficiently exactly the fragments into which it is broken. For a bond in a polyatomic molecule it must be remembered that the configuration of the atoms in the radical R when the bond R–R′ is being broken may change as the bond length increases. For example, it has been suggested that the free methyl radical, CH_3, is planar, whereas the CH_3 group in methane is certainly tetrahedral. Thus the dissociation energy of the CH_3–H bond in

methane may include not only the energy required to stretch and eventually to snap the C–H bond, but also the energy changes involved in the concomitant adjustment of the other three bonds. This latter part of the energy has been called the 'reorganization energy' and is of importance because it suggests that the dissociation energy may not be closely related to other quantities characteristic of bond strength. The bond dissociation energy has the great merit of being unambiguously related to measurable quantities.

The bond energy term is a quantity which, summed over all the bonds, gives the heat of formation of the molecule from atoms. This concept is unambiguous in a diatomic molecule, where the bond energy term is just equal to the bond dissociation energy. Again for a polyatomic molecule in which there is only one type of bond, MX_n, the energy of the MX bond is one nth of the total energy of formation of the compound. When there is more than one type of bond, the bond energy terms of all but one type must be taken as known, derived from the energy of formation of molecules containing that type only, and the bond energy term for the remaining type deduced from the energy of formation by difference. If the hypothesis that the energy term of a bond is invariant from molecule to molecule holds, then this procedure should give the same result regardless of the molecule from which the bond energy terms are deduced, apart of course from divergencies due to errors in the experimentally determined heats of formation, and possible minor effects due to thermal agitation and zero-point energy. In fact, it is found that some bond energy terms appear to vary from molecule to molecule, which introduces an element of arbitrariness into the values of bond energy terms chosen for different molecules. Two ways of assigning the resulting variations are as follows: one is to regard the bond energy terms obtained unambiguously from the heat of formation of MX_n compounds ('primary' bond energy terms) as fixed, and to throw all the variation on secondary or higher bond energy terms. This assumes that the energy terms for some bonds do not vary at all with environment, whereas others vary considerably. Since there is no reason to believe that 'primary' bonds in this sense differ from secondary bonds, this is not a very satisfactory procedure. The other method is to adopt some method of allowing all bond energy terms to vary with environment, and testing the resulting scheme for self-consistency. This has the disadvantages that considerations other than those derived from thermal data only must enter into the allocation of bond energy terms, and that there is no unique solution. Sometimes

the bond length is taken as an indication of environmental effects and the environment can then be specified in terms of bond lengths by making various assumptions about the effect of one on the other.

The third measure of the strength of a bond is its stretching force constant, derived from an analysis of the molecular vibrations. This quantity differs from the two previously considered in that it is not concerned with the difference of energy between two states, in one of which a bond exists and in the other of which it does not; it is concerned in a more intimate way with a property of the bond as it actually exists in the molecule. In fact it measures the resistance of a bond to a small alteration of its length from the equilibrium value. The drawback to this is that chemical changes are those which involve large disturbances in the molecule, and thus to a chemist the resistance of a bond to small perturbations is perhaps not very important. On the other hand, the bond length is also characteristic of the molecule as it exists undisturbed, and so force constants ought to be particularly useful for correlation with molecular geometry. There are two further drawbacks; bond stretching force constants can only be derived uniquely for diatomic molecules and for polyatomic molecules of favourable symmetry; the constants for polyatomic molecules in general therefore depend on the particular force field assumed. Moreover, it is not practicable to give a complete discussion of the vibrations of other than relatively simple molecules.

Another possible method of measuring bond strength is that due to Walsh[547], who suggested that the ionization potential of the bonding electrons is proportional to bond strength. The more tightly the electrons are bound, it is argued, the stronger is the bond and the firmness of binding is determined by the ionization potential. This method is applicable to relatively few compounds.

1.4. EXPERIMENT AND ANALOGY

In the following discussions of bond strength we shall confine ourselves to those results which can be established by more or less direct experiment, and attempt to assess the reliability of the various experimental determinations. We shall eschew as far as possible those values which have been obtained by analogy with other molecules. The literature has many examples of reasoning about bond energies based on assumed regularities for which the evidence is doubtful. It is particularly difficult under these circumstances for the investigator to avoid assuming regularities whose

existence is later 'proved' by evidence derived in this way. We therefore conclude this chapter with a cautionary tale.

When it was found that the ultra-violet spectrum of fluorine was not such as to allow a direct determination of its dissociation energy, this quantity was estimated to be 63·5 kcal, by extrapolating results from the spectra of iodine, bromine, and chlorine (*see* Section 8.2.2.9.). Now the chemical behaviour of fluorine differs in many ways from that of the other halogens. When a certain member of a series differs from the rest, and when a property of this member cannot be measured in the same way as that of the others, there is a danger that this member is not typical in that respect. Nevertheless, the value 63·5 kcal for the dissociation energy of fluorine, obtained in 1931, passed into the literature and was quoted and used for many years. In turn this value for fluorine was used to derive other bond energies by analogy. For example, in a paper published in 1948 it was stated that the N–N bond in hydrazine, the O–O bond in hydrogen peroxide, and the F–F bond in fluorine all had approximately the same strength, 64 kcal. The evidence for this was as follows. 63·5 kcal was accepted as the dissociation energy of fluorine. The O–O bond energy in hydrogen peroxide was estimated to be ~64 kcal from the considerations that the OH bond energy in this molecule is likely to be less than in OH radical, that the dissociation energy of a complex organic hydroperoxide was estimated to be 66 kcal, and that the dissociation energy of O–O in persulphates was 57 kcal, by the agreement between the force constants of O–O and F–F, and by comparison with estimates of the single bond strengths S–S and Se–Se. At that time the vibration frequency of F_2 had not been determined, and the force constant was therefore estimated by an empirical rule applied along the rows of the periodic table. A much higher estimate of the force constant of F_2 obtained from a plot of force constant against bond length for the other halogens was rejected, although the dissociation energy itself had been obtained in a similar way. Since the N–N bond length in hydrazine is the same as that of O–O in hydrogen peroxide and that of F–F, and since the stretching force constants for all these bonds were supposed to be the same, it was concluded that the N–N bond energy is ~64 kcal and hence that the N–N, O–O, and F–F bond energies are all the same and equal to 64 kcal. Much of this reasoning has lost its cogency since a reliable, experimental determination has shown that the dissociation energy of fluorine is about 37 kcal. In fact, the most probable values of the dissociation energies in these compounds are 60, 48, and 37 kcal (*see* Sections 9.7.7, 9.8.8 and 8.2.2.9).

This is not to deny the value of attempting to find regularities in bond strengths from molecule to molecule; indeed it is hoped that the present book will be of help to those who wish to do so. It is merely desired to stress the danger of an incautious mixture of experiment and analogy, in the hope that should the present author make some mistakes of this nature, his readers will be forewarned.

2

DEFINITION, MEASUREMENT, AND USES OF BOND DISSOCIATION ENERGIES

2.1. DEFINITION AND DISCUSSION

THE dissociation energy, $D(R_1\text{–}R_2)$, of a bond $R_1\text{–}R_2$ is the change in energy at absolute zero in the ideal gas state, ΔE_0°, for the reaction

$$R_1R_2 \rightarrow R_1 + R_2, \qquad \ldots . \quad (2.1.1)$$

the products being in their ground states. Unless otherwise specified, D refers to the reaction taking place under these conditions. Occasionally, however, $\Delta H(2.1.1)$ at 25° C is used in place of $\Delta E_0^\circ(2.1.1)$ for the dissociation energy. Where there is liable to be confusion, D_0° is used for the strict definition. Here the subscript refers to the zero'th vibrational level, the superscript to products in their ground states. D_e refers to the process taking place for a hypothetical molecule R_1R_2 without zero point energy. With these definitions, D_0° and D_e are quantities characterizing individual molecules. The change of enthalpy, ΔH, measured at normal temperature does not differ greatly from the true value of D, and many of the data obtained by measurement of the former quantity are not sufficiently precise to warrant the correction, for which in any case the heat capacity information is often lacking. It will be seen that D_e is equivalent to the chemical binding energy of Section 1.2, but this quantity is not often used in the discussion of experimental results.

In connection with determinations of bond dissociation energy at normal temperatures, it is useful to note that the heat capacity change of reaction (equation 2.1.1) is always positive, so that the value of ΔH for normal temperatures will always be greater than $D(R_1 - R_2)$ as defined above. This is because reactions of this type involve the creation of new translational degrees of freedom at the expense of vibrational degrees of freedom. Quanta of translational energy are very small, and translation therefore makes its full classical contribution to the heat capacity, whereas many vibrational quanta are sufficiently large not to contribute much to the heat capacity at ordinary temperatures. Rotation generally

contributes its full classical amount at ordinary temperatures. We notice that for a non-linear polyatomic molecule dissociating into two non-linear polyatomic fragments, three new translational and three new rotational degrees of freedom are created at the expense of six vibrational degrees of freedom. If none of the vibrational degrees of freedom destroyed are appreciably excited, the increase in C_v, the molar heat capacity at constant volumes, at $\frac{1}{2}\boldsymbol{R}$ per mole per degree of freedom is $3\boldsymbol{R}$. Since in dealing with ΔH we require ΔC_p, the change at constant pressure, and since one mole is added in the dissociation reaction, we must add $\boldsymbol{R}$ to obtain $\Delta C_p \sim 4\boldsymbol{R}$, and hence

$$\Delta H^\circ_{300^\circ\mathrm{K}} - \Delta E^\circ_0 \simeq 4\boldsymbol{R}T \simeq 2{\cdot}4 \text{ kcal mole}^{-1}$$

This is of course an upper limit, because in general the vibration will contribute something to the heat capacity. For a non-linear polyatomic molecule splitting into a radical and an atom, three translational degrees of freedom replace three vibrational degrees, and for a diatomic molecule, three new translational degrees of freedom are created at the expense of two rotational and one vibrational degree of freedom; in this last example $\Delta H^\circ_{300^\circ\mathrm{K}}$ exceeds D°_0 by about 0·9 kcal. For hydrogen, for example, we have

$$D^\circ_0(\mathrm{H_2}) = 103{\cdot}24 \text{ kcal mole}^{-1}$$

and

$$\mathrm{H_2} \rightarrow \mathrm{H} + \mathrm{H},\ \Delta H^\circ_{298{\cdot}16^\circ\mathrm{K}} = 104{\cdot}18 \text{ kcal mole}^{-1}$$

Dissociation energies must be considerably greater than $\boldsymbol{R}T$ if the entity $\mathrm{R_1}$–$\mathrm{R_2}$ is to be sufficiently stable to be recognized as a molecule. In practice there are wide variations in $D(\mathrm{R_1} - \mathrm{R_2})$ from molecule to molecule. At the lower end of the scale we have $D(\mathrm{NO_2} - \mathrm{NO_2})$ in dinitrogen tetroxide as low as 12·9 kcal mole^{-1} in accordance with the well-known ease of dissociation of this compound. At the other end we have the molecules carbon monoxide and nitrogen where D is probably more than 200 kcal mole^{-1}. Appreciable dissociation of CO and $\mathrm{N_2}$ can only take place at temperatures usually found only in certain flames and detonations.

2.2. METHODS OF DETERMINATION

2.2.1 *General*

Two types of method for determining bond dissociation energies can be distinguished. One is to determine the energy change for the reaction shown in equation 2.1.1 in a thermodynamically valid way, either directly or by way of a set of equilibrium measurements; the other method is to measure the rate of some process,

and relate it to thermodynamic properties by an assumption about the mechanism of the process. The former way might for example use the techniques of classical thermochemistry, or might use the relationships developed by quantum statistical mechanics to relate spectra to thermodynamic quantities. In either case the energy difference between the products and the reactants is established by methods which are valid in principle however great their practical shortcomings may be. Bond energies derived from kinetic measurements cannot have quite the same validity, since there is no necessary connection between the energy change in a process and the rate at which it takes place, although semi-empirical generalizations connecting these quantities have often proved of value. Happily enough, it is for just the type of reaction we are considering here that generalizations concerning energy and rate are most soundly based, and much useful information has been obtained in this way.

Although this distinction is fundamental, it does not lead to the most convenient classification. It has been usual to classify experimental methods according to the means of supplying the energy. The main methods are briefly characterized here, and discussed in detail in the following three chapters. References to the literature are given in these chapters; here only general principles are stated, except in Sections 2.2.2 and 2.2.7, where the methods are of such limited application that no further discussion is required.

2.2.2. *Calorimetric Methods*

Direct calorimetric measurement of the heat absorbed when dissociation takes place is not possible but for a few substances it is possible to measure the exothermic recombination of atoms or radicals. Bichowsky and Copeland[37] were able to measure the heat of recombination of hydrogen atoms by direct calorimetry; their results yield $D(H_2) = 105{\cdot}0 \pm 3{\cdot}5$ kcal, in good agreement with the presently accepted value of 103·2, which is spectroscopically derived. In their method, hydrogen was admitted to a discharge tube at a known rate of flow, and the partially dissociated gas was allowed to pass through a small hole on to a platinum calorimeter, where the recombination of the hydrogen atoms was catalysed. The rise in temperature of the calorimeter gave the energy change on recombination. The proportion of free hydrogen atoms in the gas passing into the calorimeter was determined by the difference between the pressure of the gas before passing through the small hole under steady state conditions of no dissociation (no discharge)

and the pressure under steady state conditions of dissociation (discharge). From these two pieces of information the required heat quantity was deduced. The use of measurement of effusion through a small hole to determine concentrations of atoms is discussed in Section 3.2.

2.2.3. *Thermal Equilibrium Methods.*

The heat of dissociation can be deduced thermodynamically if the equilibrium concentrations of R_1R_2, R_1 and R_2 are known over a range of temperature, or if the entropy change is known, from their values at one temperature. The difficulty here is to determine the concentrations which cannot often be measured directly. These methods have the characteristic that the only difficulty is the measurement; the interpretation of the results is unambiguous. A detailed discussion is given in Chapter 3.

2.2.4. *Chemical Kinetic Methods*

The most common form of chemical kinetic method assumes that the activation energy for the recombination of radicals is zero, and therefore that the activation energy of the dissociation reaction is equal to the heat of reaction. Whereas thermal equilibrium methods are most suited to diatomic molecules, the kinetic method is used for polyatomic molecules. The dissociation products of diatomic molecules are stable enough for equilibrium measurements to be made; the products from polyatomic molecules, on the other hand, are usually very reactive, and the kinetic method is often the only way of obtaining the dissociation energy. Although it is often easy enough to measure a rate of decomposition, it may be difficult to relate this to the rate of the desired reaction. Here the correct interpretation of the kinetic results is all-important, and techniques which can give unambiguous bond dissociation processes are particularly valuable. A detailed discussion is given in Chapter 4.

A special case of the application of kinetic methods is the study of processes initiated by excited atoms. Chemical change is brought about by the interaction of an excited atom with a molecule, the required energy being supplied by the excitation energy of the atom. For example, if we can show by kinetic analysis that the reaction

$$A^* + R_1R_2 \rightarrow A + R_1 + R_2,$$

where A* is an excited atom, takes place without activation energy, then $E(A) \geqslant D(R_1R_2)$, where $E(A)$ is the excitation energy of A.

E(A) is exactly known because the excitation is photochemical with light of a known wavelength.

A similar study is of course that of direct photoreaction, where the quantum absorbed must be greater than the energy required for the primary step, which may be a bond splitting process.

2.2.5. *Electron Impact Methods*

Electrons of known energy are allowed to interact with molecules to produce ionization and dissociation. If certain conditions are fulfilled, the lowest electron energy required to produce a given ion by dissociation and ionization is equal to the sum of the dissociation energy and the ionization potential of the fragment. The method can be used for polyatomic and diatomic molecules, but for the former, identification of the process taking place is often difficult, and the required accurate knowledge of the ionization potentials of radicals is not always easy to come by. However, apart from very few equilibrium results, it is the only method other than the kinetic for obtaining dissociation energies in polyatomic molecules. A detailed discussion is given in Chapter 5.

2.2.6. *Spectroscopic Methods*

The ultra-violet spectrum of many diatomic molecules offers the most accurate method of measuring their dissociation energy, thanks to the great accuracy with which wavelength measurements can be made. Thus if the spectroscopist can be certain what the products of dissociation are at the wavelength at which dissociation takes place, and if he can be certain that dissociation does take place at the wavelength at which he thinks it does, the accuracy of the dissociation energy is often limited only by the accuracy of our knowledge of Planck's constant and of the energy scale. Unfortunately, however, these conditions are not always fulfilled. Lack of knowledge of dissociation products may lead to two equally plausible and equally precise values of the dissociation energy, each known to one part in ten thousand and differing by fifty per cent. Here, of course, less accurate but unambiguous thermal methods may often be used to decide between the spectroscopic values, although in the most controversial examples the thermal measurements are so difficult that a decision is not possible. Often, too, spectroscopy may only provide an upper limit to the true value. The spectrum of polyatomic molecules is too complicated for it to be used to determine dissociation energies. Further discussion is given in Chapter 5.

Spectroscopically derived information is often very useful in the thermodynamic discussion of thermochemical results. Since spectroscopy is the study of molecular energy levels, it is possible to deduce various thermodynamic properties of molecules from their spectra, using the methods of quantum statistical mechanics. Since electronic energy levels are only rarely excited at room temperature, this usually requires a knowledge of the vibrational energy levels, often only of the first two or three. This, together with knowledge of the molecular geometry, itself often derived from spectroscopic measurements, gives the specific heat, entropy, and heat content and free energy relative to the molecule at 0° K. These quantities are used to deduce dissociation energies from equilibrium measurements at one temperature, and also to convert results obtained at higher temperatures to the required temperature. It is possible to do this for simple polyatomic molecules as well as for diatomic molecules.

Spectroscopic information may also be used to determine temperatures and concentrations in thermochemical experiments.

2.2.7. *Direct Calculation*

A complete theory of chemistry would permit the calculation of bond dissociation energies directly from the fundamental quantities of atomic mass and electronic charge. Moreover, the theory exists. Dirac's famous remark is as true now as it was in 1929:

> "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation'[112].

Exact solution of the equations has been possible only for one molecule, the hydrogen molecule ion H_2^+. Jaffe[246], Hylleraas[239], and others give $D_e/I_H = 0{\cdot}2053$, where I_H, the ionization potential of hydrogen, is 13·60 eV. D_e is the dissociation energy measured from the minimum in the energy curve, and when corrected for the vibrational half-quantum of zero-point energy gives $D_0^\circ(H_2^+) = 2{\cdot}649$ eV, in complete agreement with experiment. It is a pity that this is an isolated case. An heroic approximate calculation of $D_e(H_2)$ has been made by James and Coolidge[248] in which agreement with experiments is obtained, but this cannot be considered

an absolute calculation because the value of the equilibrium internuclear distance was derived from experiment. However, it is also possible to show (by applying the condition that at the equilibrium internuclear distance $2\bar{T}+\bar{V}=0$, where $\bar{T}$ and $\bar{V}$ are the electronic kinetic and potential energy) that if the wave function used by James and Coolidge is correct, the correct internuclear distance only differs from theirs by a factor of 1·0029, making a negligible difference to the energy. Hirschfelder and Kincaid[224], who discussed wave functions and the virial theorem, expressed the view that 1·0029 is a scale factor by which the wave function had to be corrected to make the virial theorem hold, but it has been shown[96] that for the wave function concerned the virial theorem must automatically hold, and thus Hirschfelder's scale factor is in this case really a correction to the internuclear distance.

Many attempts were made to carry out reliable quantum mechanical calculations of dissociation energies, particularly in the early 1930's, with the depressing results summed up by Van Vleck and Sherman[533] as follows:

> 'In most so-called calculations of heats of dissociation, doubtless influenced by the answer to be desired, the nice agreement [with experiment] achieved at the nth approximation is usually lost at the $(n+1)$th stage.'

Although we can expect no help from quantum mechanics in the direct calculation of dissociation energies, it must be remembered that on this discipline rests the whole basis of our understanding of the essentials of molecular spectra without which we should know very little of dissociation energies.

2.2.8. *Combination of Results*

Considering equation 2.1.1 we have the simple result that

$$D(R_1-R_2)=\Delta H_f^\circ(R_1)+\Delta H_f^\circ(R_2)-\Delta H_f^\circ(R_1-R_2)$$

where ΔH_f°, the heat of formation, should properly be referred to 0° K. Thus if $D(R_1-R_2)$ is determined, and $\Delta H_f^\circ(R_1)$ known from the case where $R_2=R_1$, $\Delta H_f^\circ(R_2)$ can often be derived because $\Delta H_f(R_1-R_2)$ is generally known from ordinary thermochemical results. This can be used to deduce a series of dissociation energies involving R_2, provided the heat of formation of the other fragment is known. Thus in general, the determination of one dissociation energy leads to a whole series of dissociation energies involving a common radical, simply by the systematic exploitation of Hess's

law. For example the reliable determination of any one bond dissociation energy $D(CH_3-X)$ leads to most other dissociations involving a methyl radical and an atom, because the heats of formation of most of the compounds concerned are known. The determination of bond dissociation energies is leading up to a body of knowledge of the heats of formation of radicals and atoms, which can be combined to give other dissociation energies in just the same way as ordinary tables of heats of formation of more stable molecules can be used to give the thermochemistry of reactions.

2.3. USES OF BOND DISSOCIATION ENERGIES

2.3.1. *In Theoretical Chemistry*

The bond dissociation energy is the most direct measure of the strength of a bond, and therefore of the stability of the chemical combination between the two atoms or radicals from which it is formed. The stabilities of chemical combinations are important facts for chemistry. Theoretical chemistry is concerned with deducing chemical information from general principles, ultimately from the physical laws governing the behaviour of nuclei and electrons. Energy quantities are, in the present state of theory, perhaps the most accessible numerical quantities we can hope to calculate for chemical systems, and for chemical systems it could be maintained that the most specific energy quantities are dissociation energies. The fact that it has been found possible to account qualitatively for chemical binding in general and quantitatively for the dissociation energy of the hydrogen molecule is important evidence that theoretical chemistry is on the right lines. To have reliable experimental values of dissociation energies is to have a useful touchstone to test our theoretical ideas on chemical binding.

2.3.2. *In Chemical Kinetics*

It is now established that many chemical reactions proceed via unstable intermediates, radicals or atoms. In order to discuss whether some postulated atom or radical reaction is likely to occur it is necessary to know something of the thermochemistry of these active species. Since we can rarely have a sufficiently large concentration of free radicals to carry out thermochemical measurements on them in bulk, it is necessary to deduce their heats of formation from dissociation energies involving them.

3

DETERMINATION OF BOND DISSOCIATION ENERGIES BY THERMAL EQUILIBRIUM METHODS

3.1. GENERAL

The equilibrium constant K for the dissociation reaction

$$AB \rightarrow A + B \qquad \ldots\ (3.1.1)$$

is defined by

$$K = f_A \cdot f_B / f_{AB} \qquad \ldots\ (3.1.2)$$

where the f's are fugacities, although for many purposes partial pressures may be used instead of fugacities with little loss of accuracy[304]. K is related to the thermodynamic quantities by

$$-RT \ln K = \Delta G^\circ \qquad \ldots\ (3.1.3)$$

where ΔG° is the change in Gibbs free energy at the temperature T. We have to find the energy change at absolute zero, ΔE_0°, which is equal to the change in heat content at absolute zero, ΔH_0°. This quantity is the dissociation energy, D. Two methods are available. We have:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \ldots\ (3.1.4.)$$

whence, from equation 3.1.3

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad \ldots\ (3.1.5)$$

Thus, by knowing the relationship between the equilibrium constant and the temperature we can obtain ΔH°, the change in heat content at that temperature. If the temperature is sufficiently low, this may not differ much from D, as discussed in Section 2.1. If the heat capacity data are known, ΔH° may be converted to ΔH_0°. This introduction of the experimental data by equation 3.1.5 depends on the second law of thermodynamics.

Alternatively we may write equation 3.1.3 as

$$-R \ln K = \frac{\Delta(G^\circ - H_0^\circ)}{T} + \frac{\Delta H_0^\circ}{T} \qquad \ldots\ (3.1.6)$$

Thus, from a knowledge of the equilibrium constant at a single temperature, and the first member of the right-hand side of equation 3.1.6, we can obtain ΔH_0°, or D. The first member of the right-hand side is the function $(G^\circ - H_0^\circ)/T$, known to American authors as the free energy function. It depends solely on the properties of the individual reactants concerned, not upon the heat of reaction. We have:

$$\frac{\Delta(G^\circ - H_0^\circ)}{T} = \left(\frac{G^\circ - H_0^\circ}{T}\right)_A + \left(\frac{G^\circ - H_0^\circ}{T}\right)_B - \left(\frac{G^\circ - H_0^\circ}{T}\right)_{AB} \quad . \quad . \quad . \quad (3.1.7)$$

This function may be calculated from molecular data by the methods of quantum statistical mechanics. It may also be obtained from experimentally determined heat capacity data, from which the required entropies are deduced using the third law of thermodynamics. The calculation may be put into several equivalent forms, and is discussed in the text-books. An account of the theory is given by Fowler and Guggenheim [157], and its application by Aston [13], Wenner [563], and many others.

The possibility of obtaining reliable values from this method depends upon getting sufficient dissociation for the equilibrium pressures of the dissociation products to be measurable. The dissociation products must themselves be stable under the experimental conditions. Diatomic molecules fortunately give products which do not as a rule take part in reactions other than to regenerate the parent diatomic molecule, although the possibility of the formation of higher aggregates must be considered, whereas only rarely are radicals from polyatomic molecules sufficiently stable for their equilibrium pressure to be measured. Many diatomic molecules are difficult to dissociate, and for this reason very high temperatures or very sensitive methods of detecting dissociation products are required. The former involve experimental difficulties in attaining and measuring the temperature, and often in measuring the concentration; the latter, such as the hot wire method, give results which are often difficult to interpret. Thus in spite of the attractive simplicity in principle of thermal equilibrium methods, relatively few accurate values of dissociation energies have been derived by using them.

The measurement of the variation of dissociation pressure with temperature is less accurate than that of the quantity itself, and if suitable subsidiary data are available, third law procedures give more accurate results. The most satisfactory situation is, of course, when third and second law treatments give the same answer. Where they differ, third law values are to be preferred.

3.2. DIRECT MANOMETRIC METHOD

Clearly the equilibrium constant for a dissociation reaction can be obtained directly from the pressure of a given mass of gas, provided the effect of gas imperfection is known, and provided it is certain that the molecule concerned and its primary dissociation products are the only species present. The first condition is fulfilled in almost all work at pressures near to or less than atmospheric, and only for work of the highest accuracy is it necessary to take gas imperfections into account. The second can be checked by the internal consistency of the results, if the equilibrium constant is determined over a range of temperature.

A fine example of this type of work is the determination of $D_0^\circ(I_2)$ from vapour density measurements at high temperatures by Perlman and Rollefson[388]. These workers were interested in obtaining very accurate values of the equilibrium constant to see whether they exhibited any trend which would indicate the presence of I_3 and incidentally in obtaining an accurate value of $D_0^\circ(I_2)$ for comparison with the spectroscopically derived result. They introduced highly purified iodine into a silica bulb of known volume contained in a furnace controlled at temperatures between 723° K and 1,274° K, measured the pressure, and then removed the iodine and weighed it. Gas imperfection for molecular iodine was taken into account, but atomic iodine was assumed to be a perfect gas.

Table 3.2.1

Temperature ° K	ΔH_0° cal mole^{-1}	*Average deviation*	*Error estimated from 1° temperature error*
1,274	36,515	± 21	± 25
1,173	35,504	± 14	± 30
1,073	35,528	± 30	± 55
973	35,583	± 47	±140
872	35,757	±132	±480

The main source of uncertainty was the absolute temperature measurement, which was made with a platinum, platinum–rhodium thermocouple, calibrated by the National Bureau of Standards to ±2°, but thought to be accurate to ±1° C. ΔH_0° was obtained by substituting the experimentally determined equilibrium constants and the spectroscopically derived free energy functions into equation 3.1.6. The results obtained are shown in *Table 3.2.1.*

The weighted mean of these results is 35,514 cal mole^{-1}, which is strikingly good agreement with the spectroscopic result [217] of

$$D_0^\circ(I_2) = 1{\cdot}5417 \text{ eV} = 35{,}556 \text{ cal mole}^{-1}.$$

$\Delta H^\circ(298{\cdot}1^\circ \text{K})$ is given as 36·06 kcal mole^{-1}. Here the difference between ΔH° at 0° K and at standard temperature is less than the 0·9 kcal mentioned in Section 2.1, because the vibrational frequency of I_2, 215 cm^{-1} [217], is sufficiently low for it to contribute appreciably to the specific heat at room temperature. Other investigators using thermal equilibrium methods have obtained results of slightly less precision, which appeared to show slight trends with temperature, but which lead when averaged without weighting over their temperature ranges to the following values of $D_0^\circ(I_2)$: 35·49 kcal [465], 35·67 kcal [49], and 36·00 kcal [536].*

This work shows that at temperatures of about 1,000° K molecules with a dissociation energy of about 35 kcal are sufficiently dissociated at convenient pressures to permit accurate measurements to be made. Unfortunately the atoms produced at high temperatures are often reactive, and may attack the containing vessel. To get round this difficulty, lower pressures, temperatures, and consequently lower degrees of dissociation must be used, with a resulting loss in precision. Doescher [115, 116] has described the determination of the dissociation energy of F_2, using the static manometric method, where trouble due to atomic reactivity is met with in an acute form. The equilibrium pressure measurements were made in a nickel vessel coated stepwise by heating in fluorine up to 850° C, by comparing the pressure with that of nitrogen at the same temperature using a differential manometer containing *Fluorolube*. Careful equilibration of the furnace with fluorine reduced the reaction with the walls to such an extent that the correction to the difference in pressure between nitrogen and fluorine to take account of this was only 4 per cent. An average value of ΔH, 37·7 ±0·4 kcal, for the dissociation over the temperature range was obtained by plotting $\ln K$ against $1/T$ (equation 3.1.5). Calculated values of the free energy function in conjunction with $\ln K$ at 1,000° K gave $\Delta H^\circ_{1000^\circ \text{K}} = 39{\cdot}0$ kcal. A value of $D_0^\circ(F_2)$ of about 37 kcal is indicated.

The manometric method can only be used for polyatomic molecules under favourable circumstances, such as obtain in the dissociation $N_2O_4 \rightarrow 2NO_2$, studied by several workers. The equilibrium pressure results were combined with an experimental

* See the discussion of their results by Perlman and Rollefson [388].

(third law) entropy and some spectroscopically derived thermodynamic properties by Giauque and Kemp[172] to determine ΔH_0° to be 12·9 kcal, and $\Delta H^\circ_{298\cdot16^\circ K}$ to be 13·7 kcal. Thus $D(N-N)$ in $N_2O_4 = 12\cdot9$ kcal. An example of the usual difficulty in applying the method to polyatomic molecules, that of radical reactivity, is provided by the work of Horrex and Miles[232], who tried to measure the dissociation energy of dibenzyl into benzyl radicals directly in this way. Because the benzyl radical is very stable they hoped to measure the pressure change due to the primary decomposition by using sufficiently low pressures and temperatures. Attempts to do this using a Knudsen gauge were unsuccessful.

3.3. THE EFFUSION METHOD

The effusion method originally suggested by Knudsen is essentially a method of pressure measurement which utilizes the fact that pressure is the effect of the bombardment of the walls of the containing vessel by the molecules. If a small part of the wall is replaced by a hole leading to an evacuated space, then the molecular shower will pass through the hole, and the rate at which molecules do this depends only on the mean component of velocity of the gas molecules and the number present, and may be calculated by kinetic theory to be $ap/(2\pi mkT)^{\frac{1}{2}}$ molecules per second, where a is the area of the hole, p is the pressure, m is the mass of a molecule, k is Boltzmann's constant, and T is the absolute temperature[249]. In the derivation of this formula it is assumed that:

1. The pressure on the evacuated side of the hole is negligible.
2. The hole is small in comparison with the mean free path of the gas*.
3. The thickness of the plate in which the hole is made is small compared with the diameter of the hole, although theoretical corrections can be made when this condition is not complied with.
4. There is thermal equilibrium on the high pressure side.

The application of this result to the measurement of the degree of dissociation of gases at high temperatures was suggested by Weide and Bichowsky[559]. The method is to allow a small constant flow of gas at a constant low pressure to escape through a small hole. If the gas dissociates near the hole according to the equation $A_2 \rightleftharpoons 2A$ the various molecular species will escape at a rate which

* For nitrogen at 0° C and 0·1 mm Hg pressure, for example, the mean free path is 0·45 mm.

is the sum of the rates at which they would escape at that temperature if present in a pure form at the pressure of their partial pressures in the mixture, *i.e.*

$$\begin{aligned}\mathcal{N} &= \mathcal{N}_{A_2} + \tfrac{1}{2}\mathcal{N}_A \\ &= a(2\pi \boldsymbol{k} T m_{A_2})^{-\frac{1}{2}}(p_{A_2} + 2^{-\frac{1}{2}}p_A)\end{aligned}$$

where $\mathcal{N}$ is the number of gas molecules of A_2 entering the container in time t, $\mathcal{N}_{A_2}$ and $\mathcal{N}_A$ are the number of molecules of each species passing through the hole, and p_{A_2} and p_A are the partial pressures. Now if there is no dissociation, $\mathcal{N} = \mathcal{N}' = ap'(2\pi \boldsymbol{k} T m_{A_2})^{-\frac{1}{2}}$, where p' is the pressure calculated on the assumption of no dissociation. Hence, if $p = p_A + p_{A_2}$, we have

$$p_A = 2^{\frac{1}{2}}(2^{\frac{1}{2}} - 1)^{-1}(p - p')$$

p is measured and p' may be calculated, and so the partial pressure of the dissociation product may be obtained. p' may conveniently be obtained by carrying out the experiment at a temperature T_0, which is sufficiently low for there to be no dissociation, and again at T where there is dissociation. In this case, $p' = p_0 \frac{\mathcal{N}}{\mathcal{N}_0}\sqrt{\left(\frac{T}{T_0}\right)}$, where the subscripts refer to conditions at T_0.

The method has been used by de Vries and Rodebush[536], for bromine and iodine, with results in agreement with those from other sources (*see* Section 3.2), and recently by Wise[575] for fluorine. Wise worked in the temperature range 500–650° K, and obtained $\Delta H^\circ_{298^\circ K} = 39{\cdot}9 \pm 0{\cdot}8$ kcal from a plot of equilibrium constant against temperature, in agreement with the direct manometric result (*see* Section 3.2). The sensitiveness of this method is shown by the fact that for the direct measurements it was necessary to work at a temperature several hundred degrees higher, a great disadvantage when working with a reactive gas.

Although direct dissociation measurement has not been made in this way for many compounds, the principle has been used in connection with other dissociation measurements. For example it was used by Bichowsky and Copeland[37] to determine the concentration of hydrogen atoms in their calorimetric measurement of recombination energy (Section 2.2.2), and by Brewer[51] in his determination of the latent heat of sublimation of carbon, which leads to $D(CO)$.

Attention should be drawn in particular to assumption 4 that there is thermal equilibrium on the high pressure side. This has great importance in the design of the effusion vessel, because if the

accommodation coefficient of the gas on the heated vessel surface is very low, it may require a very large value of the ratio, surface area of vessel : area of hole, for this condition to be attained (*see*, for example, Section 8.2.2.6).

3.4. EQUILIBRIUM FLOW METHOD

The possibility that reactions other than recombination will be entered into by dissociation products is the main objection to the static manometric method. In the effusion method this possibility is diminished by the use of low temperatures and pressures. In the flow method the dissociation equilibrium is established in a flow system so that although a static concentration of reactants and products is set up, the product molecules do not remain sufficiently long in the reaction vessel for side reactions to take place. The 'time of contact' or time which the gas stream takes to traverse the reaction vessel is adjusted so that the molecules are in the vessel long enough for equilibrium to be established, and, it is hoped, for a short enough time for the main advantage of the method to be obtained. The concentration of the dissociation products is usually determined spectroscopically.

Bonhoeffer and Reichardt[46] used the method to determine the heat of the reaction

$$2H_2O + O_2 \rightarrow 4OH \qquad \ldots . \quad (3.4.1)$$

and hence, using well established thermal data, the heat of formation of the hydroxyl radical and $D(H-OH)$. The absolute concentration of OH in the thermal dissociation of water vapour could not be determined directly, because the extinction coefficient was not known, and so the device of matching the intensity of OH absorption at different temperatures and at different pressures of reactants was adopted, and for this purpose oxygen addition in varying proportions at constant total pressure was used. Their results lead to

$$D(H-OH) = 115 \pm 2{\cdot}5 \text{ kcal}$$

but experimental details in the method as originally used have been criticized by Dwyer and Oldenburg[130], who have repeated the work under better conditions and arrived at the value

$$\Delta H_0^\circ \text{ (equation 3.4.1)} = 153{\cdot}4 \pm 2{\cdot}6 \text{ kcal}$$

leading to

$$D(H-OH) = 118{\cdot}5 \pm 0{\cdot}7 \text{ kcal}$$

and

$$D(O-H) = 100{\cdot}4 \pm 0{\cdot}9 \text{ kcal}$$

These differ slightly from the values given in Dwyer and Oldenburg's paper, which have been recalculated using $D_0^\circ(H_2) = 103{\cdot}24$, $D_0^\circ(O_2) = 117{\cdot}17$ and $\Delta H_f^\circ(H_2O;\ g)_{0^\circ K} = -57{\cdot}11$ kcal.

The procedure is interesting, and Dwyer and Oldenburg, following Bonhoeffer and Reichardt, give the following treatment. If $p(H_2O) = x$, $p(O_2) = y$, and $p(OH) = z$ then the equilibrium constant for the reverse of the reaction given by equation 3.4.1 is

$$K = \frac{x^2 y}{z^4} \qquad \ldots . \quad (3.4.2)$$

x and y are varied, and z obtained from the intensity of absorption of OH. The experiments are carried out at constant pressure P and at temperatures sufficiently low for $z \ll x, y$. If x/y is varied at constant T and P, z varies and reaches a maximum at $x = \frac{2}{3}P$, $y = \frac{1}{3}P$, *i.e.* for equal numbers of bound hydrogen and oxygen atoms. This is called the 'optimum mixture'. The heat of reaction, ΔH_T for the reverse of equation 3.4.1 is obtained by integrating *e.g.* equation 3.2.1 between T_1 and T_2 to give

$$\Delta H_T = [4\boldsymbol{R} T_1 T_2 \ln(z_2/z_1)]/(T_1 - T_2) \qquad \ldots . \quad (3.4.3)$$

The least ambiguous method of relating absorption spectra and pressures is to consider that if two mixtures show equal intensity of absorption they contain an equal density of absorbing molecules. This is applied to two gas mixtures at different temperatures, the partial pressure of OH at T_1 being reduced by adding more oxygen and thus changing the mixture from its optimum composition at constant P. By this means z is reduced to such a value z_1' that in spite of the higher temperature T_1, the absorption is only as intense as that of the optimum mixture at the lower temperature T_2. If primed symbols refer to values with the equilibrium shifted and unprimed to the optimum mixture

$$z_1'/z_1 = \{[27x_1'^2(P - x_1')]/4P^3\}^{\frac{1}{4}} \qquad \ldots . \quad (3.4.4)$$

Since matching absorption intensities gives matched densities, the results for partial pressures are

$$z_1'/z_2 = T_1/T_2 \qquad \ldots . \quad (3.4.5)$$

and hence

$$\Delta H_T = \frac{4\boldsymbol{R} T_1 T_2}{T_1 - T_2} \ln \frac{z_1' T_2}{z_1 T_1} \qquad \ldots . \quad (3.4.6)$$

where z_1'/z_1 is deduced from equation 3.4.4 and the known partial

pressure of water vapour x_1' which is required at constant P to give matched absorption intensity.

The experimental procedure was to select T_2 as the minimum temperature at which the absorption spectrum of OH was visible in the optimum mixture. P was 775 mm Hg. Then a new value of x, x_1', smaller than the optimum was chosen, and the temperature T_1 found at which the intensity of OH absorption matched that in the optimum mixture at T_2. The mixtures of oxygen and water vapour were prepared by passing oxygen into liquid water maintained at the appropriate temperature, and the resulting gas flowed through the furnace at a constant rate. The furnace had quartz windows at each end through which the light beam passed, and precautions were taken to maintain the temperature constant over the whole length of the furnace, for example the heating at the entrance of the furnace had to be adjusted for the cooling effect of the gas flow.

Dwyer and Oldenburg measured the intensity of single rotational lines in the OH spectrum, using a high resolution grating spectrograph, whereas Bonhoeffer and Reichardt used only a medium size quartz spectrograph, and the former authors point out that this introduces a serious systematic error into the work of the latter. A spectrograph of small resolving power which fails to resolve single lines but shows the whole band as a short, nearly continuous, spectrum requires a relatively high concentration of OH. At this high concentration, although the average absorption may be weak, the actual absorption consists of many lines each one of which at its centre is probably almost completely absorbing the incident radiation; in this case the concentration of OH affects the total intensity transmitted only by the more or less extended wings of the lines, and therefore the nature of the line broadening is important. In this method pairs of absorption spectra are matched, and the two members of such a pair are subject to pressure broadening by different mixtures of H_2O and O_2 which may have different broadening effects. The effect of neglecting this consideration cannot be estimated, but the striking difference in sensitivity between single line and average band absorption measurements is shown by the fact that with the grating spectrograph the absorption of free OH showed up clearly at 768° C, whereas Bonhoeffer and Reichardt found barely observable absorption at 1,150° C. Computed for absorption tubes of the same length the sensitivities differ by a factor of 45.

The use of a single rotational line means that, strictly speaking, equal intensities correspond to equal densities only of molecules

in the particular rotational level responsible for the transition giving rise to the line measured. The proportion of molecules in different rotational levels varies with temperature according to the Boltzmann distribution, and this needs to be taken account of in deducing the total number of molecules from measurement of the intensity of the rotational line. The effect can be calculated and allowed for, and is slight in the present example.

A similar treatment of the dissociation of cyanogen, C_2N_2, into 2CN, also using a flow method, has been given by Kistiakowsky and Gershinowitz [267]. Their estimate of $D(CN - CN)$ is, however, very much lower than all other estimates, and it has been pointed out that lack of resolving power in the spectrograph and pressure broadening effects make the result unreliable [566].

3.5. EXPLOSION, FLAME, AND DETONATION METHODS

3.5.1. *General* [255, 301]

The explosion, flame, and detonation methods of determining dissociation energies all involve the use of exothermic reactions to obtain very high temperatures and thus appreciable dissociation even of molecules with large dissociation energies. In explosions and flames very exothermic reactions occur effectively adiabatically, heating the products to high temperatures, while in detonations the products are heated even above the adiabatic explosion temperature. Under these conditions, the energy used to heat the product gases is the energy liberated in the normal reaction to ordinary molecular products less the energy used up in dissociating these molecules to the equilibrium proportions of atoms and radicals at the final equilibrium temperature. Thus the final temperature reached depends upon the dissociation equilibrium constants involved, and therefore on the dissociation energies. The final composition, and thus pressure, temperature, and other quantities dependent on them, can be calculated using an assumed value of the dissociation energy in question, and compared with experiment. Preferably all the dissociation energies involved, except one, are known, and the method is then used to fix the remaining energy. In the adiabatic explosion method the final pressure is compared with experiment, in the flame method the flame temperature, and in the detonation method the detonation velocity. Of these quantities only the detonation velocity can be measured very precisely. All three have the disadvantage that the result depends on a very large number of other data: the specific heats of a variety of gaseous species over a wide range of temperature, the heats of a number of ordinary

molecular reactions, and probably the values of dissociation energies other than the one being measured. This lack of directness necessitates great care in the choice of subsidiary data. Some estimate of the reliability of the methods can be obtained by carrying out the reaction in the presence of various inert gases, and of varying the composition of the reactants, thereby enabling the results to depend on estimates of dissociation at several temperatures.

One important point in connection with this work is the meaning of 'temperature' in very fast processes, such as are involved in all these methods. It has been known for some time that at ordinary temperatures and pressures some gases can exhibit different specific heats, depending on the rate of the process by which energy is supplied to them. Under most circumstances the specific heat of a gas is found by direct experiment to be equal to that calculated on the assumption that energy is distributed among translational, rotational, and vibrational degrees of freedom according to the postulates of quantum statistical mechanics. However, for very fast processes, there is not time for the excitation of vibrational degrees of freedom, which is a relatively inefficient process, and the apparent specific heat corresponds to translational and rotational energy only. Sometimes the rotational heat also can 'disappear'. Thus different degrees of freedom can have different effective temperatures. This was first demonstrated by the dispersion of sound velocity with frequency in carbon dioxide *. If translational–vibrational or other such relaxation effects occur in these reactions the effective temperature observed or deduced from the experiments will be higher than the true equilibrium temperature, and there will therefore be a tendency to underestimate the extent to which dissociation has taken place, and therefore to overestimate dissociation energies. It may be significant that all flame and detonation measurements of disputed dissociation energies (N_2, CO, F_2) give the higher value of the energy concerned.

3.5.2. *The Adiabatic Explosion Method*

Here the explosion takes place adiabatically in a closed vessel, and the measured pressure is compared with the calculated. It is assumed that the reactants are intially at T_1 and that after the reaction the products are present in chemical and thermal equilibrium at T_2. The calculation of T_2 is carried out by considering the process in three stages; first the reaction, usually a combustion, is assumed to take place completely at T_1, a certain amount of thermal energy being liberated; secondly some of this energy is

* For reviews, *see* Kittel[272] and Richards[417].

used to dissociate the products at the temperature T_1, so that the concentrations correspond to the equilibrium composition at T_2, P_2; thirdly the remainder of the energy is used to raise the equilibrium mixture to T_2. P_2 is easily derived from the gas laws, the gases usually being regarded as ideal. Gas imperfections have little effect. The method of calculation is a cyclic trial-and-error process; a trial value of T_2 is chosen, the equilibrium composition at T_2 calculated using the known or assumed equilibrium constants, and a value of T_2 then calculated using these equilibria, the known heats of reaction, and the known specific heats of the species present. This is repeated for different values of T_2, the choice being guided by the previous results until the calculated value agrees with the assumed value.

This calculated value of P_2 cannot be compared directly with the observed value because of the effect of non-uniform temperature distribution due to finite rates of propagation of reaction in the actual experiment. This effect can, however, be allowed for theoretically in a fairly reliable way [301]. Comparison of calculated and observed explosion pressures suggests that two different effects can cause errors. Under certain circumstances the observed explosion pressures may either be lower or higher than the theoretical figures. Low values are considered to be due to loss of energy by luminescence radiation from the reaction zone; high values to the translational temperature being higher than the equilibrium value because of the slowness of the conversion of translational into vibrational energy. This latter effect has been suggested particularly for explosions in hydrogen–oxygen mixtures containing excess oxygen or added nitrogen. The precise quantitative discrepancies introduced by these effects cannot be accurately assessed, because they may well operate simultaneously and influence the results in opposite directions. Addition of inert gases, which have no internal degrees of freedom, would be expected to reduce these effects. The most careful determination of a dissociation energy by this method, that of the reaction

$$2H_2O \rightleftharpoons H_2 + 2OH$$

carried out by Lewis and von Elbe [302] was made with that precaution, helium being used. It was found that in presence of slight excess of oxygen, the water produced in the hydrogen–oxygen reaction dissociated appreciably into OH radicals. The heat of this dissociation reaction was the only unknown quantity in the calculation of the explosion pressure, and thus ΔE_0° could be calculated from the observed pressure.

In six experiments the mean ΔE_0° was 126·0 kcal, and none of the results differed from the mean by more than 2·2 kcal. Lewis and von Elbe deduce from this value together with other accepted dissociation energies and thermodynamic data, $D(H-OH) = 114{\cdot}6 \pm 1$ kcal, and $D(O-H) = 104{\cdot}3 \pm 1$ kcal. These values differ by *ca.* 4 kcal from those obtained by Dwyer and Oldenburg [130] (Section 3.4).

3.5.3. *The Flame Method*

Whereas in the explosion method the experimental datum, the final pressure, can be obtained experimentally to an accuracy well within 1 per cent, the flame method, in which the flame temperature is measured, is not susceptible of such great accuracy. In its application to the determination of the dissociation energy of nitrogen by Gaydon and his co-workers [515] a numerical value of the desired dissociation energy was not obtained. The observed temperature was compared with the temperature calculated on the basis of the two widely different values of $D(N_2)$ indicated by alternative interpretations of spectroscopic data, and found to agree better with that calculated using the higher: $D(N_2) = 9{\cdot}76$ eV (225·1 kcal).

The cyanogen–oxygen flame has the special feature that the products of combustion, CO and N_2, are both particularly stable molecules, and therefore the heat of reaction and the final temperature are very high: sufficiently high for some dissociation of N_2 to take place. All the other relevant dissociation energies are known, except that of CO, which is too high to affect the results, and the temperature of the stoichiometric flame was calculated to be $4{,}850 \pm 50°$ K for $D_0^\circ(N_2) = 9{\cdot}76$ eV, and $4{,}325 \pm 50°$ K for $D_0^\circ(N_2) = 7{\cdot}38$ eV, the main uncertainty causing the limits of $\pm 50°$ K being the ± 6 kcal in the determination of the dissociation energy of CN [56]. It was thought that the difference of 525° K should be detectable with certainty. The temperature of the flame was determined by using the vibrational temperature of CN, a method which had already been checked by Brewer, Templeton and Jenkins [56] when they measured the heat of formation of CN. It was found that although the temperature of CN in the reaction zone in the flame was under 4,000° K, in the mantle the temperature was $4{,}800 \pm 200°$ K, in good agreement with $D(N_2) = 9{\cdot}76$ eV. The CN temperature had this value over a range of position of a few mm from the reaction zone, indicating that there was no heat loss and that equilibrium had been attained.

The result as it stands is perhaps not as certain as we might wish, because the method of temperature measurement was only checked

against an optical pyrometer at a temperature of about 2,500° K, over 2,000° K less than that measured here. On the other hand, this value of the temperature has been well confirmed in a recent study with the sodium line reversal method, using the sun as background source[87]. The temperature determined for the stoichiometric flame was 4,640 ± 150° K, and values of 4,810 and 4,375° K calculated for the high and low values of $D(N_2)$ respectively.

The status of this latter work is, however, not certain. In an earlier communication the measurement of the temperature of the stoichiometric hydrogen–fluorine flame, using the same technique was reported[86]. This was given as 4,300 ± 150° K. It has since been pointed out[5] that if the temperature of the flame is calculated assuming $D(F_2) = 37$ kcal and $D(F_2) = 63{\cdot}5$ kcal, the results are 3,956 and 4,252° K respectively. Thus the flame temperature measurements support the higher of the two suggested values of $D(F_2)$, whereas almost all the other evidence points strongly to the lower value being correct (*see* Section 8.2.2.9).

3.5.4. *The Detonation Method*

In a detonation wave, the temperature is even higher than the adiabatic explosion temperature. For cyanogen–oxygen, for example, the detonation temperature is probably over 1,000° greater than the flame temperature. This is because, in the calculation of the adiabatic temperature, the thermodynamic assumption is that the change in temperature and pressure takes place reversibly, *i.e.* infinitely slowly, with the pressure on the imaginary piston compressing the gases only infinitesimally greater than the gas pressure. In detonation waves, however, the process takes place very quickly, and in order to do this the pressure difference must be finite, and more work is done on the gases than in the reversible adiabatic process. They therefore get hotter, by an amount specified by the 'dynamic adiabatic' expression of Hugoniot for the energy change in a shock wave*. A detonation wave may be regarded as a shock wave maintained by the energy released in a chemical reaction; the wave velocity depends on this energy release, and thus on the composition of the products, *i.e.* on the

* This is true for an ideal gas. In the detonation of solid explosives, the pressures and densities reached are so high that much energy is used up in overcoming the intermolecular short range repulsive forces, and the temperature may be reduced, although the pressure will be increased. As the form of the equation of state at very high densities and temperatures is not exactly known, estimates of this effect vary: for very low estimates of the temperatures from solid detonating explosives, see Cottrell and Paterson[97].

dissociation equilibria at the very high temperatures involved. Moreover, the wave velocity can be measured very accurately, and therefore in principle provides a method of determining dissociation energies.

If we consider a stable plane shock wave, in which motion is assumed to be one-dimensional, so that no transverse losses occur, an application of the laws of conservation of mass, momentum, and energy yields three equations from which the following three equations can be deduced:

$$D = V_1[(P_2 - P_1)/(V_1 - V_2)]^{\frac{1}{2}} \quad \ldots\ (3.5.4.1)$$

$$W_2 = (V_1 - V_2)[(P_2 - P_1)/(V_1 - V_2)]^{\frac{1}{2}} \quad \ldots\ (3.5.4.2)$$

$$E_2 - E_1 = \tfrac{1}{2}(P_1 + P_2)(V_1 - V_2) \quad \ldots\ (3.5.4.3)$$

where the suffixes 1, 2 refer to the initial and final states respectively, P, V, and E have their usual significance, W_2 is the velocity of the material behind the wave relative to that ahead, and D is the wave velocity itself. Equation 3.5.4.3 is the Rankine-Hugoniot equation, called by Hugoniot the 'dynamic adiabatic' by analogy with the ordinary adiabatic, $dE = -PdV$ to which it reduces for very weak waves, involving no appreciable entropy change. In a detonation wave, where chemical reaction occurs, we must take account in the energy equation of the change in chemical identity of the material on passage through the wave. This is done as described in Section 3.5.2 although there, of course, the calculation was done for the ordinary adiabatic. We may write

$$E_2 - E_1 = \Delta E_{2,1} + \Delta E_R \quad \ldots\ (3.5.4.4)$$

ΔE_R is the energy change at constant volume V_1 and temperature T_1, in the chemical reactions to produce the products which are the equilibrium composition at V_2, T_2. $\Delta E_{2,1}$ is the change in internal energy of the products in passing from V_1T_1 to V_2T_2. These quantities can be calculated from a knowledge of heats of reaction and specific heats.

The Rankine-Hugoniot (RH) equation, expressed in terms of V_2,P_2 defines a curve in the (V,P) plane on which the terminal point V_2P_2 must lie. This is shown diagrammatically in *Figure 3.5.4.1.* For an exothermic reaction, the point P_1V_1 lies below this curve. It was originally assumed by Chapman and Jouget, and their assumption has since been discussed and confirmed by numerous workers [301], that the point P_2V_2 on the RH curve which corresponds to a stable detonation wave is the point of tangency of the

upward line from P_1V_1 (CJ point). The condition of tangency may be expressed mathematically in the alternative forms:

$$\frac{P_2 - P_1}{V_2 - V_1} = \left(\frac{\mathrm{d}P_2}{\mathrm{d}V_2}\right)_{\mathrm{RH}} = \left(\frac{\partial P_2}{\partial V_2}\right)_S \quad \ldots . \quad (3.5.4.5)$$

This condition, together with equations 3.5.4.1, 2, and 3 and the equation of state, specific heats, and equilibrium conditions of the products, suffice to determine P_2, V_2, T_2, W_2 and D. It should be noted that in calculating $(\partial P_2/\partial V_2)_S$, we should, strictly speaking, allow the chemical composition to remain in equilibrium and hence

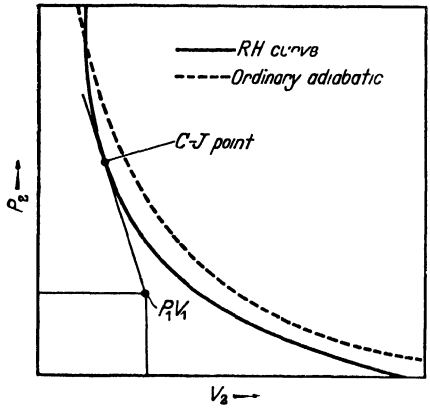


Figure 3.5.4.1. Schematic representation of RH curve for detonation, compared with ordinary adiabatic.

in general to change with V_2. If we do so, however, the labour of computation is greatly increased, and Lewis and Friauf[303], and Paterson[381] have found that for gaseous explosives only very slight errors were introduced by identifying $(\partial P_2/\partial V_2)_S$ with the value calculated for constant composition. This simplification has been made, usually without comment, in almost all calculations of detonation velocity.

These calculations refer to an infinite plane wave, and in actual explosives which propagate in tubes of finite diameter we have to consider the possibility of energy loss by lateral expansion. It is usually possible to obtain a reliable value of D_∞, the detonation velocity at infinite diameter, by measuring D at various diameters (d) and extrapolating a D against $1/d$ plot to zero $1/d$.

3.5. EXPLOSION, FLAME, AND DETONATION METHODS

It has been shown by various workers* that where all the thermodynamic quantities concerned are known, exact agreement between theory and experiment can be obtained, and measurements of detonation velocity in the system cyanogen–oxygen have been used to determine the dissociation energies of carbon monoxide and nitrogen[268]. The conceivable products from cyanogen and oxygen are CO_2, CO, N_2, CN, NO, C_2, N, C, and O, and reliable thermodynamic data are available for all reactions concerned except the dissociation of CO, N_2 and C_2N_2. The measured detonation velocities, which were obtained using piezo-electric gauges to detect the passage of the detonation wave and considered to be accurate to a few m/sec, were extrapolated to infinite diameter, the D versus $(1/d)$ plot giving a good straight line, and were corrected for the slight effect of gas imperfection. These values, D_∞° which were estimated to have a standard deviation of 9 m/sec were then compared with D_∞° calculated using various values of the disputed dissociation energies; as in the flame method, the accuracy is not sufficiently great to deduce values for these quantities; only decision between fairly widely separated values derived from other information is possible. A selection from the experimental results is given in *Table 3.5.4.1.* Best agreement was obtained with $D(N_2) = 9{\cdot}76$ eV, $D(CO) = 11{\cdot}11$ eV, and $D(CN) = 7{\cdot}6$ eV, and all

Table 3.5.4.1

Detonation velocities in $C_2N_2 - O_2$ mixtures from Kistiakowsky, Knight, and Malin [268]

Composition mole %			P atm.	D_{exp} m/sec	D_∞°	D (calc)	T °K	$D(N_2)$ eV	$D(CO)$ eV	$D(CN)$ eV
C_2N_2	O_2	A								
49·88	49·87	0·25	1	2,773	2,771	2,672	5,665	7·38	11·11	7·4
						2,679	5,691	7·38	11·11	6·3
						2,719	5,997	8·57	11·11	7·9
						2,731	6,047	8·57	11·11	7·0
						2,756	6,218	9·76	11·11	8·5
						2,772	6,287	9·76	11·11	7·6
						2,782	6,376	11·8	11·11	9·5
						2,802	6,465	11·8	11·11	8·7
						2,688	5,836	9·76	9·6	6·7
						2,665	5,500	7·38	9·6	5·8
25·0	25·0	50·0	1	2,377	2,387	2,395		9·76	11·11	7·6
						2,389	5,559	9·76	11·11	8·2

* See, for example, experiments on acetylene-oxygen mixtures by Kistiakowsky, Knight, and Malin[269], who made particularly accurate measurements of detonation velocity.

dissociation energies of N_2 and CO substantially lower than these are in disagreement with the results.

The experiments in which 50 mole per cent argon was added are important because it is shown that addition of inert gas had exactly the calculated effect. This would not be so if the gas were 'hydrodynamically' hotter than the equilibrium calculations indicate because of non-excitation of vibrational degrees of freedom in the time available, since argon has no internal degrees of freedom. Kistiakowsky, Knight, and Malin conclude that this work provides very strong evidence in favour of the high values of the dissociation energies.

One detail of the calculation which could be criticized is that apparently the authors calculated the point of tangency to the constant composition isentrope, instead of to the theoretically correct varying composition isentrope. Although Lewis and Friauf, and Paterson, have shown that the effect of this in hydrogen–oxygen and in carbon monoxide–oxygen mixtures made a difference of about 12 m/s it does not follow that this will be so for all mixtures, and the paper would have been more convincing if this point had been considered. Another possibility of error is that the dissociation of N_2 and CO is too slow to go to equilibrium by the CJ point, which would result in a high velocity.

It is unfortunate for this method that the detonation velocity is not a very sensitive parameter. If sufficiently accurate measurements could be made of the temperature (*see Table 3.5.4.1*) or some other detonation parameter the comparison with theory would be improved.

In conclusion, it should be pointed out again that all these methods require the accuracy of a vast amount of subsidiary thermochemical and thermodynamic data, and the results should therefore be interpreted with caution.

3.6. THERMAL CONDUCTIVITY METHOD

Heat transfer in gases normally takes place by gas molecules picking up translational energy when they strike a hot surface, and giving it up when a cooler surface is reached. Although this is what happens in effect, the process is modified by collisions. Details are dealt with in the usual text-books. It is necessary to mention here that not all gas molecules take up an energy corresponding to the temperature of the hot surface when they strike it. If it is assumed that molecules striking the hot surface either attain its temperature or are reflected at the incident temperature, the ratio

of the number which attain the surface temperature to the total number which collide with the surface is a, the accommodation coefficient. Other mechanisms accounting for an accommodation coefficient less than unity may exist.

Nernst[365] pointed out in 1904 that in a dissociating gas, energy transfer could take place as follows: molecules absorb energy at the hot surface and are dissociated; subsequent recombination at the cold surface releases this energy as thermal energy. He showed that this would result in a great increase in the coefficient of thermal conductivity with temperature as a gas became dissociated, and that this could be seen to occur in dinitrogen tetroxide[338]. He considered that the measured coefficient of thermal conductivity, λ_m, could be written

$$\lambda_m = \lambda + \lambda_a$$

where λ is the thermal conductivity in an undissociated gas, and λ_a, the part due to dissociation, is given by

$$\lambda_a = \frac{D.\Delta E.P}{RT^2}\left(2 + \frac{RT}{\Delta E} + \frac{\Delta E}{RT}\right)\frac{a(1-a)}{(1+a)} \quad \ldots . (3.6.1)$$

$$\sim \frac{D.(\Delta E)^2 P}{R^2 T^3}\cdot\frac{a(1-a)}{(1+a)} \quad \ldots . (3.6.2)$$

where D is the diffusion coefficient of the dissociation products through the undissociated gas, ΔE is the energy change in the dissociation, P is the pressure, and a is the degree of dissociation.

A careful test of Nernst's theory was reported by Isnardi[243] in 1915. His work consisted of the measurement of the thermal conductivity of iodine (whose dissociation as a function of temperature and pressure was well known), comparison of the experimental results with those of Nernst's theory, and the use of the method to determine $D(H_2)$ which was not then known. Isnardi measured thermal conductivities by the hot wire method, in which the rate of heat removal by conduction from the wire arranged concentrically in a cylinder containing the gas is given by

$$Q = \frac{2\pi l}{\ln R/r}\int_{T_1}^{T_2} \lambda \mathrm{d}T \quad \ldots . (3.6.3)$$

where l is the length of the wire, r and R are the radii of the wire and the cylinder respectively, T_2 and T_1 are the temperatures of the hot wire and the cylinder wall, and λ is the thermal conductivity. The apparatus gave a good check with other values of λ reported for dry air, and was then used to measure Q for iodine. Since

$\lambda_m = \lambda + \lambda_a$, the analogue of equation 3.6.3 for Q_a can be written, and a Q_a for iodine derived for comparison with experiment. Since ΔE and α are known, the only unknown in equation 3.6.2 is D, the diffusion coefficient. The kinetic theory result that

$$D = \frac{AT^{n+1}}{P}, \qquad \ldots . \quad (3.6.4)$$

Table 3.6.1

Observed and calculated Q_a for Isnardi's experiments on iodine at various temperatures ($A = 1/38{,}850$ for P in cm Hg) (*Isnardi*)

T °K	α	Q_a *calc.* W	Q_a *obs.* W
700	0·00368	0·0371	0·038
800	0·0188	0·2024	0·201
900	0·0673	0·7618	0 765
1,000	0·1838	2·086	2·15
1,060	0·3052	3·268	3·15
1,080	0·3483	3·653	3·49

where A is constant, was assumed to be correct, and n for iodine set equal to 1. On this basis, the experimental Q_a was used to deduce a value for A, and the observed and calculated Q_a compared on this basis. Some of the results are given in *Table 3.6.1.* The agreement between the observed and calculated results is good, although there is a tendency for the observed results to be lower than the calculated at the highest temperature. This may be due to an incorrect dependence of D on T being chosen, or to a dependence of D on α. The values for D, 0·027 $cm^2 . sec^{-1}$ at 273° K, 0·166 $cm^2 . sec^{-1}$ at 700° K and 1 atm., are in good agreement with what might be expected on kinetic theory. The method was then applied to hydrogen, and a value of $\Delta E = 95$ kcal for the dissociation energy in the temperature range studied was obtained. This result is a little lower than the presently accepted value.

At about the same time Langmuir studied the dissociation of hydrogen on a heated tungsten filament, using the same experimental method with a different theoretical treatment. His first result[292] gave $\Delta E = 130$ kcal, his second[294], using a more refined theoretical treatment gave 84 kcal.

The method has recently been used by Franck and Wicke[160, 567] to determine $D(F_2)$ and by Farber and Darnell[151] to determine $D(N_2)$. In both investigations, no dissociation effect was found at the temperatures employed, from which it was deduced that

$D(F_2) > 45$ kcal, and $D(N_2) > 225$ kcal, respectively. The former workers used the Nernst equation, the latter used for the power conducted away

$$\Delta Q = \frac{aP}{(2\pi MRT_1)^{\frac{1}{2}}}\left[\int_{T_1}^{T_2}(C_v + \tfrac{1}{2}R)\mathrm{d}T + a\Delta E\right]$$

where T_2 is the wire temperature and T_1 the temperature of the cold wall. a is the accommodation coefficient and was determined from its low temperature value and assumed to remain constant. For H_2, $\Delta E = 101 \pm 3$ kcal was obtained by the latter workers.

The theoretical treatment of the effect is not altogether satisfactory. Rates of recombination may have some effect on the result and therefore the assumption that the equilibrium concentration of dissociated molecules exists at all temperatures may not be valid. Moreover, it is not certain that the accommodation coefficient for dissociation will be the same as that at temperatures at which dissociation does not take place. It is known that whereas in ordinary collisions in some gases, translational energy is shared in all collisions, vibrational energy is only excited in a small proportion of collisions, and it is not unreasonable to consider that something analogous may take place in collisions with a surface. A decrease in accommodation coefficient for dissociating collisions with a surface would have the effect of increasing the temperature at which it becomes possible to detect dissociation.

It remains perfectly valid to consider the increase of thermal conductivity as very good qualitative evidence of dissociation, particularly, as Langmuir pointed out, the fact that at high temperatures in dissociating gases the heat conductivity actually increases as the pressure is lowered. The absence of such an effect does not, however, serve as completely conclusive proof that dissociation does not take place at true equilibrium at the temperature concerned, thought it must be admitted that this possibility of non-appearance of the effect has not been verified experimentally for a gas whose dissociation energy is known with certainty.

3.7. MOLECULAR BEAM METHODS

If molecules are allowed to escape from an enclosure into an evacuated space through a small hole under the conditions described for the effusion method in Section 3.3, they may be collimated into a molecular beam by the use of slits. If a pulse of this molecular beam is allowed to fall on a moving receiving plate, the condensed

molecules will be distributed along the plate according to their velocities. An experiment of this nature was first made by Stern [469], who intercepted a stream of silver atoms on a rotating plate with the object of verifying the Maxwell velocity distribution experimentally. Further direct experimental verification of the Maxwell distribution was provided, using a similar method with mercury vapour, by Lammert [288]. If the Maxwell distribution is taken as proved, the method can be used to find out the mass distribution of particles in the molecular beam. In particular, in a beam of molecules and dissociated atoms, it should be possible to deduce the degree of dissociation from the observed velocity distribution, and hence the dissociation energy, if the beam is in dissociative equilibrium with the enclosure at a known temperature. Zartman [581] studied a beam of bismuth vapour, which he allowed to fall on to a rotating cylinder, with a slit in the wall, and condensed the vapour on a glass plate coated with bismuth placed inside the cylinder opposite to the slit. If the cylinder is stationary, and the slit aligned with the beam, the bismuth condenses at a point diametrically opposite to the slit, but if the cylinder rotates, the condensation is displaced and spread out according to the velocity distribution in the beam. By rotating the cylinder at 241 rev. sec^{-1}, Zartman spread molecules having velocities from 168 m sec^{-1} to 673 m sec^{-1} over a band 3 cm wide. The extent of the bismuth deposit as a function of distance on the glass plate was found by measuring the optical density of the deposit. It was found that the velocity distribution corresponded to a beam consisting 40 per cent of atoms and 60 per cent of Bi_2 molecules from an enclosure at 1,124° K. A more detailed study using the same method was made by Ko [275], who varied the temperature of the crucible from which the bismuth was vaporized. To prevent blocking of the collimating slits by condensation it was found necessary to have them about 20° higher than the crucible and the dissociation found was taken to refer to this temperature. The degree of dissociation was found from the velocity distribution, the pressure was found from the total amount of material effused from the crucible (*see* Section 3.3), and thus the dissociation constant was obtained. The plot of $\ln K_p$ against $1/T$ gave a straight line corresponding to $\Delta H = 77{\cdot}1 \pm 1{\cdot}2$ kcal at 1,150° K. Unfortunately the spectroscopic information required to calculate $D_0^\circ(Bi_2)$ from a single value of $\ln K_p$ is not available.

A difficulty in this method is the detection of the molecular beam. Any method based on the optical density of deposited material requires the assumption that the accommodation coefficient of

bismuth atoms at a bismuth surface is the same as that of bismuth molecules, which is by no means self-evident.

Another method of analysing a molecular beam for atoms and molecules depends on the fact that atoms or molecules with a resultant magnetic moment will be deflected by a magnetic field, whereas those without a moment, *i.e.* in ^1S and $^1\Sigma$ states respectively, will not be deflected. The observation of this effect was first made by Gerlach and Stern[170] for a beam of silver atoms, and applied to the measurement of magnetic moments. However, it was realized that for some dissociation equilibria the molecules in the beam in $^1\Sigma$ states would not be deflected, whereas the atoms would be. This applies to the alkali metals, for example, where the ground state of the diatomic molecule is $^1\Sigma$ and that of the atoms is ^2S. Thus the effect of an inhomogeneous magnetic field on a molecular beam of gaseous alkali metal in dissociative equilibrium affords a method of measuring the degree of dissociation. The intensity of the beam is greatest directly in line with the slit system in the absence of a magnetic field; when the field is applied, the atoms are deflected to left and right, but the molecules are unaffected. Again the difficulty is to measure the intensity of the beam, and for alkali metals the favoured method has been to make use of the observation of Langmuir that a tungsten filament heated to 1,200° K or more in saturated caesium vapour converts all the caesium atoms which strike it into caesium ions, and that when the filament is surrounded by a negatively charged cylinder a positive ion current, which is independent of the filament temperature and of the applied potential, flows from the filament[295]. The principle was used to measure the vapour pressure of rubidium and potassium by Killian[263], and applied to the measurement of intensity distribution in molecular beams by Taylor[511]. Positive ion currents of between 10^{-8} and 10^{-7} A were expected from an ion beam.

Table 3.7.1

Substance	ΔH kcal	D_0°
K_2	15·9	14·3, 13·0 (*see text*)
Na_2	17·5	16·8
Li_2	24·0	23·4

Using Taylor's technique, Lewis[305] determined the equilibrium between atoms and molecules of lithium, sodium, and potassium by the magnetically deflected molecular beam. This was done for a

range of temperatures of the evaporating oven, and the results used by way of a $\ln K_p$ against $1/T$ plot to determine ΔH at the temperature of the investigation. $\ln K_p$ at a single temperature, together with spectroscopic information, was used to give D_0°, and the results were as given in *Table 3.7.1.*

Loomis and Nusbaum[321] pointed out that, for K_2, Lewis used an incorrect value of the moment of inertia, and that the correct value of D_0° on his data should be 13·0 kcal. Later Meissner and Scheffers[343] reported confirmation of Lewis's results, using the same method. The results are in fairly good agreement with those obtained by other methods. It should be mentioned that the exact validity of the detection method depends on the view that the carrier of the positive ion current is the alkali metal atomic ion and not the molecule ion. The overall results suggest that this is so, as does the fact that the temperature of the wire is well above the temperature of the oven from which the beam comes. Ives[245] has suggested that there is evidence that higher aggregates than atoms carry the current. The possibility of higher species than A_2 being present is so slight that it seems likely that Ives's work is at fault.

The other point to be considered in experiments of this nature is that as in the effusion method, the molecular beam must be in thermal dissociative equilibrium with the enclosure. This could fairly readily be checked by showing that the results are independent of the ratio of the hole to the surface of the enclosure, but such a test has apparently not been made in the experiments mentioned above. There is of course good *a posteriori* evidence that this was so in the work on the alkali metals, but it may not have held in the work on bismuth.

3.8. THE CHEMILUMINESCENCE METHOD

The application of chemiluminescence by Polanyi and his collaborators to the determination of the dissociation energies of sodium and potassium is an elegant but rather specialized study in the field. It was found that when sodium and halogen vapours react in a very 'dilute flame', intense chemiluminescence is produced, which can only be attributed to the reaction of halogen atoms with Na_2 molecules:

$$Cl + Na_2 \rightarrow NaCl^* + Na$$

This was established by showing (a) that the intensity of the light emitted decreased and could be almost completely extinguished by raising the temperature of the reaction zone, and (b) that the light yield increased more rapidly with pressure than would correspond

to a linear relationship. Both of these facts point to collisions with Na_2 molecules being the important reaction and Polanyi and Schay[393] were able to explain the decrease in light intensity quantitatively in terms of the dissociation of Na_2. They obtained $D(Na_2) = 18 \pm 2$ kcal. Further work, using bromine as the halogen, by Ootuka[375] gave $D(Na_2) = 19 \pm 1$ kcal, and $D(K_2) = 12{\cdot}5$ kcal.

This method is in effect a variation on the manometric method, using a very special technique for measuring the pressure of molecules.

3.9. THERMOCHEMICAL METHODS

As already mentioned in Section 2.2.8, measurement of the heats of formation of a variety of atoms and radicals allows the thermochemical derivation of a large number of heats of dissociation involving them. It is not intended to discuss these methods and results comprehensively, but mention should be made of one particular thermochemical cycle which has been widely applied. The dissociation energy of a diatomic metallic halide or oxide, $D(MX)$ is related to other thermochemical quantities by

$$\begin{aligned} D(MX) &= \Delta H_f(M; g) + \Delta H_f(X; g) - \Delta H_f(MX; g) \\ &= L_M + \tfrac{1}{2}D(X_2) + \tfrac{1}{2}\Delta H_f(X_2; g) - \Delta H_f(MX; s) - L_{MX} \end{aligned}$$

where L is a heat of vaporization.

The heat of formation of the solid oxide or halide is usually known. That of the alkali metal halides, for example, depends upon the heat of solution of the alkali metal in water, the heat of neutralization with the halogen acid, and the heat of solution of the solid in water. The first is the least accurately known of these quantities: for example the spread of the values for the heat of solution of solid sodium in water quoted by Bichowsky and Rossini[38] is 1·4 kcal mole^{-1}. Heats of formation of oxides may be determined by direct combustion of the metal, or by measurement of the heat of solution in acid.

The heat of vaporization depends on the measurement of vapour pressure. The low volatility of the metals and their salts and oxides restricts us to two methods of measurement, the Knudsen method and the rate of evaporation method. The principle of the Knudsen method, which depends on the rate of effusion of the vapour from a small orifice in a heated cell containing the material, has been discussed in Section 3.3. The rate of evaporation method, due to Langmuir[293] depends upon the assumption that there is no activation energy opposing condensation; on this view the rate of

evaporation into a vacuum from unit area of heated surface is given by $aP(M/2\pi RT)^{\frac{1}{2}}$, where a is the accommodation coefficient, M the molecular weight, and P the vapour pressure. This method appears to be generally applicable, but there is some doubt whether the assumptions are justified for graphite (*see* Section 8.2.2.6). From the vapour pressure at any temperature the heat of vaporization may be deduced if the thermodynamic functions of the solid and gas are known, using third law methods. The heat of vaporization at the temperature at which it takes place can of course be deduced from $\mathrm{d}\ln P/\mathrm{d}T$ at this temperature, using the second law (*see* Section 3.1).

Thermochemical determinations of dissociation energy obtained in this way can hardly be subject to the very large errors which may affect spectroscopically determined dissociation energies if the ground state, for example, is incorrectly identified or if the range of vibrational levels available is small. Applications to oxides are discussed, for example, by Brewer and Mastick[53], to halides by Barrow and Caunt[17]. Gaydon[166] also discusses the results for particular molecules.

4

DETERMINATION OF BOND DISSOCIATION ENERGIES BY KINETIC METHODS

4.1. HEATS OF REACTION DETERMINED KINETICALLY

MEASUREMENTS of rates of reaction may sometimes be used to deduce heats of reaction quite generally, as follows. Consider the general reaction

$$A+B \ldots \rightleftharpoons C+D+ \ldots \quad \ldots . \quad (4.1.1)$$

The rate of the forward reaction may be expressed

$$\frac{dc_C}{dt} - \frac{dc_D}{dt} = \ldots = k_1 c_A \cdot c_B \ldots \quad \ldots . \quad (4.1.2)$$

and that of the reverse reaction

$$\frac{dc_A}{dt} = \frac{dc_B}{dt} = \ldots = k_2 c_C \cdot c_D \ldots \quad \ldots . \quad (4.1.3)$$

where c_A is the concentration of species A, *etc.* At equilibrium these two rates are equal, and if the ideal gas laws hold, so that $pv = nRT$, we have

$$(RT)^{\Delta n} k_1 p_A \cdot p_B \ldots = k_2 p_C \cdot p_D \quad \ldots . \quad (4.1.4.)$$

where p_A is the partial pressure of A, *etc.*, and Δn is the change in the number of moles in the reaction. Now, for ideal gases, we have for the equilibrium constant K,

$$K = \frac{p_C \cdot p_D \ldots}{p_A \cdot p_B \ldots}$$

and since

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$$

we have, from equation 4.1.4

$$\Delta H = \Delta n RT + RT^2 d(\ln k_1/k_2)/dT$$

or

$$\Delta E = RT^2 d(\ln k_1/k_2)/dT \quad \ldots . \quad (4.1.5)$$

Hence if we know experimentally the temperature dependence of k_1 and k_2, we can obtain ΔE. This result is quite independent of any theory of k_1 and k_2, and depends on observation only. It does depend, however, on the rate being the same function of concentration throughout the range, and this is seldom experimentally established. If, within the limits of experimental error, we can describe the kinetic results for k_1 and k_2 by the Arrhenius equation,

$$\ln k_1 = A_1 - E_1/RT, \text{ etc.} \quad \ldots . \quad (4.1.6)$$

we have

$$\Delta E = E_1 - E_2 \quad \ldots . \quad (4.1.7)$$

Particular assumptions about the kinetics of dissociation reactions, and the activation energy of atom or radical recombination reactions enable the dissociation energy to be deduced from the measurement of k_1 only. These are discussed in Section 4.2; in the present section we are concerned with the more general case. The typical reaction studied is that of a molecule with a radical or atom to give a radical or atom and another molecule. If the heats of formation of the molecules and one or other of the radicals or atoms are known, the heat of formation of the other atom or radical can be deduced from the heat of reaction, and hence a dissociation energy. For example, considering the reactions

$$CH_3 + H_2 \rightarrow CH_4 + H \ldots E_1$$

and

$$H + CH_4 \rightarrow CH_3 + H_2 \ldots E_2$$

we have $E_1 - E_2 = \Delta E$ for the reaction of hydrogen molecules with methyl radicals, and $\Delta E = D(H_2) - D(CH_3 - H)$. The main difficulty in using this method is to obtain sufficiently reliable information about the kinetics of a reaction to be able to determine the activation energy of an elementary step such as those given above. A very good account of the work on such reactions is given by Steacie[467]. For example, Steacie considers that the most probable value for E_1, above, is 9 ± 2 kcal, and for E_2 13 ± 2 kcal, whence $D(CH_3 - H) \simeq D(H_2) + 4$ kcal. The temperature to which this refers is not clearly defined, but it is a few hundred degrees whence $D(CH_3 - H)$ at room temperature $\sim$107 kcal, which is not in very good agreement with the most reliable value. This value of E_1 is, however, controversial, and an estimate of 13 kcal, which makes $D(CH_3 - H) \simeq D(H_2)$, has also been given[9a].

The best known example of the determination of a dissociation

energy by this method is that of $D(CH_3-H)$ by Kistiakowsky and co-workers, using the reactions*

$$CH_4 + Br \rightarrow CH_3 + HBr$$
$$HBr + CH_3 \rightarrow Br + CH_4$$

They followed the work of Bodenstein and Jung[45], who deduced $D(H_2)$ from a similar study of the reaction between bromine and hydrogen, giving the value $D(H_2) = 106$ kcal. This result differs from the most reliable value by less than 3 kcal. It is, of course, not the most satisfactory determination of $D(H_2)$, whereas the present best value of $D(CH_3-H)$ comes from Kistiakowsky's work, which has received considerable confirmation by other methods.

Table 4.1.1

Rate of bromination of methane at 503° K (*Kistiakowsky*[266])

$[CH_4]$ mm Hg	$[Br_2]$ mm Hg	$-\left(\frac{d[Br_2]}{dt}\right)_{t=0}$ mm. sec^{-1} × 10^{-1}	k' sec^{-1} × 10^{4}
547	53·5	1·17	7·0
613	40·5	1·11	7·3
284	40·5	0·72	7·2
473	25·1	0 83	7·8
280	21·5	0·53	7·0
497	16·3	0·65	7·3

Under these circumstances it is probably better to describe Kistiakowsky's work in detail rather than Bodenstein's, although it must be remembered that the close similarity of the kinetics that Kistiakowsky studied to those of the hydrogen–bromine reaction made less necessary a closely detailed proof of every step. The occurrence of these reactions in the photobromination of methane was shown by measuring the rate of disappearance of bromine photometrically to establish the kinetics. From the plot of $[Br_2]$ against time the initial rate of disappearance of bromine was obtained as a function of the initial pressures of the reactants $[CH_4]$ and $[Br_2]$, and found to fit the equation

$$-(d[Br_2]/dt)_{t=0} = k'[CH_4][Br_2]^{\frac{1}{2}}[1/P]^{\frac{1}{2}},$$

where P is the total pressure of reactants. Some typical results are given in *Table 4.1.1.*

* The literature references to this work are a little complicated, and are as follows: preliminary note giving brief description of complete research, reference 8; study of the reaction $CH_3 + HBr \rightarrow CH_4 + Br$, reference 7; study of the bromination of methane, reference 266, and of ethane, reference 6.

The initial rate was varied by a factor of 2, and the methane and bromine pressures by factors of 2 and 3 respectively. The bromine pressure could not conveniently be raised above about 50 mm Hg because the Lambert-Beer law was only known to apply accurately to bromine up to this pressure. This dependence on the square root of the bromine pressure suggests attack by bromine atoms, and the following scheme seemed a reasonable one, particularly in view of the work of Bodenstein and Jung.

$$\begin{aligned}
&1.\ Br_2 + h\nu \rightarrow Br + Br\\
&2.\ Br + CH_4 \rightarrow CH_3 + HBr\\
&3.\ CH_3 + Br_2 \rightarrow CH_3Br + Br\\
&4.\ CH_3 + HBr \rightarrow CH_4 + Br\\
&5.\ Br + Br + M \rightarrow Br_2 + M
\end{aligned}$$

This scheme leads to

$$\frac{d[CH_3Br]}{dt} = \frac{k_2 k I^{\frac{1}{2}}[CH_4][Br_2]^{\frac{1}{2}}[1/P]^{\frac{1}{2}}}{1 + (k_4[HBr])/(k_3[Br_2])}$$

where I is the light intensity, and k a non-temperature dependent apparatus constant. The required dependence on the square root of the light intensity, and the inhibition by HBr were demonstrated experimentally, and a plot of $\ln k'$ against $1/T$ gave a good straight line of slope $18{,}250/\boldsymbol{R}$. If the A factor in the expression

$$k' = Ae^{-E'/\boldsymbol{R}T}$$

is proportional to $T^{\frac{1}{2}}$, the true activation energy E is 17·8 kcal. This temperature dependence of the rate is clearly to be ascribed to reaction 2, so $E_2 = 17{\cdot}8$ kcal. Now since the $T^{\frac{1}{2}}$ factors in two opposing bimolecular reactions will cancel, the energy change is equal to the difference in activation energies as defined above between the forward and back reactions, and we have

$$CH_4 + Br \rightarrow CH_3 + HBr,\ \Delta E = (17{\cdot}8 - E_4)\ \text{kcal}$$

E_4 is expected to be small, since it is similar to the reaction of hydrogen atoms with hydrogen bromide, whose activation energy is only about 1 kcal[356]. The study of the yield of methane in the photolysis of methyl iodide–hydrogen bromide mixtures, which is attributed to reaction 4, showed that E_4 was about 0·8 kcal greater than the activation energy of

$$CH_3 + I_2 \rightarrow CH_3I + I$$

which is estimated to be $0{\cdot}5 \pm 0{\cdot}5$ kcal, by what Steacie[467] describes

as 'a rather dubious process of reasoning by analogy'. Thus ΔE for the reaction between bromine atoms and methane is $17{\cdot}8 - E_4$ kcal, $\sim$16·3 kcal. From this result, and the value for $D(\mathrm{H-Br})$, that for $D(\mathrm{CH_3-H})$ follows. The value given by Van Artsdalen [11] is 103 kcal at 450° K, 102 kcal at 293° K, and 101 at 0° K.

4.2. DIRECT KINETIC DETERMINATION OF DISSOCIATION ENERGY

4.2.1. *General*

The direct kinetic determination of dissociation energies depends on the assumption that for the reaction,

$$\mathrm{R_1R_2} \rightarrow \mathrm{R_1} + \mathrm{R_2}$$

the activation energy of the reverse or recombination reaction is zero. Thus the activation energy of the forward reaction is equal to the energy of reaction. The assumption of zero energy of activation for recombination has considerable experimental justification. An energy of activation would imply that two atoms of appropriate spin approaching one another to form a molecule would suffer some repulsion before combining. There would be a hump on the energy–interatomic distance curve, or 'potential energy' curve, for the interaction of two atoms. Much evidence on such potential energy curves has accumulated from band spectroscopic measurements, and the results show that usually no such potential maximum exists. It has, however, been found by Herzberg and Mundie [219] that potential maxima exist in the energy curves for the ground states of AlH and BH. Herzberg [217] has shown that on his interpretation of the NO spectrum, a potential maximum of at least 1·04 eV ($\sim$23 kcal) must exist, although this interpretation has been contested by Gaydon [165], and Hagstrum's interpretation of the CO spectrum requires a potential maximum of about 0·2 eV (5 kcal) [196]. Both these interpretations are controversial, but reasons why such maxima may occur are fairly well understood [217] and they may not always be ruled out. The situation for polyatomic molecules is much more complex, chiefly because of the great experimental difficulties involved in measuring rates of recombination of radicals. However, Lossing and his collaborators have recently devised a mass spectrometric technique for measuring concentrations of methyl radicals [324] which has been applied to the measurements of their rate of recombination [240, 241]. The concentrations of methyl radicals, ethane, and methane, formed by the thermal decomposition of mercury dimethyl in a stream of helium, were measured by continuous analysis of the gas stream. A small portion of the gas

entered the ionization chamber of the mass spectrometer through a small orifice in a quartz cone projecting into the stream. The mercury dimethyl was almost completely decomposed into methyl radicals by passing through a movable tubular furnace, whose distance upstream from the orifice could be varied. When the distance was short, the time available for recombination was less than 10^{-4} sec, and the methyl radicals formed were found to be nearly equivalent to the mercury dimethyl decomposed. When the furnace was moved upstream, sufficient time was allowed for some recombination, and an equivalent amount of ethane appeared. Combination of the methyl radicals appeared to take place both by a first and by a second order reaction. The latter was studied, and found to have a small negative temperature coefficient. That the activation energy is nearly zero is also shown by the work of Gomer[182] and Lucas and Rice[327], who found a collision efficiency of approximately unity at about 450° K, although the actual value of the collision efficiency does not agree exactly with that determined above. Previous estimates of the collision efficiency of this reaction vary, but there appears to be fairly general agreement that the activation energy is low. The most important evidence that the recombination of polyatomic radicals takes place without activation is the consistency of the information deduced in this way with other estimates of dissociation energies.

The precise relationship of the experimental activation energy (derived from the Arrhenius equation, $k = Ae^{-E/RT}$ where k is the first order rate constant for the dissociation reaction) to the dissociation energy, on the assumption of no potential maximum, has been discussed by Szwarc[497]. He has shown that on certain assumptions about the shape of the potential energy curve, if $kT \gg h\nu_0$ (where ν_0 is the fundamental vibration frequency of the link broken), the observed activation energy is exactly equal to D, the dissociation energy, and if $h\nu_0 \gg kT$, $E = D + RT$. The first condition corresponds to a very weak bond or a very high temperature, the second probably applies normally, but the exact result is uncertain because of the assumptions made, which are certainly not exactly valid. It is sufficient that this treatment shows that the experimental activation energy of the dissociation reaction gives a good approximation to the bond dissociation energy.

The experimental activation energy, from the Arrhenius expression, depends on the reaction kinetics according to the equation,

$$\frac{1}{[R_1R_2]} \cdot -\frac{d[R_1R_2]}{dt} = Ae^{-E/RT} = k \quad . \quad . \quad . \quad . \quad (4.2.1.1)$$

provided of course R_1R_2 decomposes by a bond dissociation mechanism. E is given by $RT^2 \mathrm{d}\ln k/\mathrm{d}T$, and hence from a plot of $\ln k$ against $1/T$. This requires an accurate knowledge of k to give accurate values of E. Szwarc[497] has pointed out that for $1/T_1 - 1/T_2 = 10^{-4}$, which corresponds to a reasonable temperature range of about 50° if the experiments are carried out at about 500° K, if the rate constants at T_1 and T_2 are in error by 20 per cent the maximum error in the experimental activation energy is 8 kcal. This can certainly be very much reduced by careful experimental work, but such careful experimentation will only reduce the random errors, which in any case are not likely to combine to give such a large effect. The danger of error comes from the possibility of a surface effect, or of some competing reaction, which has a different temperature coefficient from that of the desired reaction, which might quite well cause a large systematic error. However, if the constant A in equation 4.2.1.1 is known, it should be possible to deduce E from the rate measured at a single temperature. There is much experimental evidence to show that for most first order reactions, A is about 10^{13} sec^{-1}. Szwarc points out that if A is known for a reaction with an activation energy of 55 kcal, an error in k measured at 800° K of as much as 100 per cent causes an error of only 1·1 kcal in the activation energy. In the same example, an error by a factor of 5 in A produces an error of 2·6 kcal in E. Szwarc concludes from a detailed study of the experimental evidence that the 'true' values of A for unimolecular dissociations do not differ by more than a factor of 5 from 10^{13} (*see* Section 9.6.35). On the two assumptions for the relationship between $h\nu_0$ and kT mentioned above, the theoretical value of A is:

$$kT \gg h\nu_0,\ A = \nu_0$$

and

$$h\nu_0 \gg kT,\ A = kT/h,$$

where k is Boltzmann's constant. The vibration frequency for 'moderately weak' bonds, such as those of dissociation energy less than 50 kcal, is usually less than 1,000 cm^{-1}, or $\nu_0 \leqslant 3 \times 10^{13}$ sec^{-1}, and for $T = 500°$ K, $kT/h \sim 10^{13}$ sec^{-1}, so that these theoretical results are in good agreement with the experimental results.

Apart from the experimental difficulty of obtaining the correct number for k, there is the difficulty of ensuring that the process for which k is measured is in fact a decomposition into radicals. If the kinetic observations measure directly the rate of radical formation, this difficulty disappears, but often the evidence that the

decomposition takes place into radicals is complex and difficult to interpret reliably. In the next sections we shall discuss various methods of measuring the rates of radical-forming reactions. This field has been fairly well covered by reviews in recent years, particularly those of Steacie[467] and Szwarc[497] already mentioned, and the treatment will therefore be fairly brief, particular attention being paid to the most recent developments.

4.2.2. *The Mirror Removal Technique*

Paneth and his collaborators[378] showed that free alkyl radicals produced by decomposition of lead tetra-alkyls at low pressures in a carrier gas could be detected by their reaction with metallic mirrors, and Rice and others developed the technique and used it for the determination of the activation energies for the decomposition of organic compounds into radicals[414]. They found that a great variety of organic compounds when heated in the range 800–1,000° C decompose into free radicals, and that the radicals can be detected using mirrors of several different metals. The technique was considerably simplified by the use of a condensible gas, such as water vapour or carbon dioxide, as a carrier, making the very high pumping speeds required by Paneth to obtain high flow rates unnecessary. It was assumed that if no recombination

Table 4.2.2.1. Ethane decomposition (Rice and Dooley[412])

Distance from end of furnace (cm)	2·5	2·1	1·5	1·0	0·7
Ratio t_{906}/t_{960} . . .	3·14	3·31	3·73	3·88	4·08
E (kcal)	61·6	64·5	71·0	73·0	76·0

occurred, the concentration of radicals in the gas flowing out from the furnace would, for constant flow conditions, *i.e.* constant contact time, depend upon the rate of their production. It was also assumed that the time of removal of a standard metallic mirror deposited downstream from the furnace was proportional to the radical concentration at that point in the system. Thus the relative rates of removal of standard mirrors at different furnace temperatures give a measure of the relative rates of radical production at these temperatures. The assumption that no recombination takes place was recognized not to be valid, and so the times of mirror removal were determined for various distances of the mirror downstream from the furnace, and the results extrapolated to zero

distance of the mirror from the furnace end. Typical results are those for the thermal decomposition of ethane, given by Rice and Dooley [412] in one series of experiments with the furnace at 906° and 960° C using a quartz tube 1·3 cm in diameter and a furnace 15 cm long. The ratio t_{906}/t_{960} is the ratio of the times of disappearance of two standard antimony mirrors for these furnace temperatures. The extrapolated value for the end of the furnace is 4·44 which corresponds to an activation energy of 80·0 kcal, which was considered to be equal to $D(CH_3-CH_3)$. Such an extrapolation requires a definite knowledge of the position of the end of the furnace, which though quite definite physically, outside the tube, is uncertain as far as the molecules inside the tube are concerned. Molecules of carrier gas which acquire energy inside the furnace may transfer this energy to the reacting substance beyond the furnace. Another drawback of the method is that relative rates of reaction only are measured, so that A, the pre-exponential factor in the rate equation, remains unknown. Steacie considers that because of these and other difficulties, Rice's activation energies may be uncertain by as much as ± 10 kcal. However, it must be remembered that despite these faults, Rice's work had the great advantage that the presence of radicals was directly demonstrated. Were it not for these experiments, other work on reactions in which free radicals are supposed to be formed would be much more speculative. This work led to the view that dissociation into radicals is very often the primary step in the thermal decomposition of organic compounds and is followed by a complicated series of radical reactions. In order to overcome the objections that such complication could not account for simple kinetic orders of reaction, and that activation energies for thermal decompositions were usually less than the expected bond dissociation energy, Rice and Herzfeld [413] put forward radical chain mechanisms which did account for these observations (*see*, for example, Steacie [467]).

4.2.3. *Mass Spectrometric Methods*

The most direct method of measuring the rate of production of radicals in a thermal decomposition would appear to be to lead the products of the reaction to a mass spectrometer, where the radicals could be identified by their mass numbers. Considerable technical difficulties are met with in the method, however, and so far relatively few communications have appeared dealing with its use, although several investigators are at present starting work on the subject. The pioneer work was done by Eltenton [142] and the principle of his method is as follows.

If a molecule R_1R_2 is bombarded with electrons of energy E_A, given by $E_A \geqslant A(R_1^+)_{R_1R_2}$, where $A(R_1^+)_{R_1R_2}$ is the appearance potential of the ion R_1^+ from the compound R_1R_2, it will dissociate and ionize. However, if the radical R_1 is itself already present, it will form R_1^+ when bombarded by electrons of energy $E_1 \geqslant I(R_1^+)$, where I is the ionization potential of the radical R_1. Now (*see* Section 5.2) $A(R_1^+) \geqslant I(R_1^+) + D(R_1R_2)$, and so it should be possible by using an electron bombardment energy between E_A and E_1 to ensure that the positive ion R_1^+ in the mass spectrometer comes only from the R_1 radicals present. In this way a positive-ion current of given mass in a mass spectrometer becomes a measure of the concentration of a given free radical. Theoretically, if the potential at which the measurements were made and the probability of ionization are known the absolute concentration of the radicals could be determined, but unfortunately ionization probabilities at low potentials are mostly unknown. Empirical calibration also presents obvious difficulties, in that a known concentration of radicals would be required.

Eltenton[143] used the method to study, among other reactions, the production of methyl radicals from methane. A quartz reaction vessel was separated from the ionization chamber by a thin diaphragm with an orifice. Using a freshly blown and outgassed quartz vessel, it was found that no CH_3 radicals could be detected in pure methane in the pressure range 0·01 to 0·3 mm up to temperatures of 1,100° C, although after heating the tube to 950° C in a stream of ethane or natural gas at about 1 mm pressure for 1 h, methyl radicals could be detected from pure methane, and this continued to be so even after outgassing, heating in air, or washing in nitric acid. The nature of the change in the surface is not known. The ion current due to CH_3^+ increased with temperature, and a plot of log $[CH_3^+]$ against $1/T$ gave a slope corresponding to an energy of 46 kcal. This is a little less than half the most reliable result for $D(CH_3 - H)$ and is presumably the activation energy of a surface process.

Robertson[424] used a similar technique to study radicals formed in the pyrolysis of hydrocarbons on a hot filament, but did not obtain activation energies.

Lossing and Tickner[324] considered that because of the uncertainty about ionization probabilities at low bombarding electron energies, and because of low sensitivity and sharp dependence of sensitivity on electron energy under these conditions, the method of Eltenton was not suitable for determination of radical concentrations. This difficulty was avoided by the use of ionizing electrons

having energies of about 50 V as is usual in gas analyses. Much higher sensitivity was obtained, but the peak occurring at the mass number of the free radical includes large contributions from fragments formed by electron impact from the stable molecules present. In the experiments, as before, there was a fine leak from the reaction vessel into the ionization chamber of the mass spectrometer. In the calibration the sensitivity of the apparatus for radicals, defined as the ratio of the peak height of the ion current of the appropriate ion to the partial pressure of the radical on the high pressure (reaction vessel) side of the leak, is required. A knowledge of the partial pressure of the radical and the contribution of the radical to the peak height is necessary. This was achieved for methyl radicals obtained by the thermal decomposition of mercury dimethyl in a flow system using helium as carrier gas. In this system the peak at mass number 15 might be expected to have contributions from CH_3, $Hg(CH_3)_2$, CH_4, C_2H_6 and possibly other substances. The contributions from the stable molecules must be subtracted from the peak. They are obtained by introducing the stable molecules at known partial pressures into the apparatus under similar conditions and noting their mass spectrum. Their partial pressures in the reacting mixture are obtained from the heights of their parent peaks in the mass spectrum, and thus the proportion of the peak height due to CH_3 may be obtained. The partial pressure of CH_3 is obtained by difference from a knowledge of the partial pressure of reacting material, the amount of decomposition, and the partial pressures of the stable molecular products, assuming 100 per cent material recovery. This gives the sensitivity to methyl radicals, which may conveniently be expressed as the ratio of the sensitivity to methane, which has nearly the same molecular weight, under the same conditions. The experimental difficulties in obtaining reliable results are considerable. In order to measure accurately the amount of decomposition in the flow system a time of several hours was required. It was shown from the mass spectrum that in the pyrolysis of mercury dimethyl under their experimental conditions, only methyl, methane, and ethane were present, and that to make analyses it was necessary to measure only the peaks at 232, 30, 16, and 15. The sensitivity to methyl was determined by the method outlined above. One major complicating factor was the large temperature coefficient of the sensitivity, which decreased with increasing temperature. Although the main reason for this was probably the increase of viscosity of the carrier gas, that specific effects were also present was shown by slight differences in the temperature dependence of the sensitivity

for different molecules. The temperature coefficient of the sensitivity to methyl radicals could not be measured, so it was assumed to be the same as that of methane. The remarkable success attained in the determination of methyl radicals in spite of these difficulties is shown by the following table, which gives the composition of the gases from decomposing mercury dimethyl at various temperatures, and the resulting carbon balance. With the pumping speeds used in most of these experiments, the contact times varied from 0·0014 sec at 6 mm He pressure to 0·0010 sec at 20 mm He pressure at 1,000° K. With the apparatus used, however, low values for activation energies at high temperatures were obtained [323].

Table 4.2.3.1

Furnace temperature °C	$Hg(CH_3)_2$ μHg		*Decomposition* %	*Pressure of products* μHg			*Carbon balance* %
	Initial	*Remaining*		C_2H_6	CH_4	CH_3	
617	8·15	7·86	3·6	0·055	0·032	0·071	97·7
650	8·12	7·37	9·2	0·172	0·107	0·70	98·4
692	8·10	6·39	21·1	0·579	0·272	1·87	99·4
850	8·06	0·35	95·8	3·46	1·13	7·59	101·5
805	8·03	1·10	86·2	3·17	0·979	6·41	99·3
672	8·01	6·95	13·2	0·335	0·204	1·42	101·1

The method has been used for the determination of the rate of recombination of methyl radicals (*see* Section 4.2.1) and for the determination of the rate of decomposition of di-*t*-butyl peroxide, but so far has not been used for the direct measurement of rates of radical production, although this will almost certainly follow. The rate of decomposition of di-*t*-butyl peroxide was followed by the decrease in concentration of the peroxide, which is not a method peculiar to mass spectrometry. The investigation has some interest in that extremely small partial pressures of reactant (about 2μHg) and very short contact times were used in a stream of helium at pressures ranging from 5·5 mm to 12·5 mm. The rate was shown to be independent of the helium pressure over this range. It is rather unusual to see values of $\log_{10}k(\text{sec}^{-1})$ of between +1 and +2 (made possible by the short contact time). The activation energy was 37 kcal, in good agreement with other work (*see* Section 4.2.6).

The complexity of these mass spectrometric techniques is making progress perhaps slower than in other branches of experimental chemical kinetics. In addition to the technical difficulties there is

the possibility of surface effects becoming important at the low pressures of reactants used.

4.2.4. *Pyrolyses of Organic Iodides*

In 1943, Butler and Polanyi[64] published an account of their work on the pyrolysis of some organic iodides in a flow system. This paper was followed two years later by one which described the application of the method to further compounds[63]. These papers chiefly describe work which had not been completed because of the war, and do not represent a thorough investigation. Further work was undertaken at Manchester after the war (Gowenlock[188], and Szwarc[492], quoted by Szwarc[497]), and the whole work has been discussed at some length by Szwarc[497].

Briefly, the object of the research was to pyrolyse organic iodides at low partial pressures in a carrier gas in a flow system with short contact times (~0·5 sec), in the hope that for small amounts of decomposition the production of iodine would give a measure of the rate of the reaction

$$RI \rightarrow R + I \qquad \ldots . \quad (4.2.4.1)$$

It was realized that another reaction, the unimolecular formation of the olefine with elimination of hydrogen iodide would also take place, but it was thought that measurement of the iodine would be a good measure of equation 4.2.4.1. This simple view depends upon the assumption that iodine atoms recombine to give iodine more rapidly than they take part in the reverse of the reaction of equation 4.2.4.1. This seems rather unlikely, because the recombination of iodine atoms requires three body collisions and the recombination of radicals with iodine atoms may well be a bimolecular process. Under these circumstances, it seems more likely that the prevention of complete reformation of the alkyl iodide is due to further reactions of the alkyl radical, such as

$$RI \rightarrow R + I$$

$$R + RI \rightarrow RH + R'$$

$$R' \rightarrow \text{olefin} + I$$

$$I + I + M \rightarrow I_2 + M$$

as suggested by Szwarc. This scheme would lead to first order kinetics, the unimolecular dissociation of RI being the rate determining step, and the activation energy would therefore correspond to $D(R - I)$. Szwarc considers that the pyrolysis of ethyl, *n*-propyl,

and *n*-butyl iodides follows this scheme. In agreement with this view, the frequency factors of these reactions are about 10^{13} sec^{-1}, but even here detailed investigation has shown that various other processes, the details of which could not be completely elucidated, take part. For other compounds the situation is even more complicated. The 'first order' rate constants varied appreciably with time of contact and with partial pressure of iodide, so that the reactions cannot be simple unimolecular bond splitting processes. Szwarc concludes his review of the method by pointing out various ways in which the results might not give the required bond dissociation energies, and although the values of D are often fairly close to more reliable estimates, the method by itself cannot be sufficient to decide a bond dissociation energy.

4.2.5. *The Toluene Carrier Gas Technique*

This elegant and useful method of ensuring that complicating side reactions do not confuse the kinetics of unimolecular dissociation reactions is due to Szwarc. (For a review, *see* Szwarc [499].) He found that toluene reacts with many radicals as follows

$$C_6H_5.CH_3 + R \rightarrow C_6H_5.CH_2 + RH$$

The benzyl radicals are particularly stable, but eventually dimerize to form dibenzyl. If a dissociation reaction is carried out in a flow system using toluene as carrier gas, the radicals R_1 and R_2 formed react preferentially with the toluene, which is present in very large excess, each radical being therefore largely surrounded by toluene molecules. This reaction with toluene gives the stable molecules R_1H and R_2H, thus preventing the back reaction and possible chain reactions. The benzyl radicals do not react in the hot zone under the experimental conditions used, and eventually dimerize outside the main reaction zone. The rate of the initial dissociation may be measured by the formation of R_1H, R_2H or dibenzyl.

To eliminate possible secondary reactions, it is essential to prevent the formation and decomposition of dibenzyl in the hot zone, and this is achieved by using very short contact times and high flow rates. The prevention of dimerization is also aided by working at low pressures, high temperatures, and low fractions of decomposition.

The first application of the method was in the thermal decomposition of toluene itself, which can be regarded both as carrier gas and as reactant if the fraction of decomposition is very small, and Szwarc restricted this to 0·01–1 per cent in his experiments [493].

The reactions are shown to be

$$\begin{aligned} \mathrm{Ph.CH_3} &\rightarrow \mathrm{Ph.CH_2 + H} \\ \mathrm{Ph.CH_3 + H} &\rightarrow \mathrm{Ph.CH_2 + H_2} \end{aligned}$$

and

$$\left.\begin{aligned} \mathrm{Ph.CH_3 + H} &\rightarrow \mathrm{C_6H_6 + CH_3} \\ \mathrm{Ph.CH_3 + CH_3} &\rightarrow \mathrm{CH_4 + Ph.CH_2} \end{aligned}\right\}$$

or

$$\left.\begin{aligned} \mathrm{Ph.CH_3 + H} &\rightarrow \mathrm{C_6H_5 + CH_4} \\ \mathrm{Ph.CH_3 + C_6H_5} &\rightarrow \mathrm{C_6H_6 + Ph.CH_2} \end{aligned}\right\}$$

and the quantity of dibenzyl recovered is one mole of dibenzyl per mole of gas (H_2 and CH_4) produced. H_2 and CH_4 were produced in approximately the ratio 40 : 60, but the benzene formed does not appear to have been quantitatively estimated. The temperature of the investigation was 680–850° C, at a pressure of 2–15 mm Hg in a flow system, and the first order rate constant was given by

$$k = 2 \times 10^{13} \exp\left(-77{,}500/\boldsymbol{R}T\right)$$

$D(\mathrm{C_6H_5.CH_2 - H})$ was thus deduced to be 77·5 kcal.

An interesting experimental point in this investigation was that toluene from different sources purified by the usual methods of shaking with sulphuric acid, distillation and crystallization appeared to contain an impurity which gave erratic kinetic results for the pyrolysis. This impurity could be removed by fractional pyrolysis, and in all Szwarc's work the toluene was purified by twice repeated partial pyrolysis at 845° C, followed by distillation over sodium. With this material reproducible kinetic results were obtained.

The use of toluene can only be considered for reactions where the bond is weaker than $(\mathrm{C_6H_5CH_2 - H})$ in toluene, so that the temperature at which the reaction is allowed to take place is below that at which decomposition of toluene itself occurs. It was first applied to the determination of the dissociation energy of the C – C bond in ethyl benzene[494]. The pyrolysis of ethyl benzene itself leads to complicating side reactions, but it was thought that in toluene the following straightforward reactions would be the main ones:

$$\begin{aligned} \mathrm{Ph.CH_2CH_3} &\rightarrow \mathrm{Ph.CH_2 + CH_3} \\ \mathrm{Ph.CH_3 + CH_3} &\rightarrow \mathrm{Ph.CH_2 + CH_4} \end{aligned}$$

the rate of production of methane being used as a measure of the rate of decomposition of the ethyl benzene. The reaction was studied over the temperature range 615 745° C. At the lower

temperatures there was no decomposition of toluene, and at the higher temperatures the decomposition was so slight that the correction for it, which of course is known because the decomposition of toluene itself was studied previously, never amounts to more than a few per cent. The usual toluene–ethyl benzene ratio was between 20:1 and 50:1 and some typical experimental observations are given in *Table 4.2.5.1*, k being the first order rate constant.

Table 4.2.5.1. Pyrolysis of $Ph.C_2H_5$

Run	T °C	P ($Ph.C_2H_5$) mm Hg	P ($Ph.CH_3$) mm Hg	*Contact time* sec	*Decomposition* %	k ($\times 10^{-2}$ sec^{-1})
1	674	0·35	7·5	0·315	0·69	2·19
2	674	0·35	7·6	0·315	0·61	1·93
16	673	0·15	8·6	0·385	1·00	2·60
12	675	0·35	13·7	1·15	2·50	2·20
13	674	0·16	13·5	0·410	1·00	2·45
15	674	0·18	8·9	1·05	2·36	2·26

That some side reactions occurred is shown by the fact that although the collected gas was mainly methane, as required by the simple scheme, 15–25 per cent was hydrogen. The experimental activation energy was 63·2 kcal which is considered to be equal to $D(Ph.CH_2 - CH_3)$.

These two results for toluene and ethyl benzene give a useful check on the method. If the heats of formation of all the molecules concerned are known, together with the heat of formation of hydrogen atoms, knowledge of $D(Ph.CH_2 - H)$ and $D(Ph.CH_2 - CH_3)$ allows us to deduce $\Delta H_f(CH_3)$ and hence $D(CH_3 - H)$, which is given as 102·9 kcal. This is in good agreement with other reliable estimates.

An interesting application of the method is to determine $D(NH_2 - NH_2)$. Here the expected reactions are

$$N_2H_4 \rightarrow 2NH_2$$

$$C_6H_5.CH_3 + NH_2 \rightarrow C_6H_5.CH_2 + NH_3$$

The rate of the bond splitting reaction is obtained by measuring the amount of dibenzyl formed. This is because hydrazine also decomposes heterogeneously to give ammonia by reactions which do not involve radicals. Dibenzyl is only produced by the required reaction. The results lead to $D(NH_2 - NH_2) = 60$ kcal [495].

A large number of other compounds have now been studied including 1-butene[443], benzyl bromide and allyl bromide[501], substituted benzyl bromides[502], *n*-propyl benzene[296], *n*-butyl benzene[297], cumene, *t*-butyl benzene and *p*-cymene[298] and bromobenzene[505]. The work is continuing.

Useful information has been obtained using this method, but it has limitations which may be summarized here. It cannot be used for the determination of dissociation energies greater than $D(C-H)$ in toluene. To prevent interference from the decomposition of toluene itself, the dissociation energy to be measured should be at least 10 kcal less than that in toluene, *i.e.* should be <67 kcal. Furthermore, the radicals produced should be sufficiently reactive to produce benzyl radicals from toluene in the manner suggested, and they should be produced at a temperature high enough for this reaction to be rapid. This requirement rules out the method for the determination of low bond dissociation energies, because here the decomposition itself takes place at a temperature below which the radicals produced react sufficiently rapidly with toluene.

4.2.6. *Direct Thermal Decomposition*

Under favourable circumstances the thermal decomposition of a compound may occur by means of an initial split into radicals, followed by fast, non-chain reactions to give the ultimate products. If the initial bond fission is rate-determining, the overall kinetics of formation of the products will be first order, and the observed activation energy will be the dissociation energy of the bond concerned. Often the interpretation of the results of kinetic experiments on the thermal decomposition of a substance is very difficult, and the allocation of the activation energy to a particular reaction is correspondingly uncertain. In some cases, for example, the initial step may not be bond scission, but a truly unimolecular rearrangement, and the activation energy will then be less than the bond dissociation energy; or both types of reaction may occur together. Sometimes it is possible to tell from the products what reaction is occurring, and sometimes the presence of radicals can be detected by various methods, although this does not suffice to show that all, or even the major part, of the reaction is proceeding by a radical mechanism. Radical chain mechanisms can usually be detected by the inhibition of the reaction by a substance such as propylene or nitric oxide, known to act as a chain stopper by combining very readily with radicals. The details of the methods used are described in text-books of chemical kinetics and in particular in Steacie's

book[467]. It is sufficient to mention here that the mechanism of the thermal decomposition to give some simple products of some quite simple compounds, such as acetaldehyde, has been for many years the subject of lively controversy[300, 355, 458]. There is a further difficulty. Even if the mechanism of the reaction is regarded as well established, the numerical values of the parameters defining the reaction kinetics are quite often far from accurately known, results obtained in different laboratories disagreeing with one another. This state of affairs may be because of the large effect of small changes of surface* and of impurity (compare the effect found for toluene by Szwarc, discussed in Section 4.2.5). Moreover, such systematic errors, as pointed out in Section 4.2.1 can lead to large errors in frequency factors and activation energies. There is possibly a deceptive simplicity about this branch of chemical kinetics particularly if the reaction is followed merely by measuring the pressure change in a static system, and the investigator may be lulled into a false sense of security.

The thermal decomposition of di-*tert*-butyl peroxide has been fairly extensively studied in order to obtain the dissociation energy of the peroxide link, which is expected to be the weakest in the molecule. Milas and Surgenor[347] found that the only products of decomposition in the gas phase at 250° C were ethane and acetone, which suggests a simple bond splitting mechanism, followed by very straightforward radical reactions,

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO \quad \ldots\ (4.2.6.1)$$

$$(CH_3)_3CO \rightarrow (CH_3)_2CO + CH_3 \quad \ldots\ (4.2.6.2)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad \ldots\ (4.2.6.3)$$

all of which are expected to be fast. The activation energy should therefore be that of bond fission. Raley, Rust, and Vaughan[408] studied the kinetics of the reaction. They found some methane among the products, which is likely to be formed by attack of methyl

* For example, Cottrell, Graham and Reid[94], found that whereas increasing the surface volume ratio with fire polished *Pyrex* capillary tubing had no effect on the thermal decomposition of nitromethane, the addition of broken capillary tubing quite altered the course of the reaction. Barton and Onyon[19] found for the thermal dehydrochlorination of *tert*-butyl chloride a frequency factor of $10^{12\cdot4}$ sec^{-1} and an activation energy of 41·4 kcal, whereas Kistiakowsky (quoted by Barton and Onyon) found $10^{13\cdot9}$ sec^{-1} and 45·0 kcal respectively for the same reaction. The former authors point out that the rates of reaction only approach complete reproducibility after many runs when the reaction vessel walls become suitably coated, and that at the temperatures Kistiakowsky used they found it possible to obtain velocity constants identical with his, although on repeating the runs many times the constants fell to the values given by them.

radicals on acetone, and they pointed out that whether the overall reaction was

$$Me_3COOCMe_3 \rightarrow 2Me_2CO + C_2H_6$$

or

$$Mc_3COOCMe_3 \rightarrow Me_2CO + CH_4 + Me.CO.Et$$

the number of moles of product per mole of starting material would remain the same at 3. By measuring the pressure increase they found that the actual number of moles of gas formed was 2·88, in fairly good agreement with expectation. Possibly some polymerization was responsible for the defect. They found that the pressure increase was first order, that the rate constant k was almost independent of initial pressure over the range studied and obtained

$$k = 3{\cdot}2 \times 10^{16} \exp(-39{,}000/\boldsymbol{R}T)\text{sec}^{-1}$$

The frequency factor is considerably higher than would be expected from an ordinary first order decomposition, but it was shown by standard methods that the reaction was homogeneous and that there was no chain. Because of this anomalously high frequency factor, the reaction was studied again by Murawski, Roberts, and Szwarc[362]. They measured the rate of decomposition in the presence of excess toluene both in a static and in a flow system, so as to cover the widest possible temperature range. The reactions found to occur were as given in equations 4.2.6.1, 2, and 3 above, together with

$$CH_3 + C_6H_5.CH_3 \rightarrow CH_4 + C_6H_5.CH_2$$
$$CH_3 + C_6H_5.CH_2 \rightarrow C_6H_5.CH_2.CH_3$$

The rate of reaction was measured by following the formation of CH_4 and C_2H_6, and in agreement with Raley, Rust, and Vaughan the reaction was found to be first order and homogeneous. The results for the decomposition in the static system in the temperature range 120–170° C were found when plotted in the form log k against $1/T$ to lie on a straight line with a slope corresponding to an activation energy of 36 kcal, as did the results obtained in the flow system in the temperature range 170–280° C. The absolute values of the rate constants determined by the two methods at the same temperature differed by 40 per cent, presumably, according to the authors, because of errors in measuring the contact time. The frequency factor was 4 or 7×10^{14} sec^{-1}, according to which set of results was chosen. The results of Raley *et al.* lay fairly well on the line obtained by extrapolation of the results of flow experiments, which is a little surprising, if the measurement of contact time were

the main source of error in Szwarc's results. In view of the discrepancy remaining, Brinton and Volman[58] in the course of other work carried out a few experiments on the decomposition using a static method over the temperature range 130–170° C. This work, because of the small temperature range, did not remove the uncertainty. The rate constants found were compatible with values of the parameters in the Arrhenius equation from

$$k = 6 \times 10^{14} \exp(-37{,}000/RT)\text{sec}^{-1}$$

to

$$k = 6 \times 10^{16} \exp(-40{,}000/RT)\text{sec}^{-1}$$

The authors concluded that D(O–O) in (t-BuO)$_2$ could be taken to be well established as 36–40 kcal. The decomposition has also been investigated by Lossing and Tickner[324] using the mass spectrometric method described in Section 4.2.3. They were able to work at very much higher temperatures, from 280° C to 350° C, and found the activation energy to be 37 kcal and the frequency factor to be $\sim 4 \times 10^{15}$ sec^{-1}. The results of all the investigations, covering the temperature range of 120–350° C, when plotted as log k against $1/T$ fall fairly well on a common straight line, corresponding to an activation energy of 38 kcal and a frequency factor of almost 10^{16} sec^{-1}. The activation energy of 38 kcal may therefore be taken as established for the thermal decomposition of di-*tert*-butyl peroxide, and the high frequency factor must be taken as real. The discrepancies between the various results are probably due to experimental errors, a salutary demonstration of the truth of the fact that small systematic errors can cause quite large variations in the rate equation parameters, and that these errors may well remain unsuspected by the investigators concerned. It is comforting, however, to note that 38 ± 2 kcal covers the whole range of suggested activation energies, and therefore, if the mechanism is correct, the corresponding O–O dissociation energy lies within these limits. Less comforting is the unexplained high value of the frequency factor. If the true frequency factor of a decomposition differs from the usually accepted 10^{13} sec^{-1} by two powers of ten, an error of 4·6 kcal will be produced in the activation energy deduced from a rate constant determined at a single temperature with the use of a standard factor.

That this high factor is not characteristic of peroxides in general is shown by the investigation of the thermal decomposition of diethyl peroxide. Harris and Egerton[203] measured the kinetics of the thermal decomposition in a static system by following the

pressure change. They found the reaction to be homogeneous and first order, with k given by

$$9 \times 10^{12} \exp(-31{,}500/RT) \text{ sec}^{-1}*$$

The gaseous products after complete decomposition were largely carbon monoxide, methane and ethane, but the relevance of final products to mechanism is not easily seen when fairly extensive secondary reactions have taken place. Harris and Egerton suggested that the peroxide initially decomposed into ethanol and acetaldehyde, the latter itself decomposing to give methane and carbon monoxide, but this suggestion is largely speculative, and neither gives a quantitative explanation of the CO–CH_4 ratio, which was nearly 3:1, nor a good explanation of the presence of much ethane. Analysis of decomposition products after various time intervals, and extrapolation of results to zero time, though it does not always give the products of the primary set of reactions, is almost essential for a mechanistic explanation of kinetic results in a static system, unless the situation is obviously one of great simplicity. The same result can be achieved rather more simply in a flow system by using short contact times and small conversions, and analysing the products. The decomposition of diethyl peroxide has also been studied in a flow system by Rebbert and Laidler[410], and the elucidation of the primary reaction was thus made easier. They found that the main products were ethane and formaldehyde, which can readily be explained on the basis of the following reactions:

$$C_2H_5OOC_2H_5 \rightarrow 2C_2H_5O$$

$$C_2H_5O \rightarrow CH_3 + CH_2O$$

$$2CH_3 \rightarrow C_2H_6$$

They used toluene as carrier gas, and in addition found small amounts of methane and dibenzyl, presumably formed from toluene by the obvious reactions. Rebbert and Laidler state that they were using the toluene carrier gas technique of Szwarc, but in fact they were attempting to use it under conditions where it has no apparent advantage. Szwarc intended that the toluene should mop up the radicals formed by the initial bond fission of the compound under investigation, but clearly this did not happen at the temperatures used here (200–240° C). In fact, the recombination of methyl radicals, which requires no activation energy, is more likely to

* In their paper they give $\log_{10}k = -(6{,}890{\cdot}4/T) + 14{\cdot}708$, without stating units, but it is clear from elsewhere in the paper that k was measured in min^{-1}.

take place than their reaction with toluene, which requires a small activation energy, as is shown by the observed products of the reaction. This is a good example of the fact, pointed out by Szwarc, that the method is not applicable to compounds with low bond dissociation energies. However, the main feature of the investigation is that the initial products establish the mechanism fairly reliably, and since the rate determining step is first order, it is reasonable to conclude that its activation energy is equal to $D(C_2H_5O - OC_2H_5)$. The rate equation found was

$$k = 2 \times 10^{13} \exp(-31{,}700/\boldsymbol{R}T)\text{sec}^{-1}$$

This is in striking agreement with the work of Harris and Egerton, particularly considering the relatively small (and different) temperature ranges over which the two sets of experiments were carried out. Although this is considerably better agreement than one might normally expect, the conclusion is clear that $D(O - O)$ in diethyl peroxide is close to 31·5 kcal.

The use of the direct thermal decomposition method has been fairly widespread, and the values obtained by it will be discussed in the appropriate sections of this book. The O – N bond in alkyl nitrates and nitrites, and the C – N bond in nitromethane are among those whose dissociation energy has been measured by this method, but in view of the possible kinetic complexities which may be encountered, such as those already mentioned in connection with the pyrolysis of organic iodides (*see* Section 4.2.4) the values obtained are often at best only tentative.

4.3. PHOTOCHEMICAL REACTIONS

4.3.1. *Direct Photolysis*

If a substance can be decomposed by the action of radiation, it is sometimes possible to identify the minimum energy of radiation required with a bond dissociation energy. This can only be reliably done if the mechanism of the absorption of radiation and the subsequent decomposition can be established, and if the usual kinetic assumption of zero activation energy for the reverse reaction is accepted.

For example, Faltings, Groth, and Harteck[150] found that carbon monoxide could be decomposed by the action of xenon resonance radiation at 1,295Å, with the production of carbon dioxide and carbon suboxide. No reaction took place with radiation of wavelength 1,470Å. From this it was concluded that $D(CO) \leqslant 9{\cdot}57$ eV.

Gaydon[166], however, has challenged this interpretation (*see* Section 8.2.2.6).

More definite evidence of the initial step in a photolytic reaction was obtained by Terenin and Neujmin[513]. They investigated photolyses in which one of the fragments produced was a radical in an excited state. This radical was identified by its emission spectrum. They obtained $D(H-OH) = 115$ kcal, and $D(I_2) = 35$ kcal, in agreement with results obtained by other methods (*see* Section 9.6.8).

4.3.2. *Photosensitized Reactions*

If a reaction can take place without activation energy by the agency of electronically excited atoms, the energy available from the excited atom must be an upper limit to the energy barrier which must be overcome for the reaction to take place. Thus if the reaction concerned can be established to be a bond splitting process, an upper limit to the dissociation energy is obtained. The energy available from the excited atom may be simply its energy of excitation, but it may be greater than this by the energy released when the atom combines with one of the atoms or radicals produced by bond fission. The method has been most widely used for bonds to hydrogen, and the energy available may either be the excitation energy of the atom or that plus the energy released by the formation of its hydride.

The experimental work on photosensitization has been done mainly with Na, Zn, Cd, and Hg, and the possible transitions have been listed by Laidler[286] (*Table 4.3.2.1*).

Excited Na (^2P) does not in general cause reaction, because of its comparatively low energy of excitation; it is quenched by hydrogen

Table 4.3.2.1

Metal	*Transition*	*Line* Å	*Excitation energy* (kcal)	*Energy of formation of hydride* (kcal)	*Total energy available*
Na	$^2P \rightarrow {}^2S_{\frac{1}{2}}$	{5,890 / 5,896}	48·3	51·6*	99·9
Zn	$^3P_1 \rightarrow {}^1S_0$	3,076	92·5	23·1*	115·6
Zn	$^1P_1 \rightarrow {}^1S_0$	2,139	133·4	23·1	156·5
Cd	$^3P_1 \rightarrow {}^1S_0$	3,261	87·3	15·5	102·8
Cd	$^1P_1 \rightarrow {}^1S_0$	2,288	124·4	15·5	139·9
Hg	$^3P_1 \rightarrow {}^1S_0$	2,537	112·2	8·5	120·7
Hg	$^1P_1 \rightarrow {}^1S_0$	1,849	153·9	8·5	162·4

* The most recent estimates of these quantities are about 4 kcal less (*see* Sections 9.1.11 and 9.1.30).

and hydrocarbons. Excited Zn, Cd and Hg, both triplet and singlet, are quenched by H_2, which is dissociated into atoms. With ethylene, the results show considerable variation according to the atom used. There are two possible primary processes: a C – H bond split or the formation of an excited olefin molecule.

Laidler[286] discusses ethylene in detail, but his interpretation does not agree with that of Steacie[467] (*see* Section 9.1.6). It appears that a very detailed study is required before a reliable interpretation of the mechanism can be made.

5

DETERMINATION OF BOND DISSOCIATION ENERGIES BY ELECTRON IMPACT AND SPECTROSCOPIC METHODS

5.1. GENERAL PRINCIPLES

5.1.1. *Electronic Excitation by Electron Impact and Radiation*

As was briefly mentioned in Section 1.2, molecules can possess energy in translational, rotational, vibrational, and electronic degrees of freedom. A molecule in the ground electronic state may as a rule be dissociated into atoms in their ground states 'quasi-statically'; that is to say, throughout the process of dissociation there is no abrupt jump in electronic energy. Such a dissociation of a molecule into two atoms or radicals can be regarded as taking place by the atoms vibrating with respect to one another with increasing amplitude until they fly apart, although because of the quantization of vibrational energy this picture is not strictly correct. In a molecule vibrational energy levels gradually get closer together with increasing energy until, when D is reached, the energy of the system is no longer quantized, extra energy beyond this merely appearing as kinetic energy of the atoms moving away from one another. As a gas becomes hotter, so the number of molecules in higher vibrational levels increases as the energy is equilibrated among all degrees of freedom, until dissociation takes place. It is this process with which we are concerned in those methods which use thermal energy to dissociate the molecule.

There is, however, a range of electronic states of higher energy in which molecules may exist, and these states can be produced when molecules are subjected to suitable radiation, or when they suffer collision with high energy particles, usually, for experimental purposes, electrons. Observations on such processes can be used to give values of the dissociation energy of the ground state. Direct absorption, from radiation, of the appropriate amount of vibrational energy is not possible, because of quantum mechanical restrictions.

Some of the excited electronic states are not stable; *i.e.*, the interaction between atoms is repulsive at all interatomic distances, and

the molecule dissociates. Others of the excited states are stable; they have a minimum in the energy–interatomic distance curve, but the molecule may be excited to them in such a way that it suffers a sufficient change in vibrational quantum number to cause dissociation. The products of dissociation from an excited electronic state may be the atoms in their ground electronic states, but often they are atoms in excited states or even ions. Thus to determine the ordinary dissociation energy to ground state atoms, we have to know the energies of the following process (* denotes an excited atom or molecule, or an ion)

$$\begin{aligned} \mathrm{AB} &\rightarrow (\mathrm{AB})^* \quad \Delta E_1 \\ (\mathrm{AB})^* &\rightarrow \mathrm{A} + \mathrm{B}^* \quad \Delta E_2 \\ \mathrm{B}^* &\rightarrow \mathrm{B} \quad \Delta E_3 \end{aligned}$$

The sum $\Delta E_1 + \Delta E_2 + \Delta E_3$ gives $D(\mathrm{AB})$.

To obtain a dissociation energy in this way is a much more complex process than to obtain it from a thermal equilibrium measurement. The amount of information required is much greater, involving as it does a knowledge of the properties of excited or ionized molecules, atoms, and radicals, as well as of normal molecules.

The two methods of exciting molecules electronically which we consider here, absorption of radiation and electron impact, differ in most respects other than in this one primary similarity; the same fundamental principle is used in the interpretation of the electronic transition. The chief difference is that most excitation by electron impact is a collision process with no very stringent energy requirements, because the electron can carry away excess energy, whereas excitation by interaction with radiation is usually a resonance phenomenon, except for direct photodissociation (*see* Section 5.3). The two methods also differ in the principles used to detect the excitation. In electron impact methods we identify the excited product by isolating it from the rest of the gas. It therefore must be capable of being separated, and in fact we are concerned with the formation of ions whose mass can be determined in the mass spectrograph. The minimum energy of the electron beam required to produce the species identified is noted. On the other hand, the only measurements which can be made with the radiation method are of the wavelengths at which absorption takes place and the nature of the transition concerned must be deduced from a knowledge of a set of energy differences only, aided by quantum-theoretical methods.

5.1.2. *The Franck–Condon Principle*

The main guide to interpretation of electronic excitation processes is the concept of electronic states in which the potential energy of the nuclei varies with internuclear distance in the way mentioned in Section 1.2. For some molecules we have a detailed quantitative knowledge of these states, for others we only make use of the concept in a qualitative way, but in either case we use the Franck–Condon principle, which governs the path on these energy diagrams taken by the point representing the molecule. The principle is that in an electronic transition neither the position nor the momentum of the nuclei is affected directly; that is to say that electronic excitation is a very rapid process compared with the frequency of vibration. Only the potential energy of the nuclei is changed by an electron jump; the point representing the molecule moves vertically upwards on the potential energy diagram.

This hypothesis was first stated by Franck[159] who used it to explain how molecules dissociate with absorption of light and how under some circumstances molecules can take up many times their dissociation energy without dissociating. He pointed out that a molecule can only dissociate if its vibrational energy is increased until it equals or exceeds the energy required to dissociate the state under consideration, and that the relevant problem is to consider how large quantities of vibrational energy can be given to the molecule in an electronic transition. If the principle is correct, a molecule may or may not dissociate after electronic excitation, depending upon the particular relationship between the potential energy curves for the ground and excited states. Consider a molecule whose upper and lower states are as shown in *Figure 5.1.2.1* (a). Apart from the effect of zero point vibration, if the absorbing molecule is at room temperature it is not likely to possess vibrational energy, and its representative point will be at the minimum of the lower curve. For an electronic transition the point moves vertically upwards to the curve representing the upper state. Therefore it will reach the position on the upper curve shown by the arrow head. If the minimum on the upper curve is exactly above the minimum on the lower the molecule will still possess no vibrational energy. If, as in the figure, the minima in the two curves are in slightly different positions, the excited molecule will possess a small amount of vibrational energy but not enough to cause dissociation in the upper state. The molecule will return to the ground state with emission of a quantum, either spontaneously or induced by the radiation, unless a collision supervenes during the lifetime of the excited state, for which a time of about 10^{-8} sec is typical.

In this case, therefore, molecules can absorb a greater energy of radiation than their dissociation energy without dissociating except perhaps by a secondary collision process. On the other hand, if the curves for the upper and lower states have the disposition shown in *Figure 5.1.2.1* (b), the nuclei will reach a position of high potential energy in the excited state, and will thus move apart along the upper curve. In this particular illustration they have just sufficient energy for dissociation to take place. Thus the molecule is disrupted in one vibrational period (about 10^{-13} sec). In this example the dissociation of the upper state takes place into excited atoms, and the excitation energy of the atoms must be subtracted from the observed dissociation energy to obtain D, the dissociation energy of the ground state, which is the one in which we are interested.

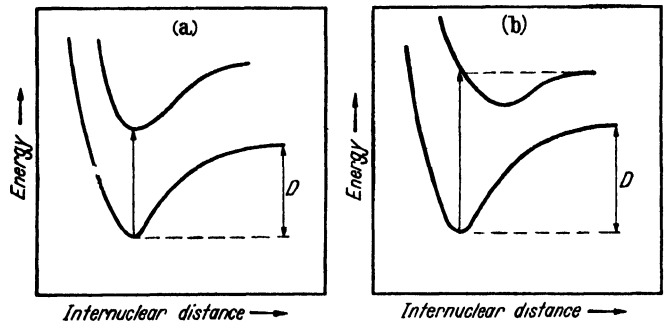


Figure 5.1.2.1. (a) Electronic transition without dissociation, (b) electronic transition with dissociation. Schematic curves showing the application of the Franck-Condon principle.

Condon[83] used the idea to explain qualitatively the intensity distribution of the vibrational structure of an electronic transition. Normally, in absorption, the molecules are in the vibrational ground state, but the vibrational level of the excited state occurring in the transition depends on the relative positions of the upper and lower potential energy curves. Shortly afterwards he was able to give a quantum-mechanical treatment of the problem[84]. From the quantum-mechanical point of view the position and momentum of an oscillator cannot definitely be given at any instant, and the system must be described by a function ψ (eigenfunction) where $\psi^2 dx$ gives the probability that the position of the representative point lies between x and $(x+dx)$*. Thus a vertical transition from an oscillator in the ground state

* *See* Pauling and Wilson[387]

will not take place from a defined position, the minimum of the curve, but very roughly speaking will take place from various segments dx of the curve with a probability $\psi^2 dx$. More exactly, the probability of transition from a vibrational state 0 in the lower curve, ψ_{L_0}, to the nth vibrational level in the upper curve ψ_{u_n} is proportional to

$$[\int \psi_{L_0} \psi_{u_n} d\tau]^2,$$

where the expression in brackets is known as the overlap integral between the two states. For low vibrational levels, the eigenfunctions are, to quite a good approximation, those for the harmonic

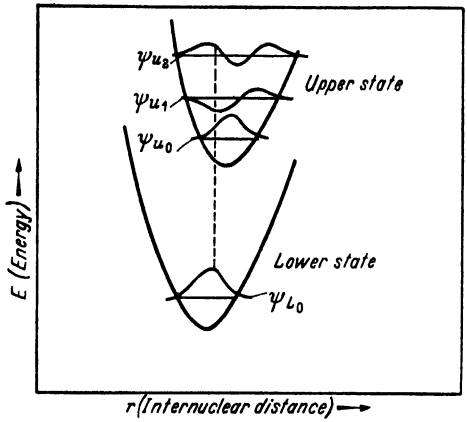


Figure 5.1.2.2. Diagram showing the vibrational wave function for the ground-state (ψ_{L_0}) and for the first three vibrational levels of an upper state ψu_0, ψu_1, ψu_2. The ψ are not plotted against E but against an arbitrary ordinate.

oscillator and are shown in the potential energy diagram (*Figure 5.1.2.2*). If the minima of the upper and lower curves were exactly above one another, the overlap integral for transition from ψ_{L_0} to ψ_{u_0} would be large, since the curves reinforce each other, whereas for transition to ψ_{u_1} the integral would be exactly zero, because the positive and negative parts cancel. Higher vibrational eigenfunctions have large maxima near the classical turning points of the motion, and a series of maxima and minima in between. These latter largely cancel in the integral, and if one or other of the main maxima is directly above the maximum in the lower curve, there is a large contribution to the integral from this region. In considering the continuous distribution of states arising when the minimum of the potential energy curve for the lower state is directly

below a portion of the upper curve corresponding to a potential energy greater than the dissociation energy for that state (where the vibrational energy no longer has a discrete series of quantum states) it is usual to reflect the square of the ground state vibrational eigenfunction on the upper curve; because all points on the upper curve are equally probable, and the transition at a given value of r simply depends on the probability of this value of r in the ground state $\psi^2 dr$. This gives the relative probabilities of various energies being found.

Although the Franck–Condon principle was first stated for electronic excitation due to the absorption of radiation, it was soon

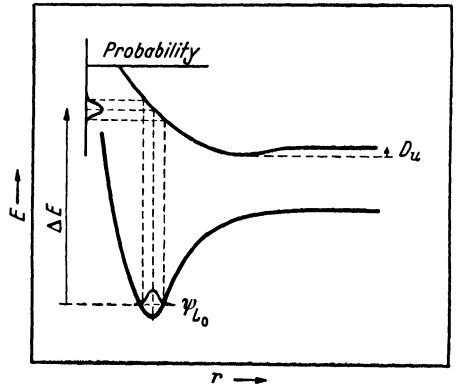


Figure 5.1.2.3. Diagram showing the application of the Franck–Condon principle to transition to a repulsive state. The probability of the transition taking place with absorption of energy ΔE depends on the relation between $\psi^2_{L_0}(r)$ and the position of the upper curve.

realized that it would apply equally well to electronic excitation however produced, and in particular to the excitation and ionization produced by electron impact[85]. It was first applied to the prediction of the types of ions resulting from electron impact in hydrogen, with complete agreement with experiment[43]. The application to the distribution of energies in the continuum shown in *Figure 5.1.2.3* is of particular importance in electron impact studies, because very often in this work particles are produced with kinetic energy in excess of the dissociation energy just because of the relative configuration of the upper and lower curves. An *a priori* knowledge of the type of distribution to be expected is essential in the analysis of the results, because selective effects in the apparatus result in distortion of the finally observed distribution.

5.2. ELECTRON IMPACT METHODS

5.2.1. *General*

In an encounter between particles without internal degrees of freedom the collision is perfectly elastic. However, if one or both of the particles have suitable internal degrees of freedom, there is a probability of the occurrence of an inelastic collision with the excitation of these degrees of freedom, provided that the relative kinetic energy involved is sufficiently great. This probability initially rises steeply with increasing relative kinetic energy of the particles, and to a first approximation it depends on the energy of the collision, the force law acting between the particles, and the matrix element for the transition (*see*, for example, Kittel[272]). Thermal dissociation in fact takes place as a result of the collisional excitation of higher and higher vibrational levels.

Electronic excitation may also take place collisionally, and, using this fact, a collision method can be used for determining dissociation energies. The obvious source of particles of known kinetic energy much greater than kT is a beam of electrons accelerated across a known potential difference, and the most feasible method of identifying the particles produced in the collisions is to examine the ionized particles in a mass spectrometer. The essential point of the electron impact method of measuring dissociation energies is to use the measurement of the mass–charge ratio of the ions produced, the kinetic energy of the electrons which is required just to produce them, and the kinetic energy which they possess, to deduce the nature of the dissociative ionization process taking place and hence the dissociation energy. Thus three types of information are required. The m–e ratio may be determined in a mass spectrometer. The kinetic energy of the electrons required just to produce the ions concerned, generally known as the 'appearance potential', is taken as the accelerating potential of the electrons at which an ion current due to the appropriate ion just appears. The kinetic energy of the ions produced is less easy to determine directly, and this problem is discussed in Section 5.2.3. If $A_0(A^+)$ is the appearance potential of the ion A^+ at rest, $I(A)$ is the ionization energy of A(to A^+), $E_a(A)$ is the electron affinity of A, and $E_e(A)$ is the electronic energy above the ground state of the atom or radical A, we have the following relationships between appearance potentials and dissociation energies for the various types of dissociative ionization.

$$AB + e^- \rightarrow A^+ + B + 2e^-;$$
$$A_0(A^+) = D(AB) + I(A) + E_e(A^+) + E_e(B) \quad . \ . \ . \ . \quad (5.2.1.1)$$

$$AB + e^- \rightarrow A^+ + B^- + e^-;$$

$$A_0(A^+) = A_0(B^-)$$
$$= D(AB) + I(A) - E_a(B) + E_e(A^+) + E_e(B^-) \quad \ldots . \quad (5.2.1.2)$$

$$AB + e^- \rightarrow A + B^-;$$
$$A_0(B^-) = D(AB) - E_a(B) + E_e(A) + E_e(B^-) \quad \ldots . \quad (5.2.1.3)$$

Appearance of a positive ion only at a given minimum electron energy indicates a process of the first type. Simultaneous appearance of a positive and a negative ion indicates a process of the second type. Appearance of the negative ion at electron energies too low for a positive ion to be formed as well indicates a process of the third type. The first two types of process are ordinary collision processes whose probability increases with increasing electron energy up to electron energies much greater than the energy required for the process, the excess energy not taken up by the molecule appearing as residual kinetic energy possessed by the electron after the collision. The third, on the other hand, which involves capture of an electron, is a resonance process.

The determination of $A_0(A^+)$, together with a knowledge of $I(A)$ and of the electron excitation E_e of the products, is sufficient to give $D(AB)$ as shown by equation 5.2.1.1. For atoms, $I(A)$ is usually known from the atomic spectrum; for radicals, $I(A)$ has usually to be obtained by direct measurement of $A_0(A^+)$ when A radicals are introduced into the apparatus, or from $A_0(A^+)$ from AC, where $D(AC)$ is known. The possible electronically excited states of the atoms $E_e(A)$ *etc.* are also known from atomic spectra, but frequently the electron impact experiment does not allow us to distinguish between several possible values of E_e, and the experiment thus leads to a choice of values of $D(AB)$, depending on the assumed values of $E_e(A^+)$ and $E_e(B)$. To decide on the correct value of $D(AB)$, a series of different dissociative ionization processes is studied. Each process yields a set of possibilities for $D(AB)$ depending on the E_e values assumed, but usually only one value of $D(AB)$ fits all the sets, and is thus the true value. This is usually only possible for heteronuclear diatomic molecules. For homonuclear diatomic molecules the possibilities may be too few, and for polyatomic molecules the complications are too great. Considerable progress in the interpretation of electron impact experiments on polyatomic molecules has been made on the assumption that the radicals and radical ions are produced in their ground states, but some discrepancies may be due to it. (*See*, for example, McDowell

and Warren[333], and Stevenson[472] on evidence relating to D(CN–CN.)

The identification of m–e for particles in the mass spectrometer is a standard technique discussed in the text-books, but in view of the fact that there is at present much interest in dissociation energies measured by electron impact and relatively little general discussion of the measurements, we shall devote the two following short sections to the discussion of measurement of appearance potential and of kinetic energy, and follow them by examples of the use of the method in Section 5.2.4.

5.2.2. *Measurement of Appearance Potential*

The measurement of the appearance potential involves the determination of the minimum energy of the electron beam required to form the ion. The voltage scale for the accelerating potential of the electron beam is calibrated by adding an inert gas whose ionization potential is known from spectroscopic measurement, to give a known point on the voltage scale. The inert gas is added at the same time or under the same conditions as the gas under investigation, and effectively the curves of ion current against

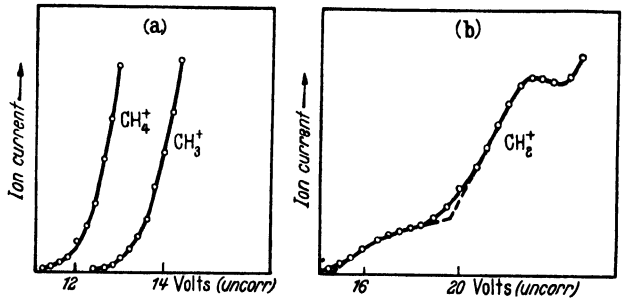


Figure 5.2.2.1. Ionization efficiency curves for methane (after McDowell and Warren[331]).

voltage for the two gases are compared. Complete congruence of these two curves is not to be expected, because the shape of the curve of ionization probability against relative kinetic energy depends upon the specific ionization process taking place. Therefore comparison of the voltages at large ion currents, for example by extrapolating the approximately linear part of the ion current voltage curve to the voltage axis and noting the intercept, is inadmissable. The typical shape of the curve is shown in *Figure 5.2.2.1* (a). The initial upward break in the curve is used in the

hope that in this way differences in the shape of the ionization probability against energy curve will disappear.

Unfortunately, the shape of the curve does not allow a sharp upward break to be clearly defined. This is because in addition to the kinetic energy imposed upon the electrons by the accelerating voltage there is superimposed the kinetic energy distribution of the electrons characteristic of their thermal motion at the temperature at which they were produced; as they are produced from a hot filament this is quite large and kT is about 0·15 eV. This effect means that the curves approach the voltage axis asymptotically, and the determination of the point of sharp upward break is somewhat subjective. Hagstrum [198] has pointed out that if the ion current voltage curves are plotted on a scale fine compared with kT, no sharp upward break will be seen, whereas if they are plotted on a coarse scale, the point becomes obvious but cannot, because of the coarseness of the scale, be located very accurately on the voltage axis. Under these circumstances, Hagstrum does not consider that measurements of appearance potential can be relied upon to better than about 0·2 eV. Honig [229] has claimed greater accuracy than this by careful matching of ion-current–voltage curves. Warren [551] has suggested that extrapolation of the voltage difference between points of equal ion current for the gas under investigation and an inert gas to zero ion current gives a measure of the appearance potential accurate to within better than 0·05 eV. Some of Warren's results for appearance potentials, obtained by this extrapolated voltage difference method, are given below. These appearance potentials are also ionization potentials because for these molecules no dissociation takes place under Warren's conditions. The voltage scale is calibrated by taking $I(\mathrm{A}) = 15{\cdot}77$ V.

Table 5.2.2.1

Molecule	*Ion*	*Spectroscopic ionization potential* V	*Electron impact result*
Kr	Kr^+	14·01	14·01 ±0·02
Ne	Ne^+	21·57	21·61 ±0·04
O_2	O_2^+	12·26	12·20 ±0·03
CO_2	CO_2^+	13·79	13·95 ±0·03

The electron impact results are 'vertical' ionization potentials. These may exceed the spectroscopic 'adiabatic' ionization potential by the vibrational energy excited in the ion because of the Franck–Condon principle. Here 'adiabatic' is used in the sense of 'without

Table 5.2.2.2. Appearance Potentials in Methane (eV)

Ion	*Investigator*						
	Honig[229]	*Hipple and Stevenson*[223]*	*Smith*[457]*	*Koffel and Lad*[278]	*Mitchell and Coleman*[350]	*Geerk and Neuert*[167]	*McDowell and Warren*[331]
CH_4^+	13·04	—	13·2 ± 0·4	13·0 ± 0·2	13·04 ± 0·02	13·3 ± 0·3	13·12 ± 0·02
CH_3^+	—	14·5 ± 0·1	14·5 ± 0·4	14·4 ± 0·3	14·57 ± 0·05	14·5 ± 0·3	14·39 ± 0·02
CH_2^+	—	—	15·8 ± 0·5	20·0 ± 0·3	—	16·5 ± 0·3	15·30 ± 0·5
	—	—	23·0 ± 0·8	—	—	21·5 ± 1·0	20·1 ± 0·1
CH^+	—	—	23·4 ± 0·6	24·3 ± 0·5	—	22·5 ± 0·5	22·4 ± 0·1
	—	—	—	—	—	27·0 ± 1·0	—
C^+	—	—	26·8 ± 0·8	—	—	21·5 ± 1	26·2 ± 0·2
	—	—	—	—	—	29·5 ± 1	⩽27·3

* The results in these columns were corrected for the new value of I(argon).

change in vibrational level'. For O_2 the ground state vibrational eigenfunctions in the molecule and the molecule ion overlap, so that the spectroscopic and electron impact ionization potentials would be expected to be the same. For atoms of course they should be identical. It should be realized that this method has no more theoretical significance than direct inspection; it is merely an attempt to lessen the subjectivity involved. Typical curves which can be treated in this way are shown in *Figure 5.2.2.1* (a), taken from a paper on ionization and dissociation in methane by McDowell and Warren[331].

Often the same ion may be produced by two different processes: for example A^+ is produced by processes given in equations 5.2.1.1 and 5.2.1.2, and thus at two different appearance potentials. The curve of ion current for ions of this mass number thus rises with increasing voltage for ions produced by equation 5.2.1.1 until the appearance potential of A^+ from equation 5.2.1.2 is reached, when it curves more steeply upwards again. The usual method of determining the point of break is to regard the extrapolation of the first ionization curve as if it were the voltage axis, and to detect the point of sharp upward break by eye, or to extrapolate back the upper curve until it meets the extrapolation of the lower one if the break is not sharp enough. The theoretical justification for this is not obvious, and unless the break is very sharp, appearance potentials of ions obtained by superimposing a higher energy process on top of a lower cannot be considered to be very accurately known. *Figure 5.2.2.1* (b) shows this type of effect occurring in the curve for CH_2^+ from methane, as given by McDowell and Warren[331]. They used the method of extrapolated straight line intercepts, shown in the figure by broken lines to determine the difference between the appearance potentials of CH_2^+ produced in different processes.

The degree of agreement between different investigators in the measurement of appearance potential is shown in *Table 5.2.2.2* from McDowell and Warren's paper, which gives the various measured appearance potentials of the heavy positive ions from methane.

As expected, the agreement is good for those ions which have a simple ionization efficiency versus voltage curve with high relative abundance, but less satisfactory for those ions produced by a higher energy process superimposed on a lower and for those ions which are only produced with low relative abundance.

It should be remembered that all measurements of appearance potential are essentially difference measurements, because of the

necessity for calibrating the voltage scale. This to some extent gets round the difficulty that the exact shape of the ionization efficiency curve is not known if the comparison is made by extrapolation of the voltage difference to zero ion current, but there is always the possibility of some change in the shape of the curve for ion currents below the sensitivity of detection. It is therefore to be expected that appearance potential measurements depend a little on instrument sensitivity, and some discrepancies in the literature have been ascribed to this, which is particularly important for ions of low relative abundance (*see* McDowell and Warren [331]). The limits of accuracy quoted by the American workers appear to be estimates of the absolute accuracy of the measurements. On the other hand, those given by McDowell and Warren depend on the precision of their measurements, and are the standard deviations of the mean of a number of determinations, usually between six and twelve, of the appearance potential.

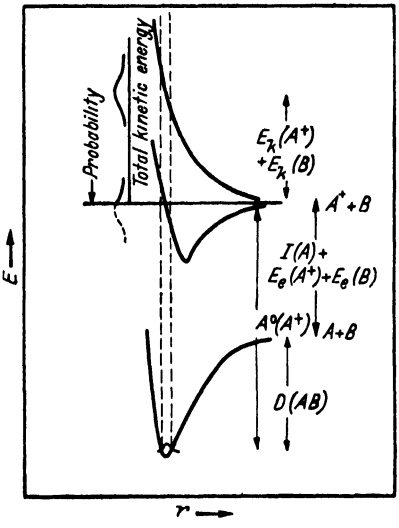


Figure 5.2.3.1. Diagram illustrating production of products with kinetic energy in electron impact experiments (after Hagstrum [198]).

5.2.3. *Measurement of Kinetic Energy*

It has already been shown in Section 5.1.2 how the particles resulting from electronic excitation may possess kinetic energy if the transition takes place under appropriate conditions. A discussion of the effect of kinetic energy and the conditions under which it is produced has been given by Hagstrum [198] in a particularly illuminating review of electron impact processes in CO, N_2, NO and O_2, and in

much of this section we follow his treatment closely. Hagstrum and Tate[199] have considered the application of the Franck–Condon principle to this problem in some detail. The situation may be described in terms of the Franck–Condon diagram in *Figure 5.2.3.1.* The particles produced possess kinetic energy, E_k, by virtue of the position on the upper curve to which transition may take place, and the distribution of kinetic energy may be obtained approximately by the reflection method. If transition to the repulsive upper state occurs, all ions produced will possess appreciable kinetic energies. If transitions to the more stable upper state take place, ions will be produced with kinetic energies including zero. For example, in a dissociative ionization process producing positive ions only, the appearance potential of the ion A^+ with kinetic energy, $A_k(A^+)$, will be given by

$$A_k(A^+) = D(AB) + I(A) + E_e(A^+) + E_e(B) + E_k(A^+) + E_k(B)$$

where E_k is kinetic energy. The total kinetic energy divides between the particles according to the principle of the conservation of momentum and in this case

$$E_k(A^+) = [m(B)/(m(A^+) + m(B))][E_k(A^+) + E_k(B)]$$

and hence

$$A_k(A^+) = A_0(A^+) + [(m(A^+) + m(B))/m(B)]E_k(A^+)$$

Thus the plot of ion kinetic energy against appearance potential should be a straight line of slope $m(B)/[mA^+) + m(B)]$ with intercept $A_0(A^+)$ on the $A_k(A^+)$ axis, but of course measurement of $A_k(A^+)$ will only be possible over the region of this graph indicated by the probability curves in *Figure 5.2.3.1.*

Ions may also be produced with kinetic energy if there is a maximum in the potential energy curve for the stable excited state, as pointed out by Hipple and Stevenson[223]. The last possibility corresponds to an activation energy for the recombination reaction (*see* Section 4.2.1). Measurement of kinetic energy, or proof that the ions are formed at rest, is essential for the reliable deduction of dissociation energies from the electron impact method.

It is desirable to measure the ratio *m–e*, the appearance potential, and kinetic energy in the same experiment, but there are considerable difficulties in doing this, and usually in the mass spectrographic experiment only the first two of these have been measured, while the retarding potential method of Lozier measured the second and third.

5.2. ELECTRON IMPACT METHODS

The retarding potential method[325] for the study of the velocity distribution of ions formed by electron impact involves an electron beam of known accelerating potential being passed along the axis of two coaxial cylinders, which contain the gas to be ionized. The beam is kept linear and narrow by a magnetic field. The thick inner cylinder is slotted and allows only ions moving perpendicularly to the electron beam to pass to the outer collecting cylinder. A retarding voltage is applied between the two cylinders. A study of the positive ion current collected as a function of the retarding voltage allows the determination of the kinetic energy distribution of the ions. Alternatively the retarding voltage is kept fixed and the appearance potential of ions of known minimum kinetic energy corresponding to the retarding voltage is measured from a plot of positive ion current against electron voltage in the usual way[326]. The original experiment gave results for hydrogen in fairly good agreement with theoretical prediction, but an instrumental effect, probably due to the magnetic field or to contact potentials gave a kinetic energy maximum at about 1·0 eV for ions which were expected to be at rest. In the later experiments the difficulty was overcome, and accurate values of $D(H_2)$ and $D(H_2^+)$ obtained. $D(N_2)$ was determined as 9·79, 7·90, 7·42, 6·23, or 5·76 eV according to the assumed states of excitation of the nitrogen ion and the nitrogen atom produced. Spectroscopically obtained values for $D(N_2)$ are 9·76 or 7·38 eV, depending on the assumptions made. The retarding potential and appearance potential measurement alone is satisfactory for the interpretation of electron impact processes in homonuclear diatomic molecules, where there can be no doubt about the mass number of the ions. Possible confusion for heteronuclear diatomic molecules is not likely to be very great, but the method by itself is clearly inapplicable to dissociative ionization processes in polyatomic molecules, where the number of possible products is large.

The difficulty in the measurement of kinetic energy in the mass spectrographic experiments is that the mass spectrograph itself may be expected to distort the kinetic energy distribution. In particular the slits in the source and analyser of the mass spectrograph discriminate against the collection of ions having large initial kinetic energies, and there is a velocity dispersion in the mass analyser. The first effect occurs because ions of low initial velocities are more easily formed into a beam and are therefore collected more efficiently, the second because the optimum setting of the ion accelerating potential and the analyser magnetic field strength (if variable field strength is used) depends upon the initial kinetic energy

of the ions. This last effect has been responsible for discrepancies in the literature*. It is, however, fairly easy even in the mass spectrometer to obtain the zero of initial kinetic energy because ions produced by direct ionization, with the loss of one or more electrons only, possess essentially the thermal velocities of the parent gas and may be considered at rest.

Hagstrum and Tate [199] studied the effect of the initial kinetic energy and of instrumental characteristics on the shape of the ion peak, and were able to distinguish characteristic shapes corresponding to different types of initial kinetic energy distribution. Hipple [222] pointed out that the use of a retarding potential applied to the positive ion beam emerging from the exit slit of the mass spectrometer before it falls on the collector should give information about initial kinetic energy. It was noted that if the retarding potential is adjusted so that ions produced effectively at rest (such as $C_4H_{10}^+$ from butane) are unable to reach the collector a so-called inverted peak will be formed; they will be accelerated back against the exit slit from which they will eject secondary electrons. Because of the polarity of the field, these electrons will be accelerated to the ion collector, where they will set up a negative current. It was found that if for butane the retarding potential was arranged to give an inverted peak for the heavy ions, the lighter ions did not produce one. An increase of several volts in the retarding potential was necessary to cause this effect for the light ions, indicating that they were formed with considerable initial kinetic energy. Because of the instrumental discrimination mentioned above, the change in retarding potential does not give a measure of the amount of kinetic energy. Hipple remarked on the importance of this observation in connection with the deduction of thermochemical quantities for polyatomic molecules from appearance potentials.

McDowell and Warren [331] point out that in their instrument, in which retarding potentials could not conveniently be applied, the effect of initial kinetic energy of an ion was to produce slight defocusing of the ion beam. If the ion beam is moved across the collector slit by varying the ion accelerating potential the voltage change corresponding to the half-width of the beam could be found. It was observed that a plot of beam half-width as ordinate against ion accelerating voltage for ions known to be formed with zero kinetic energy (usually ions formed by simple ionization) gave a good straight line, whereas the points for ions suspected to be formed with

* *See* footnote 18 in H. D. Hagstrum [198], where the failure of Newhall [367] to observe H^+ ions of zero initial energy is attributed to this effect.

kinetic energy lay above the line. The points for O^+ and N^+ from air lay at half-widths between 5 and 10 per cent greater than those corresponding to the straight line. This is, of course, a purely qualitative test. The method was used to show that CH_4^+, CH_3^+, CH_2^+, CH^+ and C^+ produced from methane were without kinetic energy. It should be pointed out, however, that in processes involving the production of light particles, such as hydrogen atoms in this example, the latter would be expected to have most of the kinetic energy and the above test may not be sufficiently sensitive.

A detailed discussion of the use of retarding potentials in the mass spectrometer has been given by Hagstrum [198]. The distribution of ion current with retarding potential was studied for ions known to be produced at rest, and its displacement when ions with kinetic energy are formed was examined. By paying careful attention to the possible sources of error mentioned above, measurements of the kinetic energy of ions formed at various electron voltages could be made. From these the appearance potential of ions formed at rest $A_0(A^+)$ could be deduced from $A_k'(A^+)$ as a function of E_k, the electron kinetic energy. This is not simply a linear extrapolation of the A_k, E_k plot, because the theoretical slope of this plot is known. Thus the appearance potential corresponding to one retarding potential is sufficient to determine A_0. Kinetic energies obtained in this way for O^+ from CO were found to agree reasonably well with those derived from analysis of peak shape by Hagstrum and Tate [199].

5.2.4. *Examples of Electron Impact Work*

In the 1930's the method was applied several times to the dissociation of simple diatomic molecules chiefly by the Minnesota school. The situation as far as CO, N_2, NO, and O_2 are concerned has been discussed in great detail by Hagstrum [198] and his paper is the chief source of the following information. There has been much controversy about the dissociation energies of these compounds, so perhaps it might be mentioned at the outset that for hydrogen Lozier [326] obtained the result $D(H_2) = 4{\cdot}43$ eV in 1933. This differs from the presently accepted spectroscopically obtained value by less than 0·05 eV so it appears that where interpretation of the appearance potentials is not in serious doubt the method is capable of good results. Similarly, for nitrogen, the results obtained by the retarding potential method allow only the two values for $D(N_2)$ most favoured by spectroscopists, the choice depending upon the assumed states of excitation of the products. Further, as Hagstrum

has shown, a proper interpretation of the electron impact results for oxygen, where greater experimental difficulties are met with, gives a value for $D(O_2)$ in agreement with the reliably obtained spectroscopic result.

The electron impact results for carbon monoxide will now be discussed in some detail, as an illustration of the method applied to a diatomic molecule. The ion current against electron energy curves for C^+ from CO and for O^- from CO are given in *Figure 5.2.4.1.* It will be seen that the initial appearance potential of C^+ is well defined at $20{\cdot}9 \pm 0{\cdot}2$ eV, and that the appearance potential of O^- is at almost exactly the same voltage, given by Hagstrum

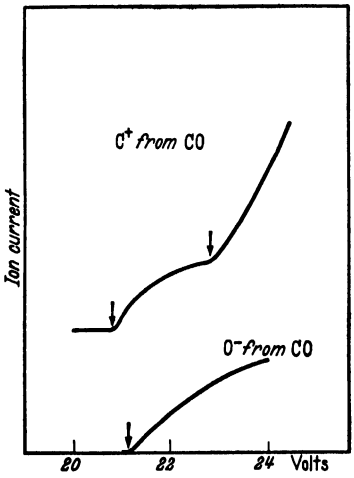


Figure 5.2.4.1. Production of C^+ and O^- from CO; ion current as a function of voltage (after Hagstrum[198]).

as $21{\cdot}1 \pm 0{\cdot}2$ eV. A plot of retarding potential and its derivative against ion current for C^+ and O^- was compared with a similar plot for the molecular ion CO^+, and the shapes were found to be similar, although the curve for the atomic ions showed a slight tail towards higher kinetic energies. This shows that the ions are formed substantially without initial kinetic energy. These curves are shown in *Figure 5.2.4.2* (a) and (b) and comparison of the figures suggests that any shift to higher kinetic energies cannot be greater than 0·1 to 0·2 eV, or well within the accuracy of the appearance potential measurements. The production of C^+ and O^- at the same appearance potential and without kinetic energy shows that A_0 for the process

$$CO \rightarrow C^+ + O^- \qquad \ldots . \quad (5.2.4.1)$$

is $20{\cdot}9 \pm 0{\cdot}2$ eV. The electronic excitation of the products is left

unspecified, as it cannot be determined from this information alone. The curve for C^+ in *Figure 5.2.4.1* shows a second distinct upward break at $22{\cdot}8 \pm 0{\cdot}2$ eV, and Hagstrum's published curve allows of little uncertainty in the estimation of its position. His estimate of

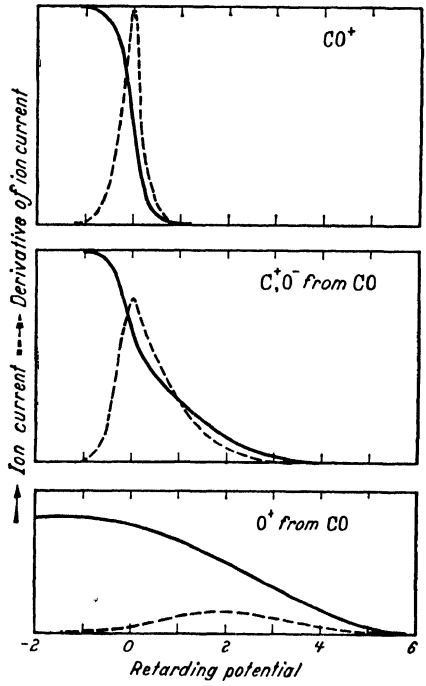


Figure 5.2.4.2. Ion current against retarding potential for ions from CO (after Hagstrum[198]). The zero retarding potential scale is taken from CO^+. The curves were taken for an electron energy of 100 V.

the possible error appears not to flatter the results. The absence of a similar upward break in the O^- curve indicates that A_0 for the process

$$CO \rightarrow C^+ + O \qquad \ldots . \quad (5.2.4.2)$$

again leaving unspecified the electronic states of the products, is $22{\cdot}8 \pm 0{\cdot}2$ eV. The appearance potential for O^+ ions is less clearly defined, and the plot of ion current and its derivative against retarding potential for this ion shows conclusively that it is produced with a large amount of kinetic energy. It has been shown that a weak positive ion current with no appreciable kinetic energy at this mass number could just be detected with an appearance potential of from 23·1 to 23·5 eV. The curve shown in *Figure 5.2.4.1* (c) was obtained with a large electron energy (100 V) and

it does not rule out the possibility of producing a small proportion of ions of almost zero initial kinetic energy at low electron energy. A_0 for this ion was determined from a knowledge of the A_k–E_k relationship, and the expected theoretical slope, and was estimated to be $23{\cdot}2 \pm 0{\cdot}3$, in good agreement with the observation that a very weak positive ion current could be detected at about 23·3 eV. C^- ions were looked for in this process, but not found, so that $A_0(O^+)$ at $23{\cdot}2 \pm 0{\cdot}3$ eV must correspond to

$$CO \rightarrow C + O^+ \qquad \ldots . \quad (5.2.4.3)$$

This definite failure to find C^- is important[197] because Gaydon[166] has suggested that this appearance potential might correspond to the production of O^+ and C^-. Finally, O^-, without kinetic energy, is produced at 9·5 eV. Earlier workers obtained O^- at voltages between 9·3 and 9·5. The production of O^- at such low energies can only be due to a dissociative electron capture process

$$CO \rightarrow C + O^- \qquad \ldots . \quad (5.2.4.4)$$

The ionization potentials of C and O are reliably known to be 11·26 and 13·61 eV respectively, and the electron affinity of O may be accepted as 2·2–2·3 eV (Gaydon[166], Chap. V)*. Thus if unexcited atoms are formed in all the processes, the following values (in eV) are obtained for $D(CO)$ from the various processes: equation 5.2.4.1, 11·6; equation 5.2.4.2, 11·8; equation 5.2.4.3, 9·6; and equation 5.2.4.4, 11·7. For equation 5.2.4.3 to give results in agreement with the other processes, assuming ground state atoms, the appearance potential of O^+ without kinetic energy would require to be about 25·2 eV, and there appears to be no doubt that O^+ may be observed at potentials less than this, and that the O^+ produced at larger electron energies possesses kinetic energy. Under these circumstances, it must be concluded that excited atoms are produced, and that the dissociation energy deduced will depend on the excitation assumed. The true dissociation energy is obtained by making all possible assumptions about the energies of the products, and writing down the resulting dissociation energies. In general this list will be different for each process, but each should contain the true value. The lists for the different processes are given in *Table 5.2.4.1.* The only value occurring in all the lists is 9·6 eV, and this is the value of $D(CO)$ deduced from the electron

* Although Gaydon states that 2·2–2·3 eV is the most reliable value for the electron affinity of O, and that the value 3·08 may be discarded, in Chap. VII he criticizes the electron impact work of Hagstrum and Tate for failing to obtain 3·08 eV for the electron affinity of oxygen.

impact results. An extraneous but perhaps interesting consideration is that values of $D(CO)$ higher than 11·1 eV are conclusively ruled out by spectroscopic evidence. Gaydon has suggested that the electron impact results giving the high values are based upon the correct interpretation of the results and that the weak O^+ ion current produced at 23·3 eV is due to some impurity, and further that all the results are about 0·5 eV high due to unspecified

Table 5.2.4.1

	Process (equation number)			
	5.2.4.1	5.2.4.2	5.2.4.3	5.2.4.4
D	11·8	11·6	9·6	11·7 10·4
	9·6	9·6	8·3	9·5
	6·5	7·4	6·9	9·0
	4·3	6·4	6·3	8·2

experimental errors. This suggestion has been indignantly repudiated by Hagstrum[197], and certainly Gaydon's explanation is very strained. It would, however, be very helpful if some more direct evidence on the state of excitation of the products could be obtained.

The application of the method to the determination of bond dissociation energies in polyatomic molecules has been carried out, at least at first, in a less rigorous manner. The results are justified mainly by their self-consistency and also by their often remarkably close agreement with results obtained by different methods. For example, $D(CH_3 - H)$ was determined in two separate ways by electron impact, and the agreement between them was taken to show that errors due to kinetic energy effects were unlikely to be present.

The 'indirect' method was put forward by Stevenson[470]; in it the appearance potentials of the same ion produced from two different but related molecules are measured, and their difference is combined with thermochemical data to give the required dissociation energy. It is thus possible to calculate bond dissociation energies from appearance potentials and thermochemical data without a knowledge of ionization potentials. The essence of the method is to produce as the non-ionized partner in a dissociative ionization process of the type

$$AB + e^- \rightarrow A^+ + B + 2e^-$$

a radical B, and in another similar process producing the same ion A^+ to produce as non-ionized partner a radical or atom B′ whose heat of formation is known. It is thus possible to obtain $D(B-B')$. $D(CH_3-H)$ was obtained by observing the appearance potential of $C_2H_5^+$ from ethane with H as the other partner, and from propane, with CH_3 as the other partner, and using the known heat of formation of atomic hydrogen together with those of the compounds concerned in the following thermochemical equations

$$C_2H_6+CH_4 \rightarrow C_3H_8+2H \qquad \Delta E=5{\cdot}08 \text{ eV}$$

$$C_3H_8 \rightarrow C_2H_5^+ + CH_3 \qquad \Delta E=A(C_2H_5^+)=14{\cdot}5_0 \text{ eV}$$

$$H+C_2H_5^+ \rightarrow C_2H_6 \qquad \Delta E=-A(C_2H_5^+)=-15{\cdot}2_0 \text{ eV}$$

whence

$$CH_4 \rightarrow CH_3+H \qquad \Delta E=4{\cdot}3_8 \text{ eV}$$

By this method Stevenson obtained $D(CH_3-H)$ as $101 \pm 4{\cdot}5$ kcal, and $D(C_2H_5-H)$ as $96 \pm 4{\cdot}5$ kcal. In view of the errors in the measurement of appearance potential, he did not consider this difference to be significant. He also was at pains to point out that if the recombination reaction between ions and methyl radicals has an appreciable activation energy, while the recombination of ions and hydrogen atoms has none, the correct results would be lower than those given above by that amount. Confidence in these results was increased when in 1943 Hipple and Stevenson[223] published measurements of the ionization potentials of the methyl and ethyl radicals, thus enabling the direct measurement of dissociation energy from the relationship,

$$AB+e^- \rightarrow A^+ + B + 2e^-; \; A(A^+)=I(A)+D(AB),$$

which holds if the fragments are produced at rest and in the electronic ground state. These measurements of the vertical ionization potentials were made by decomposing lead tetra-alkyls in a furnace built into the ionization chamber of a mass-spectrometer, and noting the initial upward breaks in the ionization efficiency curves for the ions CH_3^+ and $C_2H_5^+$. It was found that as the temperature of the furnace containing lead tetramethyl rose, the CH_3^+ current passed through a minimum and then increased at the same rate as the CH_4^+ produced, showing that at this temperature the CH_3^+ was being produced from the dissociation of methane by electron impact. The difference between the appearance potentials of CH_3^+ produced by the two processes gave $D(CH_3-H)$,

in the absence of complication from kinetic energy, as follows:

$$CH_3 \rightarrow CH_3 + e^-; \qquad A(CH_3^+) = 10{\cdot}0_0 \pm 0{\cdot}1 \text{ eV}$$

$$CH_4 \rightarrow CH_3^+ + H + e^-; \qquad A(CH_3^+) = 14{\cdot}44 \pm 0{\cdot}1 \text{ eV}$$

giving $D(CH_3 - H) = 4{\cdot}4_4 \pm 0{\cdot}2$ eV, in excellent agreement with $4{\cdot}3_8 \pm 0{\cdot}2$ eV obtained by the indirect method. Hipple and Stevenson state that the agreement between the two methods shows that the result is equal to the true value, but their argument is not conclusive. They give the following formal comparison of the two methods. In the indirect method, we have

$$\left.\begin{aligned} &R - R' \rightarrow R^+ + R' + e^-; \quad A_1(R^+) \gtrdot \Delta E_1 \\ &R - H \rightarrow R^+ + H + e^-; \quad A_2(R^+) \gtrdot \Delta E_2 \\ &R - R + 2H \rightarrow R'H + RH; \ \Delta E_3 \end{aligned}\right\} \quad \ldots . \text{ (5.2.4.5)}$$

Hence

$$D(R' - H) = \Delta E_1 - \Delta E_2 - \Delta E_3 \lessgtr A_1 - A_2 - \Delta E_3 \quad \ldots . \text{ (5.2.4.6)}$$

The equality sign in equation 5.2.4.6 holds if

$$A_1 = \Delta E_1, \ A_2 = \Delta E_2$$

or if

$$A_1 - \Delta E_1 = A_2 - \Delta E_2$$

In the direct method we have

$$\left.\begin{aligned} &(R' - H) \rightarrow R'^+ + H + e^-; \ A_4(R'^+) \gtrdot \Delta E_4 \\ &R' \rightarrow R'^+ + e^-; \ A_5(R'^+) \geqslant I(R') = \Delta E_5 \end{aligned}\right\} \quad \ldots . \text{ (5.2.4.7)}$$

Hence

$$D(R' - H) = \Delta E_4 - \Delta E_5 \lessgtr A_4 - A_5 \quad \ldots . \text{ (5.2.4.8)}$$

Now in a simple ionization process, the ion is likely to be formed at rest and so $\Delta E_5 = A_5$, and hence the estimate of $D(R' - H)$ provided by the indirect method is an upper limit. Thus if $D(R' - H)$ given by equation 5.2.4.8 is equal to $D(R' - H)$ given by equation 5.2.4.6, then the latter is also an upper limit. This would imply that

$$(A_1 - \Delta E_1) \geqslant (A_2 - \Delta E_2)$$

It does not seem impossible that the inequality sign might hold here, although there is no definite evidence on the point. It would, however, be rather remarkable if the amount by which $A_1 - \Delta E_1$ exceeded $A_2 - \Delta E_2$ was exactly equal to $A_4 - \Delta E_4$, and economy of hypothesis would suggest that all the ions are formed at rest,

and that $D(CH_3 - H) = 101$ kcal, a result which is in very good agreement with estimates obtained by quite different methods. Hipple and Stevenson are careful to point out that upward breaks in ionization efficiency curves can only be determined to $\pm 0{\cdot}1$ eV, and here they halve Hagstrum's estimate of the error, and that therefore the extremely close agreement is to some extent fortuitous. The results therefore leave room for small amounts of kinetic energy. The further application of the methods to the alkanes, and a more broadly based discussion of kinetic energy is given in a recent paper by Stevenson[476]. McDowell and Warren[331] have shown by the beam half-width method discussed earlier that CH_3^+ ions produced from methane had no appreciable kinetic energy. They recognized, however, that in this case the method is not very sensitive, because in this process the non-ionized partner will by the principle of conservation of momentum possess fifteen times as much kinetic energy as the CH_3^+. If we assume that the sensitivity of the method is as high as a tenth of a volt, the total excess kinetic energy may be as high as 1·5 eV, and remain undetected. On the other hand the application of their method to CH_3^+ produced from methyl cyanide is likely to be valid, because here the non-ionized partner is heavier than the ionized.

Further examples of the use of electron impact measurements to the determination of dissociation energies in polyatomic molecules are given in the discussion of particular values of dissociation energies in Chap. 9. It may be said here that in most cases the results are consistent with other information, suggesting that kinetic energy effects are often unimportant.

5.3. SPECTROSCOPIC METHODS

5.3.1. *General*

Spectroscopic methods may be used in determining dissociation energies in two ways. They may be used to provide ancillary information—a measure of concentration, perhaps, of temperature —or the energy differences deduced from the position of certain lines or bands in the spectrum may be used directly to give energy quantities related to dissociation energies. Essentially, the distinction is between the methods in which the quantal relationship between frequency and energy is ignored or used. This section is concerned with the direct use of spectroscopic measurements to determine energy quantities.

When an unambiguous interpretation of the experimental material is possible, this method is capable of giving the most

accurate values for the dissociation energies of diatomic molecules, essentially because of the great accuracy with which wavelengths can be measured. It cannot in general be used for polyatomic molecules, because of the complexity of their spectra. Unfortunately, the results are by no means always capable of an unambiguous interpretation. Thus, whereas for iodine the dissociation energy has been determined reliably to a high accuracy with a result in complete agreement with those obtained by other methods, the various values suggested for $D(CO)$, $D(N_2)$, and $D(NO)$ on the basis of the same spectroscopic evidence are still controversial. The following notes are intended to indicate the considerations which are most important; they do not pretend to give a complete account of the situation, because to do this would require much more space than is available here. There are two excellent modern works on the subject; an account of all aspects of the spectra of diatomic molecules by Herzberg [217], and one of the application of spectra in the determination of dissociation energies by Gaydon [166]. Both treat the fundamentals of the subject; in those applications which are controversial, the two authors generally hold opposite views.

The reader may be reminded here briefly of the main features of electronic absorption spectra, which are observed in the visible and ultra-violet regions of the spectrum. Systems of bands which may be shown to possess a line structure and continuous absorptions are both observed. This absorption is considered to be due to transitions between different electronic states; the energy separations between the bands in a system of bands correspond to vibrational energies, and thus to transitions between different vibrational levels of the electronic states responsible for the band system. The structure of the individual bands consists of lines having the separation corresponding to rotational energies.

The particular vibrational levels excited depend on the Franck-Condon principle and the relative positions of the potential energy curves for the electronic states concerned. From a study of the structure of the band systems it is often possible to deduce the dissociation energy to the products obtained from the dissociation of the upper state. Therefore to determine D_0°, the dissociation energy of the molecule in its ground state to the atoms in their ground states, we have to know the state of excitation of the products from the upper state. The spectroscopic determination of D_0° therefore consists in obtaining two pieces of information: (*a*) the dissociation energy to the upper state products, the dissociation limit, and (*b*) the identity of the products. The methods of doing this will be discussed in Sections 5.3.2 and 5.3.3.

5.3.2. *Determination of Dissociation Limit*

5.3.2.1. *Direct observation of limit*—For simplicity in the following discussion we consider the initial state of the molecule to be the ground vibrational state throughout, though in the complete spectrum there will be other transitions due to higher vibrational levels of the lower electronic state. Consider the potential energy curves given in *Figure 5.3.2.1* (a), and the spectrum to which a transition from the lower to the upper will give rise. If the nuclei in the ground state are much closer together than the equilibrium internuclear distance, say at r_1, transition will take place to a point in the upper curve above the dissociation limit for the upper state,

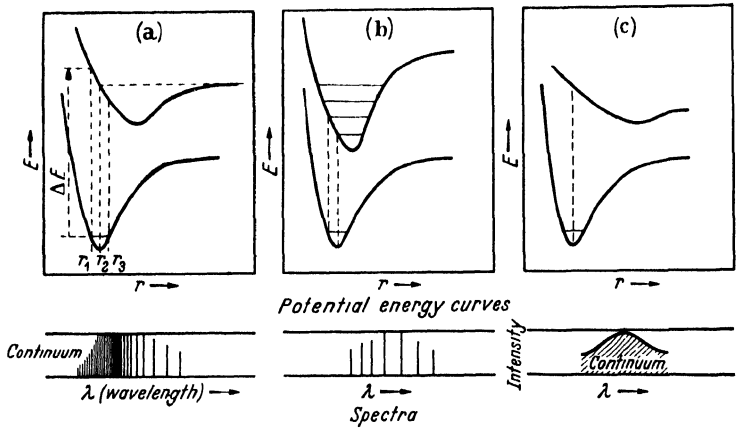


Figure 5.3.2.1. Franck-Condon diagrams for (a) absorption showing a convergence limit, (b) absorption suitable for Birge-Sponer extrapolation, (c) continuous absorption.

by the absorption of radiation of wavelength corresponding to ΔE_1. Since the energy in the upper state is not quantized in this region, the absorption will be continuous with wavelength. With the relative positions of the curves shown in the diagram the intensity will increase with increasing wavelength, because of the shape of the probability distribution of r values in the ground state (*see* Section 5.1.2). Transitions from larger values of r than r_2 take place to a region of discrete energy levels in the upper state, and absorption is no longer continuous. The highest vibrational levels in the upper state are close together, so the vibrational bands are close together. As transition takes place from larger values of r, the levels become more widely separated until the absorption

intensity falls off for transitions corresponding to larger values of r than r_3, because the probability of r values greater than r_3 in the ground state is small, and the overlap integral becomes small (*see* Section 5.1.2).

The corresponding spectrum is sketched below the potential energy curve. Going from longer to shorter wavelengths, *i.e.* with increasing energy, it is composed of bands gradually becoming closer together until the absorption becomes continuous. In these circumstances the convergence limit of a band spectrum to continuous absorption gives a very accurate measure of the energy required to dissociate the upper state. The best example of the determination of a dissociation energy by this method is that of iodine. Here the dissociation energy to excited atoms was determined directly from the spectrum and the state of the atomic products deduced to be one normal $^2P_{1/2}$ atom and one excited $^2P_{3/2}$ atom from the heat of dissociation to normal atoms known approximately from thermal data, combined with a knowledge of the atomic spectrum.

5.3.2.2. *Birge-Sponer extrapolation*—Consider the potential energy curves in *Figure 5.3.2.1* (b). Here the relative positions of the upper and lower curves is such that transition to a point on the upper curve does not take place. However, the separation of the vibrational bands becomes less with decreasing wavelengths. In this case it is possible to plot the vibrational quanta of the upper state $\omega(n)$ against the vibrational quantum number (n) and extrapolate to zero ω, that is, to a convergence limit. Such a procedure was suggested in 1926 by Birge and Sponer[41]. On the basis of the relatively small amount of evidence then available, they concluded that for non-polar molecules the curve of ω against n was strictly linear in the region in which it could be experimentally observed, and that a linear extrapolation to $\omega = 0$ seemed to give the true value of the dissociation energy to within half a volt. It is, however, now known that the slope of the curve of $\omega(n)$ against n usually becomes steeper as the n-axis is approached, and therefore a linear Birge-Sponer extrapolation is not reliable if it extends over a large number of quanta. High results are obtained for the dissociation energy since $D = \int_0^{n_0} \omega(n)\mathrm{d}n$, the area under the curve. For some molecules the extrapolation is fairly satisfactory; however, it is possible for the true curve to show a sudden steepening after the first few quanta. On the other hand for molecules in which ionic forces contribute appreciably to the binding, the form of the curve is such that the correct extrapolation is concave to the n-axis. This is shown

in *Figure 5.3.2.2.* For normal covalent molecules therefore the Birge-Sponer extrapolation gives an upper limit to the dissociation energy, whereas for ionic molecules it gives a lower limit.

It should perhaps be mentioned that the method is of course equally applicable to the ground state if the vibrational levels are known. A knowledge of the higher vibrational levels of the ground state may be derived from hot gases or from emission spectra, or

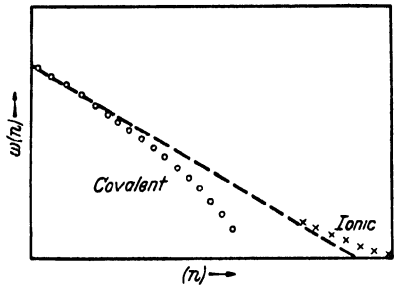


Figure 5.3.2.2. Birge-Sponer extrapolation, showing typical deviations for ionic and covalent molecules (schematic).

perhaps the intensities of the appropriate transitions may be great enough for some of them to be observable in the ordinary absorption spectrum. The extrapolation for the ground state of carbon monoxide leads to about 11 eV, which is one of the reasons why Gaydon prefers a value of $D = 11{\cdot}11$ eV for this molecule.

5.3.2.3. *Long wavelength limit of continuous absorption*—Here the situation is as shown in *Figure 5.3.2.1* (c). The position of the curves is such that no transition takes place to the region of discrete energy levels. The type of spectrum found is set out below. Clearly, when only continuous absorption is observed, the long wavelength limit of continuous absorption is an upper limit to the dissociation energy under consideration. If the upper energy curve is steep and the continuum sets in gradually, the limit may be some way above the dissociation energy. On the other hand if the energy curve for the upper state is very flat this method can be very precise; the most accurate value available for $D_0^\circ(H_2)$ is deduced in this way [36].

5.3.2.4. *Knowledge of vibrational levels*—Knowledge of any vibrational level of a state gives at once a lower limit to the dissociation energy of that state. This principle may be applied to the ground state, for which fairly high vibrational levels may occasionally be obtained, and provides a useful method of eliminating certain possible combinations of excited atoms as dissociation products of an excited state.

5.3.2.5. *Predissociation*—Although the discussion has so far been confined to the ground state and one excited state, there are a large

number of excited states possible, although transition to all of them may not be allowed by the selection rules or the Franck-Condon principle. Predissociation is a phenomenon involving three electronic states: the ground state and two excited states. If the potential energy curve corresponding to a state A to which direct transition is not possible crosses that of a state B to which transition from the ground state X is possible, and if at the level of the crossing point the nuclei have sufficient potential energy to dissociate in the state A, then a radiationless transition from state B to state A may take place, resulting in dissociation. This is known as predissociation, and may be used to fix a limit to the dissociation energy.

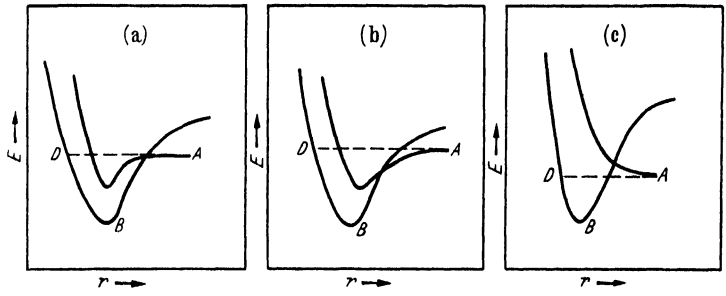


Figure 5.3.2.3. Potential energy curves showing cases I (a), (b) and (c) of predissociation. The ground state is not shown; transitions from it take place to the left branch of curve B.

This is generally known as Case I of predissociation; it concerns an electronic transition. Case II, predissociation by vibration, can only take place in polyatomic molecules. Case III is predissociation by rotation, and concerns transitions in the same electronic level. The question is treated in detail by Herzberg [217].

The Franck-Condon principle viewed classically implies that a radiationless transition between two electronic states can only take place if the two potential energy curves intersect, and the wave-mechanical viewpoint gives essentially the same conclusions, but the regions in which transitions are possible are broadened. When predissociations of Case I are interpreted in terms of potential energy curves and the Franck-Condon principle, three cases may be distinguished, Ia, Ib, and Ic. The appropriate diagrams are given in *Figure 5.3.2.3*, where only the upper two states are shown. Transition by absorption may take place from the ground state (not shown) to the left-hand ascending branch of curve B; direct transition to A by absorption of radiation does not take place. If a

vibrational level of state B above D is reached, predissociation will take place. It is shown in the spectrum by a disappearance or diffuseness of the band structure at this place, and by a weakening or disappearance of the band corresponding to the dissociation energy in the emission spectrum. In subcases (a) and (b) the point of intersection lies on (a), or below (b) the dissociation limit of state A. Thus in these cases the energy equivalent to the beginning of diffuseness in the band structure or to the breaking-off in emission, known as the predissociation limit, is the energy required to dissociate the molecule in the state A. In the third subcase (c) the point of intersection lies above the dissociation limit of A. Here the predissociation limit does not coincide with the dissociation limit but lies higher.

Predissociation is governed not only by the intersection of the potential energy curves (Franck-Condon principle) but by the selection rules which specify the types of state between which transitions may take place. These are treated fully by Herzberg. 'Accidental' predissociation is said to occur when the dissociation takes place by two radiationless transitions via the intermediacy of a third state.

The use of predissociation to determine dissociation energies is complicated by the fact that there are other effects which may cause anomalies in the structure of bands and which may be mistaken for predissociations. When two energy levels of different electronic states nearly coincide, and if transition between them is allowed by the selection rules and the Franck-Condon principle, they interact. The energy levels are perturbed and effects are produced which may be mistaken for accidental predissociation if not for a normal predissociation. Occasionally it is difficult to decide whether an alleged predissociation is real, and questions of the interpretation of certain effects as predissociations have been a fruitful ground for controversy among spectroscopists. Carbon monoxide is an example of a molecule where such a question has been controversial; the diatomic phosphorus molecule, on the other hand, provides a good example of the determination of a dissociation energy unambiguously by means of predissociation.

5.3.2.6. *Atomic fluorescence*—If a continuous absorption spectrum corresponds to dissociation into a normal and an excited atom, the excited atom may emit its excitation energy as fluorescence. Clearly the long wavelength limit which causes fluorescence corresponds to an upper limit to the dissociation energy concerned. This method has the great advantage that the state of at least one of the atoms produced is certainly known. It has been applied

successfully to the alkali halides by Terenin [512]. A similar method has been applied to dissociation in polyatomic molecules.

5.3.2.7. *Assumptions involved*—Most of the foregoing results are only correct if there are no potential maxima in the potential energy curves for the electronic upper states, such as suggested in *Figure 5.3.2.4.* If these exist, the dissociation energies derived spectroscopically will be upper limits only, the excess energy appearing as the kinetic energy of the products. The evidence about these potential maxima is somewhat controversial. For example, the interpretation of the spectrum of nitric oxide by Herzberg [217]

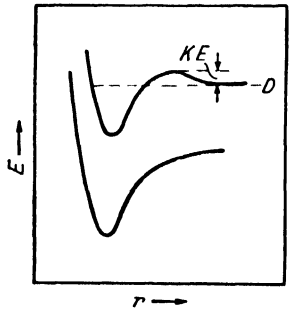


Figure 5.3.2.4. Potential maximum in upper state. This may occur in several molecules.

involves a potential maximum, but this has been contested by Gaydon [166]. Similarly, Hagstrum's interpretation of the spectrum of carbon monoxide requires a maximum [196], but this is by no means certain. The spectrum of diatomic aluminium fluoride, studied by Rowlinson and Barrow [432], taken in conjunction with thermochemical evidence, suggests that there is a potential maximum of about 0·8 eV in an upper state. A careful comparison of spectroscopic with accurate thermochemical data might reveal more of these maxima.

5.3.3. *Identification of Products*

5.3.3.1. *Energy differences*—If the dissociation limits for several excited states are known, it is possible to write down several sets of allowed dissociation energies for the ground state, each derived from a dissociation limit for an excited state together with various assumptions about the states of the atoms produced. The same procedure was followed in electron impact work on diatomic molecules. The true dissociation energy is one which appears in all the sets. Sometimes it is possible to eliminate all but one of the values in this way, but even if this is not possible it can reduce their number considerably.

5.3.3.2. *Application of the correlation rules*—The Wigner-Witmer correlation rules relate the nature of molecular states to the atomic states into which they may dissociate. The quantum-mechanical selection rules determine what electronic states may be excited by radiation, and with a knowledge of them it is often possible to deduce what type an electronic state is, and from this, using the Wigner-Witmer rules, to deduce what atomic states it may dissociate into.

The discussion of the electronic states of atoms and molecules and the correlation rules is too large a subject to be treated adequately in this book. Herzberg [217] gives a full treatment, Gaydon [166] lists the rules and gives examples of their application, and an account from the theoretical point of view is given by Van Vleck and Sherman [533].

It is necessary to mention here simply that the application of these rules is not automatic, because the theoretical treatments from which they are derived refer to ideal cases to which real molecules approximate more or less well. Indeed, the whole discussion of diatomic molecules in terms of potential energy curves and distinguishable electronic states is itself an approximation, though a good one.

5.3.3.3. *Thermochemical methods*—If an approximate value for a dissociation energy is known from thermochemical evidence, it is often possible to decide what the excited atoms formed at a given dissociation limit are, and thence to deduce an exact value of the dissociation energy. Iodine provides a good example of this.

6

THE DEFINITION, DETERMINATION, AND USES OF BOND ENERGY TERMS

6.1. DEFINITIONS

6.1.1. *Preliminary Definitions*

The bond energy term or thermochemical bond energy is a quantity assigned to each of the bonds in a molecule so that the sum over all bonds is equal to the heat of atomization of the molecule (a positive quantity, on the thermodynamic sign convention). Generally this assignment cannot be made without auxiliary assumptions, the earliest and simplest of which was that the energy term for a given bond is constant from molecule to molecule. On this assumption, they are easily derived from thermochemical information; the M – X energy term, often written $E(\mathrm{M-X})$, is $1/n$th of the heat of atomization of the compound MX_n; $E(\mathrm{M-Y})$ may then be derived from that of the compound $\mathrm{MX}_p\mathrm{Y}_{n-p}$ if $E(\mathrm{M-X})$ is known, and so on. This method would be a useful means of systematizing thermochemical information and of discussing the relative strengths of chemical bonds, if the definitions implied in the first sentence of this paragraph were clear cut, and if the assumption of constancy were exactly true. Neither of these conditions is fulfilled, and it will be the object of this chapter to examine them in more detail.

6.1.2. *The Bond Energy Sum*

The heat of atomization to which the bond energy sum is to be set equal requires further definition. It is ΔH for the reaction

$$\mathrm{A}_l\mathrm{B}_m\mathrm{C}_n \ldots \rightarrow l\mathrm{A} + m\mathrm{B} + n\mathrm{C} \ldots \text{ etc.} \quad \ldots . \quad (6.1.2.1)$$

The question of the exact specification of the states of the compound $\mathrm{A}_l\mathrm{B}_m\mathrm{C}_n \ldots$ and the atoms A, B, C . . . arises. Before considering this from the logical point of view, it is worth mentioning the experimental basis of the heat of atomization. The heat of formation of the molecule from the elements in their standard states is fairly readily accessible for most molecules, and this is combined with the heats of formation of the atomic elements from the elements

in their standard states to give the heat of atomization of the molecule. The heat of formation of a compound at room temperature consists of a number of terms which are independent of each other to a high degree of approximation. These are, for the ideal gas, the chemical binding energy, which for a diatomic molecule may be visualized as the depth of the energy minimum in the energy–interatomic distance curve of Section 1.2, the vibrational zero point energy, and the thermal energy of translation rotation and vibration. Moreover, if the substance is solid or liquid, the measured heat of formation will also include intermolecular energy. Now although we might be tempted to suppose that the chemical binding energy is the sum of a set of energy terms for the bonds in a molecule, there is no obvious reason to suppose that this will be so for the vibrational zero-point energy, the thermal energy, and still less for the intermolecular energy, which by definition has nothing to do with bonds. Derivation of the heat of formation of the compound in the ideal gas state is often easy, but on the other hand calculation of the zero-point energy and the thermal energy requires a detailed knowledge of molecular structure which is only rarely available. Thus if the heat of atomization were to be defined as ΔH for the reaction

$$A_lB_mC_n \text{ (gas at } 0^\circ \text{ K, without zero point energy)} \rightarrow l\text{A etc. (g; } 0^\circ \text{ K)} \quad \ldots . \quad (6.1.2.2)$$

only a few bond energy terms could be obtained and the method could be applied to very few compounds. Thus perhaps the most logically convenient definition is not particularly useful. An examination of the heats of formation of some simple hydrocarbons for which data to obtain chemical binding energies are available has been made. It appears that in general the use of 'binding energy terms' as suggested by equation 6.1.2.2 makes little difference to any argument based on 'bond energy terms' derived from heats of formation at room temperature[92].

Another difficulty is the energy zero to be adopted: that is, the definition of the states of the atoms. For many purposes, the energy zero does not matter, but for comparison of different bond energies, absolute values are required. We may choose the ground states of the atoms concerned: here there is no difficulty in principle, but it is an irritating fact that the heats of formation of many atoms from the elements in their standard states are not certainly known. This makes the absolute values of many bond energies uncertain. Further, however, it is uncertain that the atoms in their ground states are the most convenient to choose when discussing absolute

values of bond strengths[315, 318, 341, 453]. The ground state of the carbon atom, for example, is the ^3P state, which has the electronic configuration $(1s)^2\ (2s)^2\ (2p_x)(2p_y)$, in which there are two unpaired electrons. In most compounds, however, carbon is quadrivalent, and has four electrons which take part in bond formation. Thus it is arguable that a bond is formed, not between C(^3P) and another atom, but between C(^5S) and another atom, since ^5S is the lowest atomic state with four unpaired electrons: $(1s)^2\ (2s)(2p_x)(2p_y)(2p_z)$. The bond energy might therefore be referred to C(^5S) as zero. The energy of this state differs from that of the ground state by the promotional energy of one electron from the $2s$ to $2p$ level, 96·4 kcal[444]. Taking this into account would make a difference of 24 kcal per bond, which is from one-quarter to one-half of typical bond energy terms for carbon bonds. Once this type of argument is accepted, it is easy to continue and to point out that in tetrahedral carbon compounds the four electrons occupy completely equivalent orbitals, which is obviously not so in C(^5S), because there the $2s$ electron is more strongly bound than the others. Thus it could be argued that the correct energy zero to choose is that in which the isolated carbon atom is in a 'valence state' with the electrons occupying orbitals of tetrahedral symmetry.

This apparently more logical view involves us in two difficulties. The first is that whereas both the atomic states ^3P and ^5S are definite spectroscopic states of the isolated atoms, with energies which can at least in principle be measured, it is impossible to measure the energy of an isolated carbon atom in a hypothetical 'valence state'. Nor can the energy of such a state be calculated rigorously (*see* Van Vleck[532], who calculates the valence state of the C atom to lie 164 kcal above the ground state). The second is that the valence state will differ from compound to compound. The valencies of the carbon atom have a different symmetry in ethylene, for example, from that which they have in methane, and therefore presumably the valence state must change. These changes cannot be calculated reliably. (*See*, for example, Voge[535].) However, such changes in valence state, if not explicitly taken account of, will turn up as apparent changes in bond energy with valence state. This at present is probably the most convenient way of presenting them. Further, if we are not going to take explicit account of changes in valence state, we might as well choose a definite atomic state for our energy zero, provided we remember what we are doing; that we should remember is very important when comparing bond energy terms with dissociation energies. Except for

diatomic molecules, in which the bond energy term is equal to the dissociation energy, the dissociation of a bond will not usually lead to the atoms formed being in the states chosen as the energy zero, or in any other definite state of the free atoms, because they will be part of a molecular fragment, and therefore in some 'valence state'. Thus the bond energy term is not likely, except accidentally, to be equal to the bond dissociation energy. The contrary belief was fairly widely held a few years ago. Some of the arguments put forward to decide the heat of formation of atomic carbon (L_C) have depended on it. For example Baughan[22] pointed out that $D(CH_3-H)$ is approximately equal to the CH bond energy term in methane, if the latter is derived on the assumption that $L_C = 170$ kcal, but that the values are appreciably different if $L_C = 124$ kcal. He argued that this means that the correct value of L_C is 170 kcal. This argument depends on the identification of $D(CH_3-H)$ with the bond energy term, whereas in fact the bond energy term is the mean of $D(CH_3-H)$, $D(CH_2-H)$, $D(CH-H)$ and $D(C-H)$, in all of which processes the carbon atom must change its valence state. Baughan suggested that the energy of all the CH bonds involved must be about the same because successive halogen substitution in methane takes place with nearly equal energy per step. This example is not relevant because successive substitution involves no change in valence, although replacement of hydrogen by atoms of greater electronegativity may cause minor changes in valence state. It is interesting that the values for $D(CH_3-H)$ *etc.* are among the best evidence for the value $L_C = 120$–140 kcal (*see* Section 8.2.2.6).

It is quite possible that more refined theoretical analysis may lead to the use of valence states in the discussion of bond energies, and several moves in this direction have already been made. A term in the atomic heat of formation of a compound might well be inserted to take account of the change in the internal energy of the atoms themselves in bringing them to the appropriate valence states. Long[317] has suggested that instead of equating the bond energy sum to the heat of atomization, we might write

$$-\Delta H_f = \Sigma E_i - \Sigma V$$

where E_i is the 'gross or intrinsic bond energy' and V represents the valence state energy. Long gives references to attempts to derive valence state energies from experimental data[315, 383a, 384].

Since it is the object of this book as far as possible to deal with quantities directly related to experiment, the question of valence states will not be pursued further here.

So that the concept of the bond energy sum has the maximum usefulness we shall here define it as the heat of atomization in the ideal gas state at 298·16° K to the atomic elements in their ground states at this temperature. This is the most commonly used definition, and it is, for example, the one used by Pauling [382].

6.1.3. *The Individual Bond Energy Terms*

No matter what assumption we make about the definition of the heat of atomization to which the bond energy sum is set equal, we still have to introduce a further assumption or assumptions in order to derive individual bond energy terms from bond energy sums. For any one molecule the heat of atomization provides only one datum, from which only one bond energy term can be deduced and that only if all the bonds in the molecule are indistinguishable. Additional data are required. The earliest assumption, that bond energy terms for a given bond are constant from molecule to molecule, except under special conditions, was made by Fajans [149] and applied successfully to the discussion of molecular problems by Sidgwick [447], Pauling [382], and many others. For a molecule in which there is more than one type of bond, it is necessary to know the energies of all types except one from other data, and to obtain the remaining bond energy term as the residuum. If the assumption of constancy held exactly, this would lead to no difficulty, but if it did not, the procedure would give large differences in the energy of the 'same' bond in different molecules. This would happen because the total effects causing deviations from constancy in the bond energies as a whole are lumped into an effect on the one bond considered last.

Before discussing the idea of constancy in more detail it is desirable to examine an observation made by Butler and Polanyi [64]. They considered the theorem that the heat of formation of organic compounds from atoms can be represented by the sum of constant contributions characteristic of each chemical bond, and noted that: 'The validity of the theorem constitutes no evidence for the existence of a constant heat of *formation of the bonds* * covered by its scope.' They pointed out that for two kinds of bonds formed, say by carbon, with the two atoms X and Y, whatever the variation in the energies of the C–X and C–Y bonds with the position of the C atom, no deviation from the additivity rule would result, so long as the variations are equal for both kinds of bonds. The meaning of this depends on the definition of the 'heat of formation of bonds',

* Our italics.

which appears from the context to mean the bond dissociation energy (with sign reversed). Thus a more comprehensive statement would be that we cannot deduce bond dissociation energies in polyatomic molecules from bond energy terms, or that we cannot deduce bond dissociation energies from a knowledge only of heats of formation of molecules. If, however, we know the heats of formation of molecules from atoms, we can deduce differences between bond dissociation energies. It follows that if the 'additivity rule' holds, the difference between the bond dissociation energies $D(C-X)$ and $D(C-Y)$ will be the same regardless of what position the C atom occupies in the molecule, although we can say nothing of their absolute values. However, if the expression 'heat of formation of bonds' in Butler and Polanyi's observation is taken to mean the bond energy terms* it becomes apparently paradoxical. It would appear to imply, for example, that although the heat of formation of the compound XAY is given by the sum of bond energy terms derived from AX_2 and AY_2, we might, if we were clever enough, devise some experiment which might tell us that in fact $E(AX)$ and $E(AY)$ in XAY differed from $E(AX)$ in AX_2 and $E(AY)$ in AY_2. This interpretation would involve a mistaken notion of the logical structure of bond energy terms as we have defined them here. If we merely require that their sum should give the heat of formation of the molecule, $E(AX)$ and $E(AY)$ in XAY can be chosen in an infinite number of ways, and it is not meaningful to enquire, without further qualification, what their individual values are. Thus the validity of the 'additivity rule' does not tell us directly anything about individual bonds.

Therefore, when we ask how well the assumption of constancy of bond energy terms holds, we should more properly ask: How well can the heats of formation of molecules be represented as the sum of terms, one for each bond which we take as constant from molecule to molecule? With this in mind, we can now point out that for many simple molecules, with single bonds, the assumption of constancy holds very well.

Consider methane, methyl chloride, and carbon tetrachloride, for example. Here there are two types of bonds, C – H and C – Cl, and either could be considered 'primary' and used to deduce the others. We have the data given in *Table 6.1.3.1.*

The secondary C – Cl value does not differ from the primary value. Furthermore, the heats of atomization of the normal paraffins from ethane to hexane are given to within 1 kcal by the same values of $E(C-C)$ and $E(C-H)$ derived from the higher members of the

* As Cottrell and Sutton[99] imply.

Table 6.1.3.1

	$\Delta H_f°$(g) kcal	E(C – H) kcal	E(C – Cl) kcal
CH_4	–17·89	91·1 (primary)	—
CH_3Cl	–19·6	,,	70·0 (secondary)
CCl_4	–25·5		70·0 (primary)

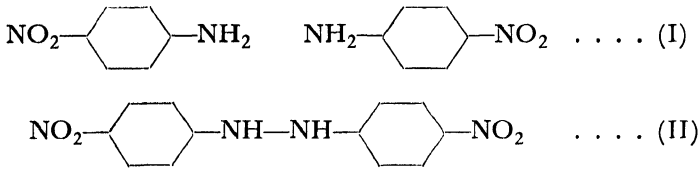
series. E(C – H) in methane differs from E(C – H) deduced from the higher paraffins by less than 1 kcal. In the 1-olefines, using E(C – C) and E(C – H) from the paraffins, E(C = C) is constant to within 0·2 kcal from propylene upwards. The value for E(C = C) in ethylene differs from that in propylene by less than 3 kcal. On the other hand for some other quite simple compounds there are indications that constancy does not hold for large changes in the molecular environment of a bond. For example E(C = O) in formaldehyde is 10 kcal less than E(C = O) in acetaldehyde, which is itself 3 kcal less than E(C = O) in ketones, E(C – H) and E(C – C) being taken as known. E(C = O) in carbon dioxide is 13 kcal higher still (*see* Section 10.6.8). Again, E(C = N) appears to vary by about 10 kcal from molecule to molecule [80]. Other and larger deviations from apparent constancy can be found in compounds for which two or more valence bond structures seem equally appropriate. Such compounds usually have higher heats of atomization than those calculated on the basis of the sum of bond energy terms for any one of these structures. This extra stability is usually ascribed to 'resonance' between valence bond structures, the excess heat of atomization above that calculated for the most stable valence bond structure being referred to as the 'empirical' or the 'observed' resonance energy. An additional brief note on this topic is given in Section 6.3.1.

For the present we consider compounds of one valence bond structure. The assumption of constant bond energy is a good first approximation, capable, for example, of being used to predict heats of formation to within two or three kcal, but there are sometimes minor effects which upset the assumption. These are about 5–10 per cent of residual bond energies in some examples. Thus although constancy is good enough for rough thermochemistry, deviations from constancy must be taken into account in more sophisticated discussions of molecular structure. Much of the interest in the subject now lies in the interpretation of these minor variations.

Lumping all the variation due to minor effects on to the 'last'

bond energy to be derived is clearly not adequate for further discussion, nor is the procedure logically sound. We can arbitrarily regard the same bond as *m*-ary or *n*-ary according to what data we take as primary, and thus we can arbitrarily throw the variation on to any particular bond. Therefore there is in the thermal data alone no necessity for us, for example, to consider that E(C=O) in formaldehyde is 13 kcal less than in acetone. We might equally well, and equally arbitrarily, say that E(C – H) in formaldehyde is 6·5 kcal less than E(C – H) in the methyl groups in acetone.

One method of getting over this difficulty of the 'last bond' effect can frequently be used in practice, though it does not remove the logical difficulty. This is to compare the heats of formation of structurally similar molecules. For example, Cole and Gilbert[81] (*see also* Anderson and Gilbert[9]) have suggested that in order to determine E(N – N) in, say 4–4′ dinitrohydrazobenzene, it is not necessary to know more than E(N – H). We consider the molecules p-nitroaniline (I) and 4–4′-dinitrohydrazobenzene (II)



It is obvious that the energy of formation of two moles of (I) in the gas state differs from that of (II) chiefly by the energy of the N – N bond and that of two N – H bonds. Thus if the difference in heats of formation is known, only E(N – H) is required.

One possibility is of course not to insist on thinking about bonds individually, but to regard the deviation from constancy as a molecular characteristic, as we already do in the definition of resonance energy. However, if it seems desirable to break this down into contributions from bonds, some regulating assumption is necessary. If allowance is to be made for the effects of differences in environment on the energy terms of the individual bonds in the molecule and this allowance is to be empirically derived, it is necessary to make an assumption of the type we wish to test about the effect of environment, on at least one sort of bond, and then to see if it leads to self-consistent conclusions. For example, for organic compounds, it might be convenient to assume a relationship between the energy and length of the CH bond. This would enable us to

deduce the energy of secondary and tertiary bonds in other compounds, to derive empirically an energy–length relationship for these bonds, and thus to check whether the form of the relationship derived is of general application.

If for convenience we regard bond length as the extra datum, together with an assumption of the form of an energy–length relationship, the problem is not uniquely solved. For example, the observed variation in length of the CH bond is from 1·059 Å in acetylene to 1·094Å in methane[216]. At first sight the question to be answered appears to be simply: 'How much does the CH bond energy change from acetylene to methane?' But this is not so, because as it stands, without further stated assumptions, it cannot be answered. The bond energy term is not an observable property of the bond but a conveniently chosen part of the energy of a molecule. The question is more properly put: 'How much of the difference between the heats of atomization of methane and acetylene should be attributed to the fact that the CH bond is shorter in the latter than in the former, in order to arrive at as generally satisfactory as possible a scheme of bond energies?' Put in this way the arbitrariness of the method of procedure is obvious. We might equally well, and perhaps more fundamentally, ask: 'How much of the difference between the heats of atomization of methane and acetylene should be attributed to the fact that the former has tetrahedral, while the latter has cylindrical, symmetry?' In brief, as soon as we abandon the simple concept of constancy, we run into fundamental difficulties of emphasis which can only be dealt with arbitrarily. The last form of the question really asks us to take into account valence states, as discussed in Section 6.1.2, and it is clearly quite legitimate to do so.

It can be argued, however, that on grounds of convenience, environmental effects should be taken account of using some energy–length relationship. This has the clear advantage over the last form of the question that bond lengths are often known, whereas valence states are not. A large number of authors have suggested relationships between bond energy and bond strength. For example, Gordy[185] has assumed that $E(\mathrm{C-H})$ is constant and thence found that CO, CN and CC links obey a simple relationship of the form $E = lr^{-2} + m$, where l and m are constants, and r is the bond length. Many others have derived energy–order and length–order relationships, which can be used to give the dependence of energy on length. Some references to this sort of exercise up to the end of 1947 are given by Cottrell and Sutton[99] and many

papers on the topic have been published since (*see*, for example, Glockler[178]).

Walsh[550] has suggested that bond energies should be chosen so that they serve as useful parameters for interconversion of bond properties, 'standard points' for the interconversion being provided by the MX_n type of molecule. He states that by the bond energy is meant an energy quantity which is a simple measure of the strength of the bond 'as it exists in the molecule'. According to Walsh it should bear a smooth relation to the equilibrium internuclear distance and to the force constant characterizing the curvature of the equilibrium minimum on the potential energy surface. This concept is thus not exact, but it does enable us to make generalizations about bond properties. The sort of procedure envisaged might be applied to the apparent difference mentioned above between $E(C=O)$ in acetone and formaldehyde as follows. The dimensions of the acetone molecule have been fully discussed by Allen *et al.*[3], who correct earlier values and after considering the electron diffraction data arrive at the results $r_0(C=O) = 1{\cdot}22 \pm 0{\cdot}03$ Å, $r_0(C-C) = 1{\cdot}55 \pm 0{\cdot}02$ Å, $< CCO = 119{\cdot}6 \pm 3°$. These are in complete agreement with an independent study by Japanese workers whose results are quoted by Allen *et al.*, and there seems to be little doubt of their accuracy. In particular they note that $r_0(C-C)$ is equal to $r_0(C-C)$ in ethane within the limits of experimental error. Moreover, there is no reason to suppose that the C – H bonds in the methyl groups differ from other C – H bonds attached to saturated carbon atoms. We may therefore use normal C – C and C – H bond energy terms in deducing $E(C=O)$ in acetone. The information on dimensions of formaldehyde is quoted by Allen and Sutton[4] to be $r_0(C=O) = 1{\cdot}225$Å, from the spectroscopically obtained moments of inertia, or $1{\cdot}21 \pm 0{\cdot}01$Å or $1{\cdot}15 \pm 0{\cdot}05$Å from electron diffraction studies. We may conclude that the C = O bond in formaldehyde is either equal in length to that in acetone, or possibly slightly shorter. Now, since we know empirically that in general the shorter the bond between two atoms the stronger it is, we can deduce that the parameter characterizing the bond energy in Walsh's sense in formaldehyde cannot be less than that in acetone[546]. Since the only other bond in formaldehyde is the C – H bond, and since the 'apparent' $E(C=O)$ in formaldehyde is 13 kcal less than in acetone, we may conclude that $E(C-H)$ in formaldehyde must be at least 6·5 kcal less than that of 'normal' CH. The length of the CH bond in formaldehyde is not known, but on this evidence we should predict it to be greater than that of CH in methane. The

only evidence bearing on this point is the force constant, which has been shown by Linnett[309] to be $4{\cdot}4 \times 10^5$ dyne cm^{-1} compared with $5{\cdot}0 \times 10^5$ in methane, implying that the C – H bond is here weaker and presumably also longer than C – H in methane, as predicted from a consideration of bond energies from Walsh's point of view. This kind of reasoning can of course only be semi-quantitative, but it is possible by using it to suggest further properties for investigation and to predict the results of certain measurements. It has the disadvantage that it is not rigorous, and that unless the data used are completely reliable, which is unfortunately very often not the case, it is possible to be led astray.

A further point in connection with this sort of reasoning about bond energies has been made by Long[317]. According to him, 'logically' these bond energy terms would not be expected to be related to other bond properties directly, because of their implicit inclusion of changes of valence state. Properly speaking, his E_i, or intrinsic bond energies (*see* Section 6.1.2), are the quantities which should be related. Long believes that such correlations of information about bond properties should in fact give information towards establishing intrinsic bond energies and valence states. This implies that if a bond energy term lies off a curve connecting, say, bond energy and force constant, the difference is to be ascribed to a change in valence state. This is in line with Pauling's[384] suggestion that diatomic molecules should normally dissociate along a Morse curve and give a linear Birge-Sponer extrapolation if they dissociate to their valence state. The discrepancy between the linear Birge-Sponer extrapolation and the experimental dissociation energy is to be ascribed to the difference between the energy of the valence state and the pure atomic state to which it actually dissociates because of the impossibility of the independent existence of the valence state of the free atom. These suggestions have the drawback that the introduction of ill-defined atomic energy states introduces yet another parameter into the description of a bond. The number of parameters required to define the bonds in a molecule of any complexity is so great, however (quantum numbers for all the electrons, for example), that the introduction of one and only one arbitrary paramenter to a set very much smaller than the total number rigorously required can never be logically necessary, and must be judged on grounds of convenience.

Attempts have been made to show that apparent deviations from constancy are not due to 'chemical' causes, but are due to the presence in the usual bond energy sum of purely thermal effects. Dewar[109], for example, suggested that there should be systematic

discrepancies between calculated heats of atomization for open chain and cyclic compounds using bond energy terms deduced from the former. These discrepancies would be due to the internal kinetic energy in the usual bond energy terms, since there should be systematic differences between the internal kinetic energy of open chain and cyclic compounds. In particular, he pointed to the 'discrepancy' between the 'observed resonance energy' of benzene obtained by the Pauling method of comparing heats of atomization with bond energy sums, and by the Kistiakowsky method from the heat of hydrogenation of *cyclo*hexene. It has been shown[98] that this is not so, and that the 'discrepancy' disappeared if $E(C{=}C)$ were obtained from an olefine with the double bond in the middle of the chain as was, in effect, done in the hydrogenation comparison. This point is more fully covered in Section 6.1.2. Another suggestion has been that lack of constancy is purely caused by repulsions between non-bonded atoms and by zero-point energies[107], but this appears not to be so[92].

These methods of discussing failure of the constancy assumption all lack precision. A determined effort to clarify the logical status of bond energy terms has recently been made by Szwarc and Evans[500]. They recognize that atomization of a molecule directly is not in general a physically realizable process, and set themselves the problem of finding a purely formal description of atomization according to which the heat of atomization can be regarded as the sum of a set of bond energy terms, each defined unambiguously only by the properties of the molecule concerned.

This programme requires a complete knowledge of the interatomic forces in the molecule which can only formally be assumed to be available, but it does result in a clear description of the process. They consider a molecule of m atoms linked by n bonds. The relative positions of the atoms in the molecule can be described by $3m-6$ independent coordinates, in the general case of a non-linear molecule. Let these coordinates be the n bond lengths $r_1, r_2, \ldots r_n$ and let the remaining $3m-n-6$ coordinates, $\alpha_1 \ldots \alpha_{3m-n-6}$ be functions of angles only. Thus a change in r_k corresponds to a change in the length of the kth bond, and a change in α corresponds to bending, twisting *etc.* Now the energy of the molecule, E, will be given by $E(r_1 \ldots r_n, \alpha_1 \ldots \alpha_{3m-n-6})$ and we will take $E(\infty)$, the energy of the infinitely separated atoms, as zero. Then we have

$$\mathrm{d}E = \sum_{1}^{n} \frac{\partial E}{\partial r_k}\mathrm{d}r_k + \sum_{1}^{3m-n-6} \frac{\partial E}{\partial \alpha_i}\mathrm{d}\alpha_i$$

The variation of E caused by bond stretching only is of course

$$\delta E = \sum \frac{\partial E}{\partial r_k} \mathrm{d}r_k$$

and consequently the heat of atomization, Q_a, is given by

$$Q_a = \sum_{1}^{n} \int_{r_{k_0}}^{\infty} \frac{\partial E}{\partial r_k} \cdot \mathrm{d}r_k, \qquad \ldots . \quad (6.1.3.1)$$

where the path of integration is on the surface determined by the $3m - n - 6$ equations $\alpha_i = \alpha_{i_0}$. The zero subscripts refer to the values of the coordinates in the original molecule. This equation simply implies that the atomization process can be regarded as one of stretching all the bonds to infinity. We now define the integration path exactly by specifying the further n equations, $r_k = \gamma r_{k_0}$ where γ is a variable which changes from 1 to ∞. This implies that the path is one along which all bond lengths change proportionately. Thus the value of every term in the set of integrals in equation 6.1.3.1 is now defined, and Szwarc and Evans suggest as a definition of 'average' bond energy, for the kth bond $\bar{q}_{ak}$, the value of the integral

$$\bar{q}_{ak} = \int_{r_{k_{0_L}}}^{\infty} \frac{\partial E}{\partial r_k} \cdot \mathrm{d}r_k \qquad \ldots . \quad (6.1.3.2)$$

where L denotes the particular integration path defined above. These $\bar{q}_a$ have the following properties:

1. $\sum_k \bar{q}_{ak} = Q_a$.
2. $\bar{q}_{ak}$ and $\bar{q}_{ai}$ for any two bonds k and i which are indistinguishable in the molecule are equal.
3. For a molecule containing n indistinguishable bonds only, $\bar{q}_a = (1/n) \cdot Q_a$.

These properties are common to all definitions of bond energy terms. The advantage of the present scheme is that the $\bar{q}_a$ in any molecule are defined rigorously by the properties of that molecule only. The definition does not imply constancy of bond energy terms from molecule to molecule. These $\bar{q}_a$ 'can be visualized as the work done to stretch two bonded atoms from their original position in a molecule to an infinite distance, while at the same time

the whole molecule swells infinitely without losing its original shape.'

These authors then proceed to discuss bond dissociation energy in similar terms and, as the comparison is instructive, we continue to follow them here. The dissociation energy of a bond k is given by

$$D = \int_{r_{k_0 P}}^{\infty} \frac{dE}{dr_k} dr_k \qquad \ldots . \quad (6.1.3.3)$$

where

$$\frac{dE}{dr_k} = \frac{\partial E}{\partial r_k} + \sum{}' \frac{\partial E}{\partial r_i} \cdot \frac{dr_i}{dr_k} + \sum \frac{\partial E}{\partial a_j} \frac{da_j}{dr_k} \qquad \ldots . \quad (6.1.3.4)$$

the primed summation sign indicating the omission of the term, $i = k$. In the integral for D, the symbol P represents the reaction path of the dissociation reaction, which may be formally defined as follows: For every fixed r_k, the other parameters are given by $\frac{\partial E}{\partial r_i} = 0$ for $i \neq k$, $\frac{\partial E}{\partial a_j} = 0$, all j. This is a statement of the requirement that the rest of the system adjusts itself to the configuration of minimum energy throughout the change in r_k. Thus the distinction between $\bar{q}_a$ and D is seen to lie essentially in the reaction path, the path P being a natural and in principle an observable one, the path L being an unnatural one corresponding to a purely imaginary process. For a diatomic molecule, where there is only one coordinate, the interatomic distance r, the two paths are identical. Using equations 6.1.3.3 and 6.1.3.4 we may write

$$D = \int_{r_{k_0 P}}^{\infty} \frac{\partial E}{\partial r_k} \cdot dr_k + \int_{r_{k_0 P}}^{\infty} A \cdot dr_k \qquad \ldots . \quad (6.1.3.5)$$

where A is the last two terms of the right-hand side of equation 6.1.3.4. Here the first term represents the part of the dissociation energy due simply to the dissociation of the kth bond, and the second term represents the part due to the concomitant changes in the configuration of the rest of the molecule. This term represents the entity called by Long and Norrish[318] the 'reorganization energy'. Szwarc and Evans hazard the guess that the first term may represent Walsh's 'bond energy' as discussed earlier in this section. Another possible way of considering the bond energy would be as the energy required to break a bond while the rest of the molecule

is retained in the configuration of the initial state, and here the 'reorganization energy' would be the work performed in transforming the radical from the initial state to that in which it actually exists. The former quantity is represented by the integral

$$\int_{r_{k_0 C'}}^{\infty} \frac{\partial E}{\partial r_k} \cdot \mathrm{d}r_k \qquad \ldots . \quad (6.1.3.6)$$

where C is an integration path defined by $r_i = r_{i_0} = \text{const.}\ i \neq k$, $\alpha_j = \alpha_{j_0} = \text{const.}$ all j. It is pointed out that neither of these last definitions of bond energy leads to the heat of atomization being given by the bond energy sum.

As the application of this treatment depends on a knowledge of the function $E(r, \alpha)$, which depends on the nature of the molecular force field, it is relevant next to enquire whether any simple force field leads to a simplification of the results. A good first approximation to the molecular force field is the simple valence force field (*see* Linnett[310]). This approximation implies that $\partial E/\partial r_k$ for all r_k and $\partial E/\partial \alpha_j$ for all α_j are functions only of one r_k or α_j respectively. Then $\int_{r_{k_0}}^{\infty} (\partial E/\partial r_k)\mathrm{d}r_k$ must be independent of the integration path. This implies that in simple valence force field the average bond energy is equal to the dissociation energy of the bond and to the entities defined by equation 6.1.3.5 or 6.1.3.6, or more simply, that the distinction between bond energy term and bond dissociation energy in a polyatomic molecule disappears if we assume that a change in one bond can occur independently of any change in any of the others. Szwarc and Evans go on to say: 'It thus becomes evident that the identification of the average bond energy with the dissociation energy of the bond, so generally accepted in the early days of the theory, arose from the belief that the molecular force field is represented by the simple valence force field.' As it stands this statement is not true, since it implies a process of conscious reasoning on the part of those who identified bond and dissociation energies based on the assumption of a special molecular force field, and there is no reason to suppose that such a process took place. The identification probably arose from the habit of neglecting interactions between non-bonded atoms, and thus tending to treat bonds in polyatomic molecules as entities as distinct as bonds in diatomic molecules. It is of course true to say that this treatment implies a molecular force field of this form.

This result of Szwarc and Evans is formally correct, but in view

of the usual context in which molecular force fields are discussed it is perhaps a little misleading. In the first place it carries the suggestion, admittedly not rigorously, that the assumption of the constancy of bond energies and their approximate equality to dissociation energies is as good or as bad an approximation as that of simple valence force field. We have, however, seen that the assumption of constancy of bond energies from molecule to molecule in the chlorinated methanes is completely justified within the experimental error, whereas it is known that although the simple valence force field judged by its success in representing molecular vibrations is a good approximation for methane it is a poor one for carbon tetrachloride. Further, molecular force fields are usually judged by their ability to describe molecular vibrations, where the movement of the atoms from their equilibrium positions is so small that the motion can usually be taken to be simple harmonic, whereas the conditions under which Szwarc and Evans require knowledge of the molecular force field are over the entire range of internuclear distance from the equilibrium position to infinity.

This leads us to a discussion in general of the usefulness of Szwarc and Evans's treatment as applied to actual molecules. The treatment requires a knowledge of the molecular force field over a range of values of the coordinates, that is to say, a specification of the energy surface representing the ground electronic state of the molecule. This is only available very approximately for a few three-atom systems, and not at all for bigger molecules. Thus the average bond energies they propose, although logically unassailable, are practically unobtainable. This does not detract from the value of their contribution, which shows that average bond energies as practically used must be vaguely defined entities. They indeed suggest that attention should be directed mainly to bond dissociation energies, and to heats of atomization, both of which can be measured.

Another attempt to give a more complete treatment of the bond energy concept has been made by Glockler [177]. This introduces explicitly the effect of neighbouring atoms on bond strength, and considers the atomization to take place in two stages, the alteration of the bond to its length in the corresponding diatomic radical and its subsequent dissociation. This scheme is not a fundamental attempt to produce a logical description of bond energies in a given molecule, as was that of Szwarc and Evans, but is concerned to make explicit some of the effects considered to be operative in determining bond strength. Numerical values for these effects are to be obtained empirically in the usual way. The present author

doubts the value of such a scheme, because it can never be rigorous, and it merely introduces a vast amount of complexity into a concept which in its earlier treatment by Pauling and others had the merit of simplicity if not of rigour. Furthermore, to remove extraneous thermal influences, as we have already seen, it is necessary to obtain chemical binding energies, which immediately restricts the number of molecules which can be discussed. Whereas it has been shown that the inclusion of thermal energy in ordinary bond energy terms appears to have no adverse effect on any conclusions which may be drawn from them, it does not follow that this will be so on a closer analysis. For example, it can be shown that the 'substitution effect' in olefines, which can be represented as an apparent variation of $E(C{=}C)$ depending on its position in the molecule, persists when binding energy alone is considered. If here we are concerned with deviations from constancy to a first approximation, the situation is satisfactory. But the proportion of the bond energy that the apparent variation represents changes when binding energy terms rather than bond energy terms are considered. For example the percentage of the effect due to change in zero point energy is about 20 for some isomers of l-butene [92].

Thus for the purposes of this book bond energy terms will be defined as entities the sum of which gives the heat of atomization at 298·16° K, and which are derived primarily from MX_n molecules.

6.2. DETERMINATION OF BOND ENERGY TERMS

If the definition given at the end of Section 6.1.3 is accepted, the determination of bond energy terms is straightforward enough until we are confronted with a breakdown of the constancy assumption. The information we require is simply the heat of formation of the molecule in the ideal gas state from its elements in their standard states, *i.e.* $\Delta H_f^\circ(g)_{298\cdot16^\circ K}$. This is ΔH for the reaction

$$\frac{l}{p}A_p + \frac{m}{q}B_q + \frac{n}{r}C_r \ldots \rightarrow A_lB_mC_n \ldots (g) \quad \ldots . \quad (6.2.1)$$

where A_p *etc.* are the elements in their standard states. We further require the heats of formation of the monatomic gaseous elements from the elements in their standard states, *i.e.* $\Delta H_f^\circ(g)$ for the atomic elements, which is ΔH for the reactions

$$\frac{l}{p}A_p \rightarrow A(g) \text{ } etc. \quad \ldots . \quad (6.2.2)$$

ΔH for the atomization is then $-\Delta H(6.2.1) + \Sigma\Delta H(6.2.2)$ the latter term being summed over all the atoms in the molecule, and is a positive quantity. The heat of formation from atoms, Q_a, is also often expressed as a positive quantity on the old thermochemical sign covention. The sum of the bond energies, which are positive quantities, is equal to either of these positive quantities. It may be useful to put these quantities in an energy level diagram (*Figure 6.2.1*). For some compounds such as NO_2 the level of the

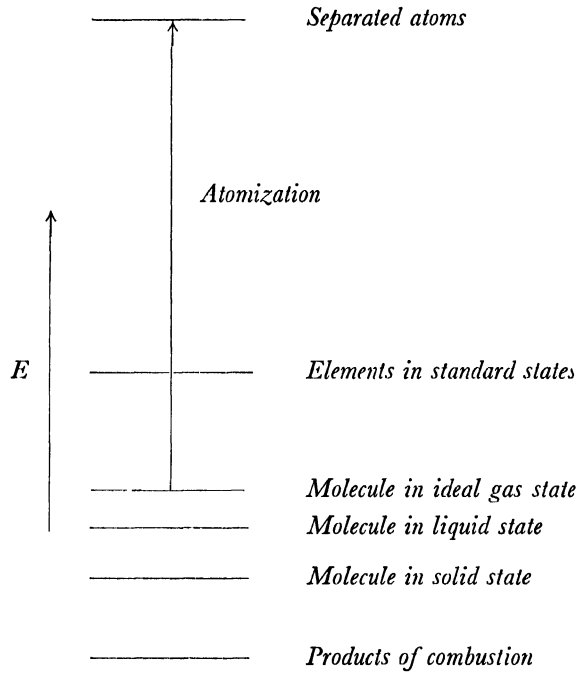


Figure 6.2.1. Energy level diagram

molecule is above that of the atoms in their standard states, but it must always be below that of the free atoms or the molecule will not be stable. Also included in the diagram are the levels of the molecule in the liquid and solid state, which are lower because of the stabilizing effect of the intermolecular forces. The likely level of the combustion products of the molecules is included,

because for most organic compounds the heat of formation is determined from the heat of combustion to products such as carbon dioxide and water whose heats of formation are known. The methods of determining heats of formation and atomization are detailed in the following chapters.

When the heats of atomization of the relevant compounds have been obtained the bond energies are deduced from them using the principles outlined in Section 6.1.3, the chemical intuition of the observer being used to decide which compounds are likely to yield the most widely applicable values of bond energies.

6.3. USES OF BOND ENERGY TERMS

6.3.1. *In Theoretical Chemistry*

If the concept of constant bond energy terms is correct, the heat of formation of a molecule calculated using them should be equal to its observed heat of formation. If this is true for most molecules, it may be considered that there is something abnormal about a molecule for which it is not true, and that the energy of such a molecule requires some special explanation.

It is usually found that where there is a large difference between the calculated and the observed values of heats of formation, the calculated value of $-\Delta H_f$ is less than the observed; that is, the actual molecule is more stable than the hypothetical molecule consisting of normal bonds. This difference has been ascribed to stabilization by 'resonance' between a variety of valence bond structures, and is sometimes known as the 'observed' or 'empirical' resonance energy. The concept of resonance is derived from a procedure used for obtaining approximate solutions of the wave equation. Its use is therefore a matter of convenience rather than theoretical necessity. Moreover it is often applied to systems of such complexity that no question of even an approximate solution of the wave equation arises; in these cases its status is therefore that of an empirically used concept similar to the earlier notion of 'mesomerism'.

In the hands of Pauling this treatment has been successful in correlating many facts in terms of a number of possible structural formulae, and it has been widely developed by Wheland and many others. Sometimes the valence bond structures between which resonance is considered to take place are natural and plausible, such as the two Kekulé forms of benzene; on other occasions it is necessary to postulate less plausible structures of high energy such as the ionic forms of carbon dioxide (*see* Long[316]). The

explanation of observed resonance energies has been a major preoccupation of theoretical chemistry in the past twenty years, and a discussion of the theory is outside the scope of this book.

A useful feature of the observed resonance energy is that it is independent of the heats of atomization used. Glockler[179], for example, notes this for benzene in a recent discussion of resonance energies.

Deviations from the expected ΔH_f in the opposite sense admit of other special explanations, such as steric strain. Discussion of this is outside the scope of this book; reference may be made, for example, to the treatment of steric strain in P_4 by Pauling and Simonetta[386].

6.3.2. *In Thermochemistry*

It is useful to be able to predict the heats of formation of compounds. This cannot be done theoretically, so some empirical procedure is needed; one such is given by Kharasch[262]. Another is the use of bond energy terms for the purpose. Provided they are used with discretion good results can be obtained. This proviso is due to the fact that various specific effects, particularly that known as resonance, can cause the true heat of formation to differ from that given by the bond energy sum. This deviation is usually characteristic of particular chemical groupings, and retains its value throughout a series of molecules. Thus it is necessary when calculating the heat of formation of a compound using bond energy terms to know whether there is likely to be any resonance energy, and, if so, how much. It is also necessary to know whether there is likely to be any other effect causing deviation from additivity.

An extensive list of observed resonance energies is given by Pauling and Sherman[385], and a slightly shorter list is given in Pauling's book[382]. Using these lists and the bond energy terms given it is usually possible to predict heats of formation of organic compounds at least to within a few kcal.

A further deviation from additivity which should be taken account of is the substitution effect, or increase of stability on substitution in hydrocarbons, mentioned in Section 10.6.6. This, for example, causes the observed resonance energy to be greater in toluene and the xylenes than in benzene.

Since the main interest in this book is in the strengths of the bonds themselves, it is not intended to give a detailed account of the estimation of the heats of formation of organic compounds.

7

HEATS OF FORMATION OF ORGANIC COMPOUNDS

7.1. HEATS OF COMBUSTION OF ORGANIC COMPOUNDS CONTAINING CARBON, HYDROGEN, AND OXYGEN

THE most widely applicable method of determining the heat of formation of an organic compound is to determine its heat of combustion. This is essentially a determination of its heat content relative to compounds of very accurately known heat of formation. From this by application of Hess's law, the heat of formation of the compound of interest is obtained. Conventionally, the heat of combustion is defined as the change of heat content per mole, ΔH_R° when the compound reacts with oxygen in its standard state to form gaseous carbon dioxide at one atmosphere and liquid water at 298·16° K(25° C), and with the formation of other products in their standard states, discussed in Section 7.2, if elements other than carbon hydrogen and oxygen are present. This process is not exactly realizable in practice but ΔH_R° can be derived very precisely from a knowledge of the heat evolved when the substance is burned in oxygen under pressure in the calorimetric bomb (*see*, for example, Sturtevant[483]). The heats of formation of carbon dioxide and water from the elements in their standard states have been determined very accurately by the National Bureau of Standards in Washington, the following values being obtained[543]:

$$H_2(g, 1\text{ atm}) + \tfrac{1}{2}O_2(g, 1\text{ atm}) = H_2O(l)$$
$$\Delta H^\circ_{298\cdot16^\circ K} = -68{,}317\cdot4 \pm 9\cdot6 \text{ cal mole}^{-1}$$
$$C(\text{graphite}) + O_2(g, 1\text{ atm}) = CO_2(g, 1\text{ atm})$$
$$\Delta H^\circ_{298\cdot16^\circ K} = -94{,}051\cdot8 \pm 10\cdot8 \text{ cal mole}^{-1}$$

where 1 cal$\equiv$4·1833 J int.$\equiv$4·1840 J abs.

We now discuss the probable accuracy of measurements of heats of combustion in the bomb calorimeter. In general, we shall not be concerned with details of the calorimetric technique, which are to be found in the references cited, but in the accuracy actually obtained. We shall deduce this chiefly from a comparison of

results obtained by different investigators using differences in technique. For general purposes of obtaining bond energy terms, very high accuracy is not required. For example, the heat of combustion of a saturated carbon compound containing about six carbon atoms is about 1,000 kcal mole^{-1}. This compound may contain about eighteen bonds so that in a favourable case to obtain these to 1 kcal we may tolerate an error of about 1 per cent in the heat of combustion. However, if we assume that seventeen of these bond energy terms are accurately known, that the bond energy terms are all of about the same magnitude, and that we require to know the eighteenth to 1 kcal, or about $1\frac{1}{2}$ per cent, we require to know the heat of combustion to 1 kcal mole^{-1}. Since in general the constancy assumption is good enough to give heats of formation to within 2–3 kcal, it is clear that we require to know heats of combustion to slightly better than this limit. The percentage accuracy to which we require the heat of combustion will vary with molecular weight and constitution, but for the imaginary compound cited we need an accuracy of about 0·1- 0·2 per cent. If we intend to discuss fine differences we shall require greater accuracy than this, but in view of the vagueness of the bond energy term concept itself, it is doubtful whether such discussions, at least if carried out with reference to bond energy terms rather than to heats of atomization of the whole molecule, are very profitable.

In general chemistry, in particular in discussion of isomerization equilibria, we may well require accuracy a good deal higher than this. Our only information about heats of isomerization of 1 or 2 kcal mole^{-1} may well come from combustion experiments where the total heat quantities measured are perhaps some thousands of kcal mole^{-1}. At present the greatest accuracy normally attained is about $\pm 0{\cdot}02$ per cent, but Parks[379] has pointed out that inaccuracies in thermal data have such a large effect on equilibrium constants that a tenfold improvement in accuracy is desirable. Thus it would appear that modern calorimetric technique is setting out to satisfy more strenuous demands than are made on it by the requirements of knowing bond energy terms.

The knowledge of isomerization equilibria is particularly important in hydrocarbon chemistry, and this is reflected in the body of very accurate measurements of heats of combustion of hydrocarbons which has become available since 1939. The spate of results has been such that determinations of the heats of combustion of various compounds have been replicated in several laboratories, and it is of interest to compare their results. The heats of combustion of several *cyclo*paraffins, for example, have been deter-

mined using advanced techniques and comparative results are given in *Table 7.1.1.*

The results are in very good agreement. For *cyclo*hexane all four sets of investigators obtained a result within 0·2 kcal mole^{-1} of the mean, or within 0·02 per cent, which amply confirms the claimed accuracy of ±0·02 per cent. It is noteworthy, too, that while investigators *a*, *c*, and *d* used approximately the same calorimetric technique, *b* used one which differed in important respects. The Amsterdam workers, *b*, used a Beckmann thermometer to measure the temperature rise and measured the amount of combustion by

Table 7.1.1. Heats of combustion, $-\Delta H_R(l)$ *at* 25° C, *for* cyclo*paraffins* (kcal mole^{-1}; *all results corrected to same energy units*)

Investigators	(*a*) *Johnson, Prosen and Rossini*[252]	(*b*) *Kaarsemaker and Coops*[256]	(*c*) *Spitzer and Huffman*[461]	(*d*) *Moore, Renquist, and Parks*[353]
cyclo*pentane*	786·5	786·7	786·6	—
methyl cyclo*pentane*	941·1	—	—	940·7
cyclo*hexane*	936·9	936 6	936·5	936·7
methyl cyclo*hexane*	1091·1	—	—	1090·7
ethyl cyclo*pentane*	1097·5	—	—	1096·8
cyclo*heptane*	—	1098·9	1099·1	—
cyclo*octane*	—	1258·5	1258·4	—

knowing the weight of substance put into the calorimeter and checking combustion to be complete by testing for carbon monoxide. On the other hand, *a*, the National Bureau of Standards, used a platinum resistance thermometer and measured the amount of combustion by measuring the amount of carbon dioxide formed.

A more detailed comparison of the results of the National Bureau of Standards with those from the Amsterdam calorimeter is given in *Table 7.1.2*, which contains results for some benzene derivatives and for 2, 2, 3-trimethylbutane. Although the agreement for one or two of the compounds is not so strikingly good as in *Table 7.1.1* the results for benzene agree to 0·2 kcal mole^{-1} or less than 0·025 per cent, and the results for ethylbenzene, the worst in the table, differ by 0·8 kcal mole^{-1} in about 1,000 kcal, an error which, though outside that claimed, is still not very large, and is below that which would cause any difficulty in the determination of bond energy terms.

One general feature of the calorimetric technique which reduces the likelihood of a systematic error is that the energy equivalent of the calorimeter is not found by direct electrical calibration but by

measuring the heat of combustion under bomb conditions of a standard substance, usually benzoic acid, the heat of combustion of which has been determined very accurately. The heat of combustion, under the bomb conditions specified by Washburn (for a definition of which see the literature cited), of benzoic acid, q_B at 25° C is given by Jessup[250a] as 26,428·4 int. J/g (vac.) or 6317·6 cal/g. Jessup also gives the correction to be applied to heats of combustion determined using the previous 'best' value[250b]. Values given in this chapter have been corrected as far as possible to take account of this.

Table 7.1.2. Heats of combustion, $-\Delta H_R$ *at* 25° C, *for some hydrocarbons* (kcal mole^{-1})

	N.B.S.	*Amsterdam*
Benzene (1)	781·0[404]	780·8[89]
Toluene (1)	934·5	934·1
Ethyl benzene (1)	1,091·0	1,090 2
o-*Xylene* (1)	1,088·2	1,087·7
m-*Xylene* (1)	1,087·9	1,087·2
p-*Xylene* (1)	1,088·2	1,087·7
2, 2, 3-*trimethylbutane* (1)	1,148·3[406]	1,148·1

It may be taken on the basis of these results that modern combustion calorimetry can obtain results which are usually reproducible from laboratory to laboratory to within 0·02–0·05 per cent. To obtain this precision it is necessary to have the substances concerned very pure; it is probable that differences between the results of different authors are due rather to differences in purity of the samples than to defects of calorimetric technique. This is illustrated by the results given in *Table 7.1.3* for some polynuclear aromatic hydrocarbons, where the agreement is much less satisfactory, presumably for this reason. Bender and Farber[32] attribute their high results to superior purity of sample, and point out that the most carefully purified materials used in previous work were those of Fries *et al.*[163] with whom they are nearly in agreement. Magnus *et al.*[337] also obtain high results, presumably for the same reason. Again there are differences in calorimetric technique. The calorimeter used by Magnus *et al.* is of interest, the measurement being made of the change in temperature between a metal block containing the combustion bomb and another metal block of the same size, using thermocouples[336]. The technique is claimed to be very accurate, the standard deviation of a single measurement being 0·012 per cent.

Only a relatively small proportion of the data available in the literature is of such high precision. There are three types of calorimetric information available: the modern high precision work, older work done before high precision work was undertaken, and modern work carried out for some reason to a lower standard of precision. A vast amount of thermochemical work was carried

Table 7.1.3. Heats of combustion, $-\Delta H_R$ at 25° C, for some polynuclear aromatic compounds

Anthracene(s)	*Phenanthrene(s)*	*Dibenzyl(s)*	*Triphenylmethane(s)*
1,689·5[337]	1,684·6[337]	—	—
1,685·2[418]	1,675·4[418]	—	—
1,683·8[380]	—	1,805·5[380]	2,372·2[380]
1,687·1[32]	1,685·3[32]	1,806·2[89]	2,374·2[89]
1,688·9[32]	—	—	—
1,688·2[163]	1,683·1[163]	—	—

out at the end of the nineteenth century. Part of it has been tabulated and discussed by Kharasch[262] together with more recent work, in a very valuable compilation of heats of combustion. An idea of the general reliability of the earlier data is provided by *Table 7.1.4*, taken from Prosen, Gilmont and Rossini[404] comparing results on the heat of combustion of benzene with that obtained using the high precision calorimeter at the National Bureau of Standards, which is itself compared with the recent Amsterdam result in *Table 7.1.2*, and shown to agree closely. The values have been corrected by these authors to the same energy units, and the uncertainty limits of the deviations have also been assigned by them. The root mean square deviation is 2·0 kcal mole^{-1}, or 0·25 per cent. Although this is ten times the difference between the results for benzene given in *Table 7.1.2* it is still not very large compared with the standard of accuracy required in bond energy term determinations. These results suggest that the older determinations of heats of combustion are probably sufficiently accurate for our purposes, provided there is no reason for doubting the purity of the compound.

There are relatively few modern determinations of the heats of combustion of organic compounds containing carbon, hydrogen, and oxygen only which have not been carried out to high precision standards. The advent of fairly accurate commercially available combustion calorimeters for determining the calorific value of fuels such as the Griffin-Sutton bomb calorimeter[489] has meant that very many laboratories are now equipped to do combustions of

moderate precision. Some work towards the derivation of bond energy terms has been done using such instruments. Usually, however, these researches have been concerned with organic compounds containing elements other than hydrogen and oxygen only, because here such high precision is not always attainable even in the best calorimeters.

Table 7.1.4. Heat of combustion of benzene $-\Delta H_R(1)$ *at* 25° C *as obtained by various investigators compared with the value* 781·0 kcal mole^{-1} *obtained by the National Bureau of Standards* (1945)*

Investigator	*Date*	*Deviation from N.B.S. result* (kcal)	*Estimated uncertainty of deviation*
*Berthelot**	1878	−3·8	±3·9
Stohmann et al.	1886	0·0	±1·6
Stohmann et al.	1889	−0·6	±1·6
Richards et al.	1907	−2·5	±1·6
Richards et al.	1910	+1·5	±1·6
Roth et al.	1915	+2·1	±1·6
Richards et al.	1915	−0·2	±1·6
Richards et al.	1920	+1·9	±1·6

* References given by Prosen *et al.*[404]

7.2. HEATS OF COMBUSTION OF ORGANIC COMPOUNDS CONTAINING OTHER ELEMENTS

7.2.1. *Nitrogen*

The combustion of a nitrogen-containing organic substance in the bomb calorimeter gives carbon dioxide, water, nitrogen gas, and a little nitric acid. Heats of combustion are referred to the first three compounds, and a correction is applied to the observed figure to take account of the nitric acid, which is determined by titrating the washing from the bomb with standard alkali. For all compounds, in accurate work, a correction is always necessary for nitric acid formation; this may in CHO compounds be due to nitrogen in the oxygen used for combustion and in nitrogen-containing compounds of course to this and to the compound itself. Huffman[233] reports that with CHO compounds the correction is usually less than 1 cal in several thousand, whereas with nitrogen-containing compounds it may become as high as 0·6 per cent of the total heat evolved in the calorimeter.

The accuracy attainable in combustion of nitrogen-containing compounds is no less than that already discussed for CHO compounds, if the most advanced techniques are used. An example is hippuric acid, the use of which as a secondary standard in the com-

bustion calorimetry of nitrogen-containing compounds was proposed by Huffman[233]. He determined ΔH_R at 25° C to be −1007·8 kcal, which, corrected to the revised value for the energy equivalent of benzoic acid, becomes −1008·2 kcal. The determination was repeated some thirteen years later by Cole and Gilbert[81], who obtained −1008·3 kcal, a result differing by only 0·01 per cent.

Older work has similar accuracy to that discussed for CHO compounds, and a fair amount of modern work not of the highest precision is available. Some examples of the situation are given below. For *p*-nitraniline, Cole and Gilbert[81] give 759·34 kcal mole^{-1} for $-\Delta H_R$, whereas the value quoted by Kharasch[262] in his 1929 compilation is 761·0 kcal, differing by less than 0·25 per cent. Typical precision attained by modern work in the Griffin-Sutton bomb calorimeter is shown by that quoted by Coates and Sutton[80], who standardized their bomb with benzoic acid and obtained a value of hippuric acid 0·15 per cent greater than that of Huffman[233].

Once again differences in purity are likely to be an important cause of differences in recorded heats of combustion. For example, Cottrell and Gill[93] obtained for aniline nitrate $\Delta H_R = -795 \pm 1{\cdot}2$ kcal mole^{-1}, whereas Willis[571] obtained $-787{\cdot}9 \pm 0{\cdot}7$ kcal for the same compound, the discrepancy between the two results being 0·9 per cent. Another example of a larger discrepancy than might be desired is in the heat of combustion of nitromethane. This compound does not present any of the difficulties in purification which are shown by the amine nitrates, and the discrepancy is more difficult to explain. Holcomb and Dorsey[227] measured the heats of combustion of several nitroparaffins and obtained for liquid nitromethane $-\Delta H_R$ at 20° C $175{\cdot}25 \pm 0{\cdot}18$ kcal mole^{-1}. Three previous determinations are quoted by Bichowsky and Rossini[38]. Thomsen[523] measured the heat of combustion of gaseous nitromethane, while Berthelot and Matignon[35] and Swientoslawski[490] measured that of liquid nitromethane. Their respective results lead to the following values of the heat of combustion $(-\Delta H_R)$ of liquid nitromethane: 171·7, 169·4, 169·8 kcal mole^{-1}. Thus Holcomb and Dorsey's result is 5 kcal or 3 per cent higher than the mean of those of previous investigators, who are themselves in quite good agreement. On the other hand Holcomb and Dorsey's results for nitroethane and nitropropane are in fairly good agreement with the earlier work. Here the question arises of whether the investigator is to choose the mean of three not very precise but concordant results or one modern precise result which differs appreciably from the others. This case is of some interest in the

interpretation of the kinetics of the thermal decomposition of nitromethane. Cottrell, Graham, and Reid[94] found the activation energy for this reaction to be 53·6 kcal, in agreement with the estimate of ~53 kcal for $D(CH_3-NO_2)$ which may be made using Holcomb and Dorsey's value for the heat of formation of nitromethane. Hillenbrand and Kilpatrick[221] found an activation energy of 50 kcal, which is still just compatible, taking into account experimental error, with the view that the reaction rate is determined by C–N bond fission. However, if the older work is correct, $D(CH_3-NO_2)$ is about 58 kcal, and since the activation energy of the reaction is certainly not as high as this, the reaction can no longer be interpreted as simple bond fission, and Hillenbrand and Kilpatrick's suggestion that the mechanism involves an intramolecular rearrangement becomes compelling.

Difficulty is of course also met with in compounds which are hygroscopic or which have high vapour pressures, such as the aliphatic amines. For example, for gaseous methylamine, Bichowsky and Rossini[38] quote values of 258·1 and 261·4 kcal for $-\Delta H_R$, and the higher value is supported by heat of combustion of methylamine nitrate, which leads to 262·0 ± 1·5 kcal for methylamine[93].

The way is clearly open for further accurate work on heats of combustion of nitrogen-containing compounds.

7.2.2. *Sulphur*

The combustion in the bomb calorimeter of organic compounds containing sulphur leads to the formation of sulphuric acid, but for quantitative conversion the conditions must be carefully controlled. Huffman and Ellis[234] state that complete combustion of sulphur to SO_3 and hence formation of sulphuric acid only takes place in the presence of nitrogen. Accordingly in their determination of the heats of combustion of sulphur-containing compounds an atmosphere of air was left in the bomb to supply the necessary nitrogen. The large heat of dilution of sulphuric acid (approximately 3 kcal are evolved in the reaction $H_2SO_4 . H_2O + H_2O \rightarrow H_2SO_4 . 2H_2O$) makes it necessary to know accurately the concentration of sulphuric acid formed in the bomb. Huffman and Ellis found that when water was introduced into the bomb before a combustion there was a large difference in the concentration of the solution in the bottom of the bomb and the condensate on the walls. For this reason they did not introduce water into the bomb in their accurate experiments. They also found that nitrogen appeared in the products both as nitrous and nitric acid; these had to be determined and

corrected for. They determined the heats of combustion of cystin and cystein.

It is usual now for American workers to quote the heat of combustion of sulphur compounds to form H_2SO_4 1·7 H_2O, the heat of formation of which ($\Delta H^{\circ}_{298\cdot16^{\circ}K}$) from rhombic sulphur, liquid water and oxygen gas at one atmosphere is $-135{\cdot}010$ kcal mole^{-1} (*see* work of Moore, Renquist, and Parks [353]). With careful attention to these points, modern determinations of heats of combustion of sulphur compounds can be very precise. For example, Moore, Renquist, and Parks obtained $-\Delta H_R$ for thiophen as 667·4 kcal, and a more recent determination in a different laboratory gave 667·2, in excellent agreement [541]. The value given in Kharasch's compilation [262] is 670·5 kcal, differing by 0·5 per cent. Kharasch points out that many of the older determinations of the heat of combustion of sulphur compounds cannot be used for calculating reliable heats of formation, because the amount of water added to the bomb is not always specified and hence the dilution of the sulphuric acid is not known.

Sunner [486] doubts whether the technique of Huffman and Ellis [234] of putting no water in the bomb originally is sufficient to ensure a uniform concentration of sulphuric acid in the products, and prefers to use a 'moving bomb' calorimeter in which the bomb is rotated so that the liquid initially placed in the bomb washes the whole internal surface of the bomb after the ignition. This certainly achieves the object of a uniform concentration, but leads to considerable mechanical difficulties. These difficulties have been surmounted and a test of the accuracy of the moving bomb calorimeter using paraffin oil has shown that it is possible to reproduce values of heats of combustion in two different calorimeters to within 0·01 per cent. This accuracy is comparable with the best attainable in stationary calorimeters [488]. Sunner [486] compared his results for cystin and cystein with those of Huffman and Ellis [234] and found those of the latter to be 0·4 per cent low. It is not certain whether the difference between the two sets of results is due to the differences in calorimetric technique or to differences in purity of the samples.

Becker and Roth [29] have also burned these substances, obtaining results much lower than those just mentioned; Sunner suggests this may be because they burned other allotropic modifications of these compounds. Their determination of the heat of combustion of thiourea, on the other hand, agrees with that of Sunner to 0·1 per cent. The basis for comparison used by Sunner throughout is conversion of the sulphur to H_2SO_4 . 10,000 H_2O.

The dilution of the sulphuric acid in the moving-bomb experiments was achieved by having water present to the extent of about 10 per cent of the bomb volume, or later about 3 per cent. The corrections for the solubility of carbon dioxide in this liquid have been determined. Becker and Roth [29] on the other hand, corrected for variations in sulphuric acid concentration in the bomb.

Further work on the heats of combustion of sulphur compounds is being actively pursued both in the United States and in Sweden [487, 538, 539].

7.2.3. *Halogens*

The chief difficulties in the combustion calorimetry of halogen compounds are to obtain the products in a clearly defined state, and to ensure complete combustion. The latter difficulty is not surprising, because for the lower highly halogenated paraffins, for example, one is trying to burn liquids commonly used as fire extinguishers! For chlorocompounds and bromocompounds the attempt is usually made to obtain the halogen after combustion as the aqueous hydrogen halide, but unless special precautions are taken, the usual product in the bomb calorimeter is a mixture of the free halogen and the hydrogen halide. Berthelot found that the introduction of an aqueous solution of As_2O_3 into the bomb before the combustion served completely to reduce the chlorine to hydrochloric acid. This has been questioned by Smith [456], at the University of Lund, who found that the efficacy of this procedure could be increased by moistening a quartz wool coil with arsenious acid solution. In order to obtain complete combustion, Smith found it necessary to burn the halogenated compounds mixed with paraffin oil. The results of this investigation were compared with those of Berthelot, who used bomb calorimetry, and of Thomsen who burned the vapour in his 'universal burner'. Berthelot's values for heats of combustion were much lower, and those of Thomsen were somewhat higher than the new results but generally in much better agreement with them. This is not surprising, because it is probable that in the burner method HCl is the only product. At Lund the heats of combustion of halogenated compounds have also been measured using the moving bomb calorimeter described in Section 7.2.2, which has as its object the complete washing of the inside of the bomb by the liquid placed therein. The results of the two methods were in agreement.

In these experiments in which a large quantity of liquid is initially placed in the bomb, there is a correction to be applied for the heat of solution of carbon dioxide, which may be about 0·1 per

cent. This is not large in view of the usual accuracy with which the heats of combustion of such compounds are obtained, but it is of course ten times greater than the estimated uncertainty of the best work on compounds containing C, H, and O only.

An illustration of the general level of accuracy and reproducibility attained in practice for chlorocompounds may be given by ethyl chloride, which has been burned by Berthelot, Thomsen, and more recently by Casey and Fordham, and for which two independent estimates of the heat of combustion may be obtained by other thermochemical means. Berthelot[34] obtained 334 kcal for $-\Delta H$(combustion) with products of combustion carbon dioxide (g), liquid water, and hydrochloric acid (dil. aq.). Thomsen[523] gives 321·9 kcal for the heat of combustion with gaseous HCl as product, hence 339 kcal with dilute aqueous HCl as product.* Casey and Fordham[71] burned ethyl chloride vapour in an all-glass calorimeter with a large excess of hydrogen to ensure complete combustion, and found the heat of combustion to be $341 \pm 2{\cdot}5$ kcal mole^{-1}, in good agreement with Thomsen's value. When ethyl chloride is burned under these conditions, the chlorine appears entirely as hydrochloric acid. This was shown by bubbling the products directly through water, which was tested for hypochlorite, with negative results. Recently, Lane, Linnett, and Oswin[290] measured the equilibrium constant for the reaction

$$C_2H_4 + HCl \rightleftharpoons C_2H_5Cl$$

as a function of temperature and deduced ΔH to be 17·1 kcal at 298° K. This, combined with the known heats of formation of ethylene and hydrogen chloride, yields $\Delta H_f(C_2H_5Cl; g)$ as $-26{\cdot}7$ kcal, whence $-\Delta H_c = 338$ kcal, in good agreement with the other results. Here we have agreement between modern determinations and those of Thomsen, with Berthelot's result slightly low. The accuracy appears to be about ± 3 kcal, or a little less than 1 per cent, which is good enough for the purpose of deducing bond energy terms but not very good for the deduction of other thermodynamic properties, such as equilibrium constants.

For iodine-containing compounds the position is simpler, solid iodine being the sole product of combustion[429]. The accuracy

* There appears to be a misprint in Thomsen[524], the reference given to his work given by Fordham. Here the heat of combustion to gaseous chlorine is given as 344·1 kcal, which should presumably be 334·1 kcal, giving 339 kcal, as above, for the heat of combustion to aqueous HCl. 339 kcal is the figure used by Bichowsky and Rossini[38], who give the heat of formation of gaseous ethyl chloride as 25·7 kcal.

actually attained appears to be similar to that mentioned for ethyl chloride. For example, Thomsen[523] gives 359·2 kcal for the heat of combustion of gaseous ethyl iodide to carbon dioxide, liquid water and solid iodine, and a modern determination by Springall and White[464] gives 357·6 ± 0·5, in reasonably good agreement. The heat of formation of methyl iodide is discussed in Section 7.3.

7.2.4. *Silicon*

There is very little recorded information in the literature about the heats of combustion of organic compounds containing silicon. This is perhaps surprising in view of the fact that the stoichiometry of the combustion reaction should be straightforward if complete combustion is attained. The silicon-containing product of combustion is expected to be SiO_2, the heat of formation of which is known. The crystal form of the SiO_2 present can be determined by x-ray methods. For example Thompson[521] has found the product to be finely divided amorphous silica. This product was found to occur to the extent of 13 per cent in the combustion of silicon itself by Humphrey and King[238] and Thompson deduced its heat of formation ($\Delta H^{\circ}_{f\,298\cdot16^{\circ}\,K}$) to be $-208\cdot14$ kcal mole^{-1} from their results.

Tanaka, Takahashi, Okawara, and Watase[508] give the heats of combustion of five silicon-containing compounds without mentioning any particular difficulty involved in the measurement. This is not in accord with experience in the author's laboratory, where it was found that although a silicone ignited easily in the bomb calorimeter, combustion was usually incomplete. Part of the carbonaceous matter appeared to be entrapped in the ash and could not be burnt off except at high temperature. Combustions carried out on a thin film of silicone gave results with a spread of ±3 per cent.

A similar result is described by Thompson[521], who found that combustion was incomplete in the bomb under the conditions normally employed, and that an insulating skin of silica was formed on the surface of the burning liquid which prevented combustion of the liquid beneath. Thompson got round this difficulty by arranging that a glass ampoule containing the liquid should burst explosively at the time of firing; under these conditions the liquids were found to burn quantitatively to silica, carbon dioxide and water. In his paper are given the heats of combustion of four linear polydimethylsiloxanes, which are used to deduce Si – O and Si – C bond energy terms. In view of the difficulties, the reliability of these results is perhaps doubtful.

7.2.5. *Organo-metallic Compounds*

Little work has been reported on the heats of combustion of organo-metallic compounds, which is not surprising in view of the difficulties involved. The compounds are spontaneously inflammable and form solid products of combustion; moreover the products are not always well defined and often undergo slow reactions among themselves. The literature on the subject is summarized by Long and Norrish[319] in a paper which contains the results of measurements in zinc dimethyl, diethyl, di-*n*-propyl, and di-*n*-butyl, cadmium dimethyl, and boron and aluminium trimethyl. An illustration of the difficulties is given by zinc dimethyl, on which no less than fifty separate experiments were carried out with nearly twenty variations in technique, but combustion always fell short of 100 per cent. The heats of formation of these compounds are therefore difficult to obtain with accuracy by combustion methods, and a check on the results by other means is helpful. This is forthcoming for some of the compounds examined by Long and Norrish from measurements on the heats of hydrolysis, which lead to heats of formation (ΔH_f) of zinc dimethyl and zinc diethyl (liquid) of $6{\cdot}3 \pm 1$ and $4{\cdot}3 \pm 1$ kcal[68] respectively, values which compare very well with 6·5 and 4·1 from heats of combustion.

7.2.6. *Other Elements*

Very little work on organic compounds containing other elements is available: so little in fact that it is not possible to make any worthwhile general observations other than to make the point that the establishment of the stoichiometry of the combustion reaction is probably the most important difficulty. Thompson[522] discusses the difficulties for phosphorus compounds, and reports the heat of combustion of disodium methyl phosphonate.

7.3. OTHER METHODS OF DETERMINING HEATS OF FORMATION

The other methods of determining heats of formation of organic compounds lack the specificity of the combustion reaction. They involve the systematic application of thermochemistry in just the same way as is required in the determination of the heats of formation of inorganic compounds. From a knowledge of a heat of reaction, in which all the participants except one have known heats of formation, it is possible to obtain the heat of formation of the remaining reactant simply from Hess's law. Combustion calorimetry is of course just a special case of this. The heats of reaction

may be determined directly by calorimetry, or indirectly from the temperature dependence of the equilibrium constant, or from a knowledge of the equilibrium constant and entropy change at one temperature.

The application of non-combustion thermochemistry to organic compounds is chiefly of interest in two respects; in the determination of small differences in heats of formation of similar compounds with large heats of combustion, and in the determination of heats of formation of compounds such as halogen compounds and organo-metallic compounds, where combustion calorimetry is attended by special difficulties.

Examples of the first type are to be found in the determination of the heats of formation of olefins. For example, Prosen and Rossini[407] give the heats of formation of a number of olefines in the ideal gas state, calculated from the known heats of combustion of the paraffins and the known heats of hydrogenation of the olefins[33, 271]. It is possible to compare some of these results with heats of combustion measured directly. For instance, Coops *et al.*[89] give for $-\Delta H_R$(*n*-heptene-1; l.) 1,111·5 kcal (corrected to the more recent benzoic acid result) whereas Prosen and Rossini's value is 1,113·6 kcal (corrected to the liquid state using the value given for the latent heat of vaporization by Bent *et al.*[33]) a difference of 2 kcal, or 0·2 per cent. The differences for the pentenes are less than this. On the other hand, the differences between the heats of formation of isomers are known better than this. The accuracy of these differences obtained by hydrogenation calorimetry has been confirmed by some recent hydrobromination calorimetry. Lacher *et al.*[283] have measured the vapour phase heats of hydrobromination of the isomeric butenes, from which may be derived some heats of isomerization to compare with those of Kistiakowsky *et al.*[271]. We have the following results for $-\Delta H$ (cal):

Butene-1 → *trans*-butene-2	2,804 (Lacher[283])
	2,720 (Kistiakowsky[271])
→ *cis*-butene-2	1,800 (Lacher)
	1,771 (Kistiakowsky)
cis-butene → *trans*-butene	1,004 (Lacher)
	949 (Kistiakowsky).

The agreement is excellent. The actual heat quantities measured were about 30,000 cal mole^{-1} for hydrogenation, and about 20,000 cal mole^{-1} for hydrobromination.

The other type of work is the determination of heats of formation

of moderate accuracy which cannot easily be obtained in another way. The various determinations of the heat of formation of methyl iodide may be taken as an example.

Thomsen[523] determined the heat of combustion of gaseous methyl iodide, from which can be deduced $\Delta H_f(CH_3I;\ g)_{25°C} = 4{\cdot}9$ kcal mole^{-1}. (Small differences of two- or three-tenths of a kilocalorie in these values from those quoted elsewhere are due to the use here of the most modern subsidiary thermal data.) For some reason this result has not been looked on with much favour, and two recent thermochemical researches have been carried out a main result of which is essentially the determination of the heat of formation of methyl iodide, though it is expressed as the C – I bond energy[335, 368]. In two other recent researches, the heat of formation of methyl iodide has been in the one the main object, and in the other an important incidental result[69, 205]. Moreover, direct determination of $D(CH_3 - I)$[330] may be combined with other dissociation energy data to give $\Delta H_f(CH_3I)$. It is interesting to compare these methods and results.

Mackle and Ubbelohde[335] essentially measured the heats of the two following reactions,

$$Me\,.\,Mg\,.\,I + I_2 \rightarrow MeI + MgI_2$$
$$2Me\,.\,Mg\,.\,I + I_2 \rightarrow C_2H_6 + 2MgI_2,$$

from which, by combination, the heats of formation of the Grignard reagent and the magnesium iodide may be eliminated, leaving a simple relationship between the measured heats and the heats of formation of iodine, ethane and methyl iodide. The reactions were carried out in ethereal solution. The major experimental difficulty, that of controlling the extent to which the two competing reactions occur, was solved by the discovery that the relative extents could be controlled by alteration of concentrations and that ethane formation could be suppressed entirely by the addition of excess magnesium iodide to the initial solution of Grignard reagent. It was found that methyl iodide formation comprised 90 to nearly 100 per cent of the reaction, and ethane formation could occur up to 10 per cent. Side reactions were almost completely absent. From the point of view of obtaining the heat of formation of methyl iodide from the raw information about heats of reaction, the main difficulty lies in the volatility of the solvent. The ethane formed is saturated with ether vapour, and the correction of the heat of reaction to that for the reaction producing pure ethane is quite large (2·7 kcal). The other heats of solution and vaporization are small or accurately known, and present little difficulty.

They used simple calorimetric techniques, concentrating rather on the chemistry of the reactions, so that the results are not of the highest precision. They are:

$$MeMgI(Et_2O) + I_2(Et_2O) \rightarrow MeI(Et_2O) + MgI_2(Et_2O);\ \Delta H = -45{\cdot}4 \pm 1 \text{ kcal}$$

$$2MeMgI(Et_2O) + I_2(Et_2O) \rightarrow C_2H_6(\text{gas, sat. } Et_2O) + 2MgI_2(Et_2O);\ \Delta H = -103{\cdot}4 \pm 3 \text{ kcal}$$

Hence

$$2\Delta H_f(CH_3I;\ Et_2O) - \Delta H_f(I_2;\ Et_2O) - \Delta H_f(C_2H_6;\ g,\ Et_2O) = 12{\cdot}6 \pm 3{\cdot}5 \text{ kcal}$$

Thus if we have

$$\Delta H_f(I_2;\ Et_2O) = 1{\cdot}6 \text{ kcal}$$

and

$$\Delta H_f(C_2H_6;\ g) = -20{\cdot}2 \text{ kcal}$$

and if we know that the heat of vaporization of the amount of ether vapourized per mole ethane formed is 2·7 kcal, we deduce

$$\Delta H_f(CH_3I;\ Et_2O) = -1{\cdot}7 \text{ kcal}$$

whence

$$\Delta H_f(CH_3I,\ g) = 4{\cdot}9 \text{ kcal}$$

with an uncertainty of about ±4 kcal in agreement with Thomsen.

The Belfast school followed this by the study of the following Grignard reactions[368]:

$$MeMgI + I_2 \rightarrow MeI + MgI_2$$

$$MeMgI + HI \rightarrow CH_4 + MgI_2$$

To avoid the difficulty of the volatility of ether, *p*-xylene was used instead of ether as solvent. In addition the calorimetric technique was improved. The compounds whose heats of formation are to be compared with that of methyl iodide are hydrogen iodide and methane. The new method has the advantage that the comparison compound, methane, is in this case produced as a main reaction product. On the other hand the ethane in the previous scheme was a product of a competing side reaction. The precision of the work is therefore much greater, and combination of their results for the two reactions yields:

$$\Delta H_f(CH_3I;\ p\text{-xylene}) + \Delta H_f(HI;\ p\text{-xylene}) - \Delta H_f(CH_4;\ \text{gas sat. with } p\text{-xylene}) - \Delta H_f(I_2;\ p\text{-xylene}) = 13{\cdot}21 \pm 0{\cdot}96 \text{ kcal}$$

Whence, using the data of Nichol and Ubbelohde[368], we have in agreement with the previous work.*

$$\Delta H_f(CH_3I;\ g) = 2{\cdot}8 \text{ kcal}$$

The use of organometallic compounds for thermochemical studies is very attractive, once the experimental difficulties of handling them have been overcome; and they have been the subject of a range of systematic investigations by the Manchester school under H. A. Skinner. Two of these investigations lead to values of the heat of formation of methyl iodide.

The first[69] involved combination of the heat of hydrolysis of cadmium dimethyl to produce methane with the heat of iodination of cadmium dimethyl to produce methyl iodide. This scheme does not have quite the attractive simplicity from the point of view of determining the heat of formation of methyl iodide of the Belfast work, because different cadmium compounds are produced in the two reactions, and thus a knowledge of the heats of formation of metallic salts is required. Of course, if the heat of formation of the organometallic compound itself is required, as indeed it was by Mackle and Ubbelohde[335] to make an estimate of the C – Mg bond strength, and by Carson *et al.*[69] for the corresponding C – C bond strength, the heat of formation of a metallic salt or salts must be known. This need not always be objectionable, but in this particular instance the iodination of the cadmium dimethyl is carried out in ethereal solution, from which the cadmium iodide is precipitated as a fine microcrystalline powder, the heat content of which may well be influenced by its high specific surface. Nichol and Ubbelohde[368] have also pointed out that the lattice energy of cadium iodide precipitated from ether may differ from that of the salt crystallized from saturated aqueous solution. Thus there is some doubt whether the heat of formation of the cadmium iodide formed in these experiments was sufficiently accurately known to allow a very reliable value of $\Delta H_f(CH_3I;\ g)$ to be deduced. However, their value of 2·8 kcal does not differ very greatly from those quoted already.

The reactions of mercury dimethyl studied by Hartley, Pritchard, and Skinner[205] give yet another estimate of the heat of formation of methyl iodide. Mercury dimethyl reacts under suitable conditions with bromine and iodine (X) according to the equation,

$$HgMe_2 + X_2 \rightarrow HgMeX + MeX,$$

* The molar heat of solution of iodine in *p*-xylene given by Nichol and Ubbelohde (3·10 kcal) seems rather low. An increase in this figure would increase the final value of $\Delta H_f(CH_3I)$ by a like amount, and make it closer to the other determinations.

and with the mercuric halides as follows:

$$HgMe_2 + HgX_2 \rightarrow 2HgMeX$$

The heats of these reactions were measured. From them can be deduced the heats of the reactions

$$HgMe_2 + 2X_2 \rightarrow 2MeX + HgX_2$$

The heat of formation of mercury dimethyl was deduced from a knowledge of the heat of this reaction when X = Br, together with a knowledge of the heat of formation of methyl bromide and that of mercuric bromide. This was then used with the heat of reaction when X = I to deduce

$$\Delta H_f(CH_3I,\ l) = -2{\cdot}3 \pm 1{\cdot}2 \text{ kcal}$$

whence

$$\Delta H_f(CH_3I;\ g) = 4{\cdot}3 \text{ kcal}$$

in excellent agreement with previous results.

Finally, it may be mentioned that Cox and McDowell[330] obtained $D(Me-I)$ by direct measurement of the appearance potential of CH_3^+ from methyl iodide as $52{\cdot}6 \pm 2{\cdot}3$ kcal, which may be combined with the value 32 kcal for $\Delta H_f(CH_3)_{25°C}$ given in the National Bureau of Standards Circular 500[529] (derived from $\Delta H_{f\,25°C}$ for the reaction $CH_4 \rightarrow CH_3 + H$, 102 kcal), to give $\Delta H_f(CH_3I;\ g)$ 4·9 kcal.

Reaction thermochemistry is particularly important in determining the heats of formation of organic compounds containing unusual elements, and the most important recent studies in this field are those being carried out by Skinner and his collaborators. Their work on cadmium dimethyl and mercury dimethyl has already been cited. Carson, Hartley, and Skinner[68] measured the heats of reaction of cadmium diethyl, zinc dimethyl, and zinc diethyl with dilute acid and water, and of zinc diethyl and cadmium diethyl with iodine. These measurements gave values for the heats of formation of these compounds, and also of the heat of formation of ethyl iodide by a similar process to that used earlier for methyl iodide. It has already been mentioned (Section 7.2.5) that the heats of formation of the metal alkyls thus obtained agree to within 0·2 kcal with those obtained from combustion measurements, while the value of heat of formation of ethyl iodide $\Delta H_f(C_2H_5I;\ l) = -9{\cdot}1 \pm 1$ kcal, is in good agreement with that derived from a modern combustion, −8·4 kcal (Section 7.2.3). Further studies of organo-mercury compounds[206, 357] showed disagreement between the heats of formation deduced in this way and those derived from

earlier combustion measurements, and the desirability of a further investigation on the heats of combustion of the mercury dialkyls was indicated. Attention has since been turned to organo-arsenic compounds[72, 358] and organo-boron compounds[74, 454, 455a].

Earlier work of this school was concerned to establish heats of formation of halogen-containing organic compounds by measuring heats of hydrolysis. Heats of hydrolysis of acetyl fluoride, chloride, bromide, and iodide[70, 402], of the chloro-substituted acetyl chlorides[401] of the benzoyl halides[69a] and of chloral and bromal[403], have also been made. Comparison with heats of formation derived from heats of combustion is not normally possible, but there is a large discrepancy between the two methods for benzoyl chloride, where an early combustion measurement is available, in the sense that the determined heat of combustion appears to be about 14 kcal low.

7.4. HEATS OF FORMATION IN THE GAS PHASE

For discussion of intramolecular forces it is essential to remove from consideration effects due to intermolecular forces, that is, to have heats of formation referring to the ideal gas state. In general the correction of heats of formation of real gases at 1 atmosphere pressure to the ideal gas state is very small compared with the accuracy to which heats of formation are known; for example, approximately 0·002 kcal mole^{-1} for methane and 0·02 kcal for methyl chloride. This means that for all purposes connected with bond energies, a knowledge of the heat of formation of the real gas is adequate. Thus for substances whose heat of formation is known directly for the liquid or solid, a knowledge of the heat of vaporization at the appropriate temperature is required. Strictly, however, the quantity concerned is the heat of vaporization to the ideal gas state.

The heat of vaporization may be obtained accurately by direct calorimetric measurements or from the dependence of vapour pressure on temperature, and roughly by empirical methods using rates of vaporization, or by using empirical relationships between heat of vaporization and boiling point.

The accuracy of the best direct calorimetric measurements is very high. For example, Osborne and Ginnings[376] report the calorimetric determination of the latent heats of vaporization at 25° C of 59 hydrocarbons, to an accuracy which they believe to be within 0·1 per cent. This is confirmed by the results of other recent calorimetric determinations. For example, Waddington and

Douslin[540] measured calorimetrically the heat of vaporization of *n*-hexane at 68·7, 54·8, and 35·6° C, from which they obtain by extrapolation 7·540 kcal mole^{-1}, at 25° C. The value thermodynamically derived from the vapour pressure measurements of Willingham, Taylor, Pignocco, and Rossini[570] is $\Delta H_v = 7{\cdot}54_3$ kcal mole^{-1}, in excellent agreement. Lemons and Felsing[299] obtained a value 1 per cent lower than this by calorimetric measurement, but because they only claimed an accuracy of 1 per cent, the agreement may still be considered very good. Furthermore, Jahn[247], using the Bunsen ice calorimeter, obtained 7·68 kcal at 0° C, which corresponds to 7·4 kcal at 25° C. This suggests that the accuracy to which calorimetrically determined heats of vaporization are known is certainly good enough for all purposes concerned with bond energies. It must be pointed out, however, that although *n*-hexane was taken at random as an example, it would appear that it is a slightly favourable case for the experimenters. A literature search reveals heats of vaporization calorimetrically determined by different investigators which differ by as much as 0·5 kcal[289]. Even so, a discrepancy of 0·5 kcal is usually not serious for bond energy purposes.

Direct calorimetric measurement for solids and liquids of low vapour pressure is not so convenient, and most of the experimentally determined values for such substances are derived from the variation of vapour pressure with temperature, using the Clausius-Clapeyron equation. Such a value is in principle likely to be less accurate than a direct measurement, because it involves the differential of a measured quantity, *i.e.* $\mathrm{d}p/\mathrm{d}T$, rather than a directly measured quantity itself. This is reflected in the greater spread of such results as obtained by different investigators, although very careful work such as that mentioned above for *n*-hexane, together with an adequate theoretical treatment taking into account gas imperfections, still allows the method to give sufficient accuracy. In this connection it is interesting to note that Waddington and Douslin[540] point out that use of the virial coefficient derived from the Berthelot equation, rather than that derived from measured vapour densities, makes a difference of 0·75 per cent in the derivation of the heat of vaporization of *n*-hexane from the vapour pressure measurements. Thus an accuracy of better than 2–3 per cent is not to be expected for values derived directly from the approximate Clausius-Clapeyron equation, assuming a perfect gas. This is, however, rarely as much as 0·5 kcal. A typical example of the agreement to be expected is given by l-heptene, for which Lister[312] gives the heat of vaporization as $8{\cdot}5 \pm 0{\cdot}30$ kcal mole^{-1}, as deduced

from the vapour pressures. Bent *et al.*[33] give $8{\cdot}1 \pm 0{\cdot}1$, a difference of 0·4 kcal. Values for solids with low vapour pressures, say below 10^{-2} mm Hg, often differ by more than this, unfortunately. For example, Bright[57] derives $15{\cdot}3 \pm 0{\cdot}7$ kcal mole^{-1} for the heat of vaporization of diphenylmethane from his vapour pressure data in the range 5–25° C, whereas Wolf and Weghofer[576] give $17{\cdot}2 \pm 0{\cdot}2$ kcal at 20° C, from vapour pressure data which are not given in their paper. The usual method for determining low vapour pressures is some variant of the effusion method, the principle of which was explained in Section 3.3, and the chief experimental difficulty is the accurate determination of the amount of material which has effused through the hole. Unless the experiment has gone on for an inconveniently long time, the amount effused is quite small (about 1 mg is often obtained) and unless careful precautions are taken the accuracy of an individual measurement of vapour pressure is not very high. In Bright's work quoted above, for example, the standard deviation of an individual determination was ± 10 per cent.

A serious source of error in the determination of the vapour pressures of solids of low volatility is the possible presence of impurities of higher volatility. For example, Menzies[344] determined the vapour pressure of trinitrotoluene at various temperatures, his results leading to a heat of vaporization of 12 kcal mole^{-1}. However, he stated that: 'Any attempt at purification other than desiccation in the absence of light was omitted.' It might therefore be assumed that his measured vapour pressures would be high and the resultant heat of vaporization would be low. Robertson[423] measured the temperature of condensation of α-T.N.T. vapour at various pressures, ranging from 76 to 3 cm, the corresponding temperatures ranging from 345° C to 232° C. From these results he deduced $\Delta H_v = 17{\cdot}5 \pm 1{\cdot}0$ kcal mole^{-1}, in this temperature range. The vapour pressure has also been measured by the effusion method in the temperature range 50–143° C[135], and the results lead to $\Delta H_v = 22{\cdot}7$ kcal mole^{-1}, if it is assumed constant over this temperature range. However, this is not so, and Edwards combines his results with those of Robertson to obtain $\Delta H_v = 37{,}680 - 41{\cdot}79T$ cal mole^{-1}. (The equation as given on page 427 of Edwards' paper has been corrected for misprints.) This gives ΔH_v (25° C) as 26·2 kcal mole^{-1}, which is a long way from Menzies 12 kcal. This also illustrates the possible danger of using vapour pressure measurements at high temperatures to deduce heats of vaporization without taking into account the variation of heat of vaporization with temperature. This is usually unimportant

for rough work if the temperature for which the heat is known does not differ much from 25° C, but it can be very important when long extrapolations are considered.

Sometimes vapour pressure data are not available, and a rough experimental measure of the heat of vaporization is required. Belyaev [31] has suggested a method which depends upon the measurement of the rate at which a small sample (1–2 mg) of the substance vaporizes from a hot plate at a known temperature. If the time of disappearance τ, of the sample is inversely proportional to the vapour pressure, then $\Delta H_v(T)$ at the temperature T is given by

$$\Delta H_v = (\ln\tau - D)\boldsymbol{R}T$$

where D is a constant to be empirically determined. The method was originally put forward for determining the boiling points and heats of vaporization of explosive substances, and its use has been critically discussed in this connection by Ahrens [2]. It may be seen from the equation that variation of temperature is more important than that of time, because if the constant D is of the same order of magnitude as $\ln\tau$, but somewhat larger, a very great difference in time will be required to make much difference to ΔH_v. The values expected for τ may be deduced from Belyaev's observation that at the boiling point, 1–2 mg substances take 4–5 sec to vaporize. This he used as the basis of a method for determining boiling points. The present author has tested the method for a number of substances, and found fair agreement with other experiments. Benzoic acid was used to standardize the apparatus. The work was carried out in 1947 and used to determine the then unknown heats of vaporization of oxamide and oxamic acid, for which ΔH_v(250° C) was found to be 26 and 23·8 kcal mole^{-1} respectively. Since then the heat of vaporization at about 100° C has been determined from vapour pressure determinations by the effusion method [47] to be 27 and 25·8 kcal mole^{-1}. Belyaev's method is purely empirical, and is not to be confused with Langmuir's rate of evaporation method, where we are concerned with the rate of vaporization into a vacuum from a known area of material.

An ingenious method has been applied to a number of aromatic hydrocarbons by Magnus *et al.*[337]. They point out that a complete destruction of the crystal lattice and separation of the molecules takes place when a substance is dissolved in a suitable solvent. Thus the lattice energy, which corresponds to the heat of vaporization, is lost, but the energy of solvation is gained. Now if the solvent has no specific interaction with the molecules, and if solution

takes place under similar conditions, it might be expected that the heat of solvation of a set of isomeric molecules will be the same for all. Magnus *et al.* therefore assume that differences in the heat of solution of isomeric aromatic hydrocarbons in benzene, toluene or xylene are due to differences in heats of vaporization. This assumption was checked for anthracene and phenanthrene, for which Wolf and Weghofer[576] have measured the heats of vaporization to be 22·3 and 20·1 kcal mole^{-1} respectively. The heats of solution of these substances in xylene are 5·58 and 3·72 kcal mole^{-1} respectively. The difference between the heats of vaporization is 2·2 kcal, and in heats of solution 1·9 kcal, in the same sense. Thence the solvation energy is 16·7 or 16·4 kcal mole^{-1}. It was further assumed that the solvation energy is proportional to the number of benzene rings in the compounds; thus the heats of solvation in xylene of 3, 4, 5 and 6 ring aromatic systems are 16·7, 22·2, 27·8, and 33·4 kcal respectively. With this assumption, and using measured heats of solution, these workers derived the heats of vaporization of a large number of polynuclear aromatic compounds. It would be valuable to have experimental confirmation of these results.

The heat of vaporization may also be estimated from boiling points by various empirical rules. Most of these rules lead to the heat of vaporization at the boiling point, whereas we require the heat at 25° C. The specific heat of the liquid is greater than that of the gas, the latter often being between one-half and two-thirds of the former, for organic liquids. Thus the heat of vaporization decreases with rising temperature, quite sharply, for liquids of high specific heat. For example, for *n*-hexane, the heat of vaporization at the boiling point (69° C) is 0·6 kcal less than at 25° C. This means that such rules for the heats of vaporization of liquids as Trouton's ($\Delta H_v = 21\,T_b$ cal mole^{-1}, where T_b is the boiling point), Nernst's ($\Delta H_v = T_b\,(9{\cdot}5 \log_{10} T_b - 0{\cdot}007 T_b)$ cal mole^{-1}), and Von Wartenberg's ($\Delta H_v = T_b\ 7{\cdot}4 \log_{10} T_b$ cal mole^{-1}) which are all fairly useful, require to be supplemented by a knowledge of the temperature dependence of the heat of vaporization. The following approximation, due to Sidgwick, may be used

$$\Delta H_v(25^\circ\text{ C}) = \Delta H_v(x^\circ\text{ C}) - 0{\cdot}013(25 - x)\text{ kcal mole}^{-1}$$

and works very well. For example it gives the heat of vaporization of *n*-hexane at 25° C from the known heat of vaporization at the boiling point to within 0·03 kcal mole^{-1} of the true value. Klages[273] has suggested a rule which takes into account the variation with temperature, giving the relations

$$\Delta H_v(25^\circ\text{ C}) = 5{\cdot}4 + 0{\cdot}036 t_b\text{ kcal mole}^{-1}$$

for ordinary liquids, and

$$\Delta H_v(25^\circ\text{ C}) = 6{\cdot}8 + 0{\cdot}045 t_b \text{ kcal mole}^{-1}$$

for highly associated liquids, where t_b is the boiling point in ° C. This rule gives fair agreement with experiment over a wide range of temperatures. These rules apply to liquids, and for solids a knowledge of the heat of fusion is required. This may be estimated from Walden's rule ($\Delta H_f = 13{\cdot}5 T_m$ cal mole^{-1}) where T_m is the melting point in ° K. The specific heat of the liquid is usually greater than that of the solid, and Sidgwick's approximate rule

$$\Delta H_f(25^\circ\text{ C}) = \Delta H_f(x^\circ\text{ C}) + 0{\cdot}013(25 - x) \text{ kcal mole}^{-1}$$

may be used to correct for this effect. It should be noticed that the correction for this is of the opposite sign.

When the necessary data for substitution in these empirical relations are not available, the heat of vaporization must be estimated by analogy, or frankly guessed. For example, Pauling and Sherman [385] give the heats of formation in the gas phase of a number of compounds such as uric acid, for which the estimate of the heats of vaporization can only be guesses of unknown accuracy. This may introduce errors of as much as 10 kcal, in the most unfavourable case, and Pauling and Sherman are careful not to draw conclusions from differences less than this.

8

HEATS OF FORMATION OF INORGANIC COMPOUNDS AND HEATS OF ATOMIZATION OF THE ELEMENTS

8.1. THE HEATS OF FORMATION OF INORGANIC COMPOUNDS

No simple general method, such as measurement of heat of combustion, is available for the determination of heats of formation of inorganic compounds. Thus the topic does not lend itself to such detailed discussion as was given in the previous chapter, and a few examples only are given to illustrate the type of measurement and the likely accuracy. In this last respect, however, each individual value must be considered on its merits to a much greater extent than with organic compounds. The need for a detailed discussion is perhaps the less because Long has recently produced an interesting review article on just this subject[317].

Not only is there no general method for determining these heats of formation, but it is rarely possible to relate compounds by only one or two reactions to the elements from which they are formed, and quite elaborate thermochemical cycles are sometimes required. This means that to a much greater degree than in organic chemistry, heats of formation of inorganic compounds are closely interrelated. An amendment of one heat of reaction might produce effects on the validity of heats of formation at first sight completely unrelated. For example, an amendment to the value of the heat of combustion of oxalic acid given by Becker and Roth would affect our estimate of the heat of formation of ammonia!

One of the most common of inorganic compounds, water, is an exception to the generalization that most heats of formation are obtained indirectly. It is very accurately known, and was most carefully determined by Rossini[426], who burned oxygen in hydrogen and hydrogen in oxygen in a flame calorimeter (*see* Section 7.1 for the value at present accepted, deduced from his results with small correction due to changes in the accepted values of atomic weights *etc*). Hydrazine is another substance whose heat of formation has been determined by direct combustion, and is mentioned here because the results obtained for it show the reproducibility possible

in careful calorimetric work. Hughes, Corruccini, and Gilbert[235] obtained for the heat of combustion of hydrazine $-\Delta H_R(N_2H_4;$ liq.) $148{,}635 \pm 30$ cal mole^{-1}. More recently, Aston *et al.*[14] measured the heats of combustion of methyl substituted hydrazines and incidentally remeasured that of hydrazine itself and found $-\Delta H_R$, 148,619 cal mole^{-1}, in very close agreement with the previous result. Hughes, Corruccini, and Gilbert[235] also measured the heat of combustion of hydrazine hydrate. From this, knowing the heat of hydration of hydrazine, they deduced $\Delta H_f(N_2H_4;$ liq.) $= 12{\cdot}10$ kcal mole^{-1}. This is to be compared with 12·00 kcal deduced from the heat of combustion of hydrazine itself, and the authors took the mean of these two results as their final estimate of the heat of formation, 12·05 kcal mole^{-1}.

Ammonia forms an interesting contrast. Although its heat of formation was first simply determined by combustion, by Thomsen using the constant pressure flame calorimeter method and by Berthelot and Matignon using the bomb calorimeter, the results were not of the highest accuracy, and other methods have been adopted. The earlier work was criticized by Haber[195], who concluded that the uncertainty was about 1 kcal mole^{-1}. These workers then determined very carefully the heat of decomposition of ammonia to nitrogen and hydrogen on a heated catalyst in a calorimeter at 25° C. They concluded that $\Delta H_f(NH_3;$ g) $=$ $-10{\cdot}95$ kcal mole^{-1} at 0° C, and $-11{\cdot}09$ kcal mole^{-1} at 25° C. Another estimate was provided by Kraus and Ridderhof[280], who measured the heat of the following reaction using a liquid ammonia calorimeter:

$$NH_4Br + NaNH_2 \rightarrow NaBr + 2NH_3 \text{ (in liquid ammonia)}$$

They then used the values given in the *International Critical Tables* for the heats of formation of ammonium bromide, sodium amide, and sodium bromide, together with heats of solution which they determined, to obtain 17·00 kcal for the heat of formation $(-\Delta H)$ of liquid ammonia at $-33{\cdot}4$° C. This they combined with the heat of vaporization and specific heat data to obtain $\Delta H_f(NH_3;$ g) $= -10{\cdot}93$ kcal at 0° C, in good agreement with Haber. On the other hand Becker and Roth[28] interpreted the data of Kraus and Ridderhof to yield 11·64 kcal mole^{-1} for $-\Delta H_f$ at 20° C. In any case whichever interpretation is correct, this method is not an absolute one for determining the heat of formation of ammonia because the determined heats of formation of ammonium bromide and of sodium amide themselves involve a knowledge of the heat of formation of ammonia. For example, the

heat of formation of sodium amide was determined by de Forcrand [156a] by measuring the heat of the reaction,

$$NaNH_2 + H_2O \rightarrow NaOH(aq.) + NH_3(aq.)$$

to be 31·0 (*ca.* ±0·3) kcal. A knowledge of the heats of formation of water, aqueous ammonia, and aqueous sodium hydroxide is required to arrive at the heat of formation of sodium amide from this result.

Becker and Roth [28] concluded from their study of the literature that a confirmation of Haber's result by another method would be desirable. An accurate direct determination of the heat of combustion of ammonia in the bomb calorimeter offers several difficulties, so the burning of an ammonium salt, together with the determination of its heat of formation from the acid and ammonia and other subsidiary data was suggested. The programme was therefore to neutralize ammonia with a solution of a stable oxygen-containing acid with a low heat of combustion, and to dissolve and burn the solid acid and its ammonium salt. There are thus five new thermochemical quantities to determine. The use of carbon dioxide instead of a solid acid appeared at first sight attractive, but preparation of really pure ammonium carbonate presented difficulties. Oxalic acid, used for convenience in the form of its dihydrate, was the most suitable choice, and the following scheme of reactions used:

		$\Delta H =$
$2NH_3 + (COOH)_2$ aq.	$\rightarrow (NH_4 . COO)_2$ aq.	a
$(COOH)_2 . 2H_2O$ + aq.	$\rightarrow (COOH)_2$ aq.	b
$(COOH)_2 . 2H_2O + \frac{1}{2}O_2$	$\rightarrow 2CO_2 + 3H_2O$	c
$(NH_4 . COO)_2 . H_2O$ + aq.	$\rightarrow (NH_4 . COO)_2$ aq.	d
$(NH_4 . COO)_2 . H_2O + 2O_2$	$\rightarrow N_2 + 2CO_2 + 5H_2O$	e
$3H_2 + 1{\cdot}5O_2$	$\rightarrow 3H_2O$	f
$N_2 + 3H_2$	$\rightarrow 2NH_3$	x

$$x = [f + c + (-b)] - [a + (-d) + e]$$

Of these heats of reaction f, the heat of formation of water, was already accurately known [426], and the rest were determined. The largest of these quantities is e, the heat of combustion of ammonium oxalate. Here $-\Delta H$ at 20° C is 189·27 ±0·10 kcal mole^{-1}. The uncertainty quoted here is 0·05 per cent, and it has been shown in Sections 7.1 and 7.2 that such accuracy can as a rule be reliably

attained in careful modern combustion calorimetry. This is also the largest in any of the single terms, and the resultant uncertainty claimed by Becker and Roth in x is $\pm 0{\cdot}14$ kcal. This leads to $\Delta H_f(NH_3;\ g)$ at 20° C $= -11{\cdot}01 \pm 0{\cdot}07$ kcal mole^{-1}, or $-11{\cdot}04$ at 25° C in complete agreement with Haber. There is little doubt that this particular quantity is well established.

On the other hand, for very many compounds there is no check on the information available, and we have to rely on nineteenth-century measurements which were certainly not carried out with the refinement now possible, although it is unlikely that many of the values are wildly in error. This is shown by the fact that most corrections to the work of the classical thermochemists have involved increases in precision, rather than large changes in value. Going from ammonia, NH_3, to arsine, AsH_3, illustrates the difference in reliability of the thermochemical results. For ammonia, as we have just shown, we have two completely independent and precise results in complete agreement, with the older results only uncertain by about 1 kcal. The heat of formation of arsine at present accepted depends upon the measurement of one heat of reaction reported by Ogier [373] in 1878. He found for the reaction,

$$2AsH_3 + 8Br_2 + 5H_2O + \text{aq.} \rightarrow As_2O_5\ \text{aq.} + 16HBr\ \text{aq.} \qquad \Delta H = 425{\cdot}8\ \text{kcal},$$

whence may be deduced

$$\Delta H_f(AsH_3;\ g) = 41{\cdot}0\ \text{kcal mole}^{-1}$$

at 25° C [529], with an unknown uncertainty. However, it is reassuring to note that it requires an error of 3 kcal mole^{-1} in the heat of formation to make an error of 1 kcal in the As – H bond energy term. As we have seen, we have no guarantee that a bond energy term will be constant to much better than this anyway.

Sometimes, usually because of the difficulty of obtaining some elements completely pure, one is faced with a bewildering variety of values for the same heat of formation. For example, the thermochemistry of boron compounds has been hampered for some time by lack of a reliable value of the heat of formation of boric oxide, B_2O_3. Recent values for $\Delta H_f(B_2O_3;\ c)$ at 25° C have ranged from -349 kcal mole^{-1} [430] to -281 kcal mole^{-1} [141]. The original thermochemical relation of elementary boron to its compounds was by Troost and Hautefeuille, who used 'amorphous' boron which was almost certainly impure. They allowed it to react in a calorimeter with chlorine to give BCl_3, the heat of formation of which was thus found to be $\Delta H_f = -104$ kcal. Berthelot later applied an arbitrary correction to this to give $-89{\cdot}1$ kcal. He hydrolysed

boron trichloride to aqueous hydrochloric acid and boric acid solution, and combining the heat of this process with his amended value of $\Delta H_f(BCl_3)$ obtained for $\Delta H_f(B_2O_3;\ c) - 282$ kcal. Combination of the original Troost and Hautefeuille value with Berthelot's heat of hydrolysis gives -311 kcal (*see* references in Roth and Börger[430]). The more recent values by Roth and Börger, and Eggersgluess *et al.*, as well as a value of -335 kcal[525] were obtained by direct combustion of boron in a calorimeter. (For a correction to this last result, *see* Long and Norrish[319].) This operation is difficult because boron alone does not burn satisfactorily in oxygen. Viscous B_2O_3 is formed which acts as a protective layer round the unburned boron, and there is also a possibility of reaction between the combustion aid and boron. Further, if the combustion aid contains hydrogen, the water formed from it in the combustion will hydrate the B_2O_3, introducing an uncertain correction. Eggergluess *et al.* suggest that the high values obtained by Roth, and by Todd and Miller, may be due to the presence of higher boron hydrides in the boron used by these workers. A further result of -303 kcal for the heat of combustion of solid boron to solid B_2O_3 has been given by Stegeman and Nathan[468], but no details appear to have been published. These differences reflect not only the difficulty of combustion of boron, but the difficulty of preparing the material in a pure state. Prosen *et al.*[405] have measured the heat of hydrolysis and of thermal dissociation of diborane, from which a value of $\Delta H_f(B_2O_3;\ c)$ of -306 kcal mole^{-1} has been deduced. Full details of this work have not been published in the usual literature, but it is reasonable to conclude that this value, agreeing as it does with one value of the heat of combustion and lying between the extreme values reported, is likely to be correct. Lacher, Scruby, and Park[284] have measured the heat of the vapour phase chlorination of diborane and obtain:

$$B_2H_6 + 6Cl_2 \rightarrow 2BCl_3 + 6HCl;\ \Delta H(25^\circ C) = -343 \text{ kcal}$$

This enables $\Delta H_f(BCl_3)$ to be deduced as -102 kcal, if the value of Prosen *et al.* for $\Delta H_f(B_2H_6)$ of 7·5 kcal is correct. This is in fairly good agreement with the original Troost and Hautefeuille value of $\Delta H_f(BCl_3) = -104$ kcal, and therefore suggests that Berthelot's correction to their results was not justified. Using Berthelot's value for the heat of hydrolysis of BCl_3 together with the new value of $\Delta H_f(BCl_3)$ we obtain -307 kcal for the heat of combustion of B_2O_3, in agreement with the result obtained by Prosen. On the other hand, as Lacher, Scruby, and Park point out, their result is inconsistent with the value of $\Delta H_f(BCl_3) = -94{\cdot}5$ given in

the National Bureau of Standards Circular 500 [529]. The situation has been clarified by Skinner and Smith [455], who remeasured the heat of hydrolysis of boron trichloride. Combination of this result with Prosen's value for H_3BO_3 gives $\Delta H_f(BCl_3;\ \text{liq.}) = -103{\cdot}0 \pm 1$ kcal, or $-97{\cdot}5$ kcal for the gas. This is in agreement with a preliminary result obtained by Prosen by direct chlorination of boron: the agreement of course confirms Prosen's results for B_2O_3 and H_3BO_3. For further details the reader is referred to Skinner's paper.

Heats of vaporization of inorganic compounds may be determined in the same way as for organic compounds (Section 7.4), although the Knudsen vapour pressure method has perhaps been used more for inorganic compounds. No further discussion is called for here.

Further discussion of heats of formation of inorganic compounds occurs as required in the discussion of individual bond energy terms.

8.2. THE HEATS OF ATOMIZATION OF THE ELEMENTS

8.2.1. *General*

It is necessary to know the heats of atomization of the elements; that is, the heats of formation of the elements as monatomic gases from the elements in their standard states, in order to obtain bond energy terms relative to the separated atoms as we have defined them in Chapter 6. On the other hand, as long as bond energy terms are used only to predict heats of formation of compounds, the heats of atomization of the elements are irrelevant. For this purpose the chief value of the use of bond energy terms referred to the heat of atomization of the molecule is that the results are always positive and usually come out at convenient numbers. Bond energy terms referred to the elements in their standard states would lead to precisely the same answers for heats of formation, since the heats of atomization appear implicitly in the bond energy terms exactly as they appear in the total heat of atomization of the compound. Indeed, bond energy terms, the sum of which gives the heat of combustion of the molecule have been used for organic compounds (*see*, for example, Klages [273]), giving a satisfactory account of the facts, and avoiding the use of doubtful thermochemical data on the heat of atomization of carbon. However, for the comparison of bond strengths between different atoms, it is necessary to refer them to separate atoms, to avoid irrelevant considerations such as the lattice energy of the solid element and so forth.

A list of heats of atomization of the elements has been prepared,

and is given in *Table 8.2.1.1.* Other recent lists have been made [317, 529], but relatively little discussion has been given to some doubtful values. The principles adopted in the present list have been to give an account of the reliability of each value, or to give a reference to such an account. This is of some importance in considering values given in N.B.S. Circular 500 [529], where the references are occasionally uninformative.

8.2.2. *Numerical Values*

In view of the fact that bond energy terms have usually been calculated for 25° C, the heats of atomization are given for this temperature. Thus the numerical value quoted for the atom A is $\Delta H_f^\circ(A)$ at 25° C. The discussion of each value is subheaded by the atomic number of the element concerned; thus Section 8.2.2.14 refers to silicon.

8.2.2.1. *Hydrogen*—$D_0^\circ(H_2)$ has been accurately determined to be 36,116 ± 6 cm^{-1} by Beutler [36, 166, 217]. Using modern conversion factors, this is 103·24 kcal $mole^{-1}$, and conversion to 25° C gives $D = 104{\cdot}18$ kcal $mole^{-1}$, whence $\Delta H_f^\circ(H)_{25^\circ C} = 52{\cdot}09$ [529]. In the original paper, Beutler gave $D_0^\circ(H_2) = 102{\cdot}72$ kcal $mole^{-1}$, an older value for the conversion factor from cm^{-1} having been used. This is the origin of the commonly quoted value of $\Delta H_f^\circ(H)_{18^\circ C} = 51{\cdot}7$ kcal $mole^{-1}$. There are no results in disagreement with this well established value.

8.2.2.3. *Lithium*—The vapour pressure date on liquid lithium reported in the literature do not agree, but Kelley [259], Gordon [184], and Bichowsky and Rossini [38], who have considered the data, all prefer those of Hartmann and Scheider [207]. However, Kelley deduces $\Delta H_{25^\circ C}$ 35·66 kcal, while Gordon and also Bichowsky and Rossini deduce 38·24 kcal for Li(liq.) → Li(g). Bichowsky and Rossini explicitly neglect the effect of Li_2 molecules in the gas phase, and Kelley implicitly does so, whereas Gordon takes account of Li_2. Values between 36·4 and 39·0 kcal for $\Delta H_f(Li; g)_{25^\circ C}$ may apparently be derived from the data. The National Bureau of Standards has chosen 37·07 kcal [529]. Clearly the data do not warrant the ascription of figures after the decimal point.

8.2.2.4. *Beryllium*—The most recent measurement of the vapour pressure of beryllium is due to Holden, Speiser, and Johnston [228], who used both the Langmuir rate of evaporation method and the Knudsen method. A third law calculation of ΔH_0° for vaporization showed no drift over a temperature range from 1,172° to 1,552° K, with a mean value of 76·57 ± 0·37. Previous measurements in this temperature range [442] gave a bad trend in third law

Table 8.2.1.1. Heats of formation of gaseous atoms from the elements in their standard states

Atomic number	*Element*	*Standard state*	*Heat of formation of gaseous atom* (kcal) *at* 298·16° K (25° C)		
			Bichowsky and Rossini [38]	*N.B.S.* 500 [529]	*This work*
1	*Hydrogen*	H_2; g	51·90	52·089	52·09
3	*Lithium*	Li; c	39·0	37·07	38
4	*Beryllium*	Be; c	75	76·63	76·5
5	*Boron*	B; c	115	97·2	?
6	*Carbon*	C; c (graphite)	170>, >110	171·698	~138?
7	*Nitrogen*	N_2; g	85·1	85·57	85·57?
8	*Oxygen*	O_2; g	59·10	59·159	59·16
9	*Fluorine*	F_2; g	31·75	18·3	18·5
11	*Sodium*	Na; c	25·9	25·98	26·0
12	*Magnesium*	Mg; c	36·3	35·9	35·9
13	*Aluminium*	Al; c	55	75·0	75
14	*Silicon*	Si; c	85	88·04	89
15	*Phosphorus*	P; c (*yellow*)	31·6	75·18	75·3
16	*Sulphur*	*S*; c (*rhombic*)	66·3	53·25	66·3?
17	*Chlorine*	Cl_2; g	28·90	29·012	28·94
19	*Potassium*	K; c	19·8	21·51	21·5
20	*Calcium*	Ca; c	47·8	46·04	46
21	*Scandium*	Sc; c	70	93	?
22	*Titanium*	Ti; c	100	112	112·6
23	*Vanadium*	V; c	85	120	122
24	*Chromium*	Cr; c	88	80·5	94·0
25	*Manganese*	Mn; c	74	68·34	68
26	*Iron*	Fe; c	94	96·68	99
27	*Cobalt*	Co; c	85	105	102
28	*Nickel*	Ni; c	85	101·61	101
29	*Copper*	Cu; c	81·2	81·52	81
30	*Zinc*	Zn; c	27·4	31·19	31·2
31	*Gallium*	Ga; c	52	66·0	65·0
32	*Germanium*	Ge; c	85	78·44	89
33	*Arsenic*	As; c	30·3	60·64	60?

Table 8.2.1.1. Heats of formation of gaseous atoms from the elements in their standard states—continued

Atomic number	*Element*	*Standard state*	*Heat of formation of gaseous atom* (kcal) *at* 298·16° (25° C)		
			Bichowsky and Rossini [38]	*N.B.S.* 500 [529]	*This work*
34	*Selenium*	Se; c	61·0	48·37	49 ?
35	*Bromine*	Br_2; l	26·88	26·71	26·71
37	*Rubidium*	Rb; c	18·9	20·51	20·5
38	*Strontium*	Sr; c	47	39·2	39·2
39	*Yttrium*	Y; c	90	103	?
40	*Zirconium*	Zr; c	110	125	142
41	*Niobium*	Nb; c	—	184·5	185
42	*Molybdenum*	Mo; c	160	155·5	155·5
44	*Ruthenium*	Ru; c	120	160	?
45	*Rhodium*	Rh; c	115	138	?
46	*Palladium*	Pd; c	110	93	?
47	*Silver*	Ag; c	68	69·12	65
48	*Cadmium*	Cd; c	26·8	26·97	27
49	*Indium*	In; c	52	58·2	?
50	*Tin*	Sn; c	78	72	70
51	*Antimony*	Sb; c	40	60·8	61
52	*Tellurium*	Te; c	55	47·6	48
53	*Iodine*	I_2; c	25·59	25·482	25·48
55	*Caesium*	Cs; c	18·8	18·83	18·8
56	*Barium*	Ba; c	49	41·96	42
73	*Tantalum*	Ta; c	—	185	185
74	*Tungsten*	W; c	210	201·6	202
75	*Rhenium*	Re; c	—	189	?
76	*Osmium*	Os; c	125	174	?
77	*Iridium*	Ir; c	120	165	?
78	*Platinum*	Pt; c	127	121·6	122
79	*Gold*	Au; c	92	82·29	84
80	*Mercury*	Hg; l	14·60	14·54	14·65
81	*Thallium*	Tl; c	40	43·34	43
82	*Lead*	Pb; c	47·5	46·34	46
83	*Bismuth*	Bi; c	47·8	49·7	?
92	*Uranium*	U; c	220	125	?

values, but gave a second law value in fair agreement with Holden *et al.* For $\Delta H_f^\circ(\mathrm{Be;\ g})_{25^\circ\mathrm{C}}$ the N.B.S. chose 76·63 kcal[529], but here again the absolute accuracy is less than indicated by this.

8.2.2.5. *Boron*—The present author does not know of any direct experimental evidence relating to the heat of atomization of boron. The N.B.S. suggest 97·2 kcal, which is 'calculated'[529]. Bichowsky and Rossini[38] estimate 115 kcal. The International Critical Tables give, rather dubiously, 2,550° K for the boiling point of elementary boron. This may be derived from the observation that boron volatilizes to a considerable extent when melting in a vacuum at a temperature about 2,500° C[560], which would favour the lower estimate. Some experimental work is clearly called for, both on boron itself, which is of course very difficult to obtain pure, and perhaps if possible on the stepwise dissociation of BCl_3 by electron impact methods.

8.2.2.6. *Carbon*—The heat of atomization of carbon has been a controversial topic for many years[166, 313, 463] and there is no final agreement on its value. The present discussion does not pretend to offer a certain solution to the problem, but outlines the evidence and reaches the tentative conclusion that $L_C = 138 \pm 3$ kcal, where L_C is written for convenience for $\Delta H_f^\circ(\mathrm{C;\ gas})$ at 0° K.

The heat of atomization may be arrived at in two ways: (*a*) by direct measurement of the pressure of C atoms in equilibrium with solid carbon (graphite) at various temperatures, or (*b*) by determining the heat of atomization of a carbon-containing compound of known heat of formation. This is only useful, of course, if the other atoms formed themselves have known heats of formation. Carbon monoxide is the compound most commonly used in this connection.

(*a*) *Direct methods**. In 1933 Marshall and Norton published a brief account of their measurement of the rate of loss of weight of carbon rings heated by high-frequency induction in a vacuum. More recently, in 1950, they published details of the work[340]. They assumed that the rate of evaporation in a vacuum was given by Langmuir's expression[293],

$$m = a(M/2\pi RT)^{\frac{1}{2}}p$$

where m is the rate of evaporation, p is the vapour pressure, a is the accommodation coefficient and the other symbols have their usual significance. They further assumed that $a = 1$, and that carbon atoms were the main species evaporating from a heated carbon

* References to early work on this subject are given by Bichowsky and Rossini[38]; only the more recent work is discussed here.

surface. From their measurements and with these assumptions they derived $L_C = 175{\cdot}2$ kcal (g atom)$^{-1}$. More recently, measurements of the rate of evaporation of carbon from a heated carbon surface in a vacuum in which the atomic and molecular species evaporating were identified by means of a mass spectrometer have been made by Chupka and Inghram [77, 78]. Their method employs mass analysis of the ions produced by electron bombardment of the vapour from the hot carbon. The ionizing electrons were of such low energy that ions were generally produced only from the corresponding neutral species; an electron-multiplier for ion detection was used to overcome the disadvantage of low ion intensities. It was found that the relative intensities of the ions C^+, C_2^+, and C_3^+ from a graphite filament at 2,450° K using 17 V electrons were 1·0, 0·5, and 1·6, and it was considered that these figures expressed the approximate relative concentrations of these species. Thus the view that the main evaporating species is atomic carbon is not correct. However, the dependence of the intensity of C^+ on temperature should give the dependence of the rate of production of C on temperature, and thus the activation energy of sublimation, or, assuming Langmuir's expression, the heat of vaporization. From this information the value 176 ± 6 kcal for L_C was deduced in remarkably good agreement with the value obtained by Marshall and Norton. The temperature dependence of C_2^+ and C_3^+ formation has also been determined: a value of $\Delta H(2{,}500°\text{ K})$ of sublimation of 200 ± 10 kcal mole^{-1} for both these species were obtained.

Two questions now arise; does the temperature dependence of the rate of evaporation give the heat of evaporation, and is atomic carbon directly produced at all in such experiments? The first question has been discussed by Herzberg, Herzfeld, and Teller [218], who suggest that the velocity of evaporation of carbon atoms from graphite in a vacuum yields an apparent heat of evaporation which is higher than the true one. This conclusion is based on a very simple treatment of the graphite lattice.

This is composed of planes, a corner of one of which is shown in *Figure 8.2.2.6.1.* It is assumed that all bonds in the plane are equal; the energy required to break one bond is ε. As there are three bonds originating in every carbon atom and as each bond joins two atoms the energy of evaporation per atom, L, is given by $L = \frac{3}{2}\varepsilon$. To remove an inner atom, H, from the plane three bonds must be broken, requiring an energy $3\varepsilon = 2L$. To remove an atom A from the edge of the plane two bonds only must be broken with energy $2\varepsilon = \frac{4}{3}L$. Then the atom B remains, bound

by only one bond, and this requiring an energy $\varepsilon = \frac{2}{3}L$ for its removal. Evaporation of the crystal takes place by the alternate breakage of two bonds and one bond, giving an average heat of vaporization of $\frac{3}{2}\varepsilon = L$. The same result is found on consideration of the other edge of the plane. The successive removal of atoms E and F requires the breakage of two bonds each, but thereafter the alteration of one bond and two bonds is again found.

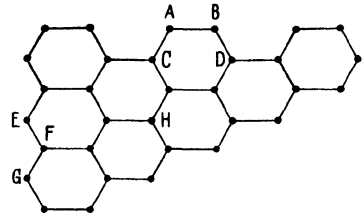


Figure 8.2.2.6.1

On the average an atom bound by two bonds will evaporate in time t_1 given by

$$t_1 = a_1 \exp\left(\frac{4}{3}\frac{L}{kT}\right)$$

where a_1 has the dimensions of time and is about 10^{-13} sec, and is almost independent of T. Similarly, t_2, the time for evaporation of atoms bound by only one bond, is

$$t_2 = a_2 \exp\left(\frac{2}{3}\frac{L}{kT}\right)$$

where a_2 is about the same as a_1.

Because t_1 is much longer than t_2 and because the second step cannot take place until after the first, the first process is rate determining. Hence the absolute rate and the temperature dependence of evaporation in a vacuum depend on the factor $\exp\left(-\frac{4}{3}\frac{L}{kT}\right)$. If Marshall and Norton's result[340] and the above argument are accepted, it follows that $L = \frac{3}{4} \times 175$ kcal mole^{-1}, or 132 kcal. The factor $\frac{3}{4}$ must only be very approximate, of course, because of the crudity of the above treatment.

We now consider the further implications of this argument. It may be shown that the correct result is obtained for the temperature dependence of the equilibrium vapour pressure. At equilibrium it is assumed that there are n_1 atoms bound by two bonds and n_2 bound by one bond. Because of the difference between t_1 and

t_2, n_1 will be very much greater than n_2 Now if it is assumed that every atom from the vapour which hits an edge sticks, and that any one which hits one of the n_1 doubly bound atoms forms a single bond, and any one which hits one of the n_2 singly bound atoms forms two bonds, it follows that most of the condensing atoms will be singly bound. Thus at equilibrium most of the evaporating atoms will be singly bound atoms which are replaced by condensation from the vapour. On the other hand, evaporation in a vacuum takes place by means of the loosely and strongly bound atoms in equal quantities.

A consequence is that the accommodation coefficient, measured by the number of atoms condensing, can be unity, but the rate of evaporation in a vacuum can be very much slower than that calculated from Langmuir's expression using an accommodation coefficient of unity.

These considerations apply generally to lattices in which each atom is surrounded by an odd number of neighbours and in which all bonds are of equal strength and are unaffected by the removal of neighbouring bonds.

It is this last assumption which has been criticized by Kynch and Penney[282]. They consider that such an over-simplification of the chemical structure of graphite robs the argument of even qualitative significance, apparently chiefly because atoms A and B are in different valence states from atoms C and D. However, the removal of A would result in a change of valence state of C, and the removal of B would result in a similar change of valence state of D, so that the effect of valence state is equal for the removal of both atoms. It is still true that the removal of A involves the breakage of the bonds AC and AB, whereas the removal of B only requires the breakage of bond BD. They also argue that after removal of A, the bond BD is likely to become more strongly bound; they suggest by a double bond to D. Though this may be, it will involve the expenditure of some promotional energy in altering the valence state of D, and the qualitative conclusion that it is likely to be more difficult to remove A than to remove B, and that the heat of evaporation per atom must be the average of these two quantities, remains valid. It may be concluded, therefore, that measurement of the rate of evaporation of carbon atoms from graphite is liable to give a high result—by a proportion up to 25 per cent for the heat of evaporation, and that the apparent 'accommodation coefficients' for condensation and evaporation may be different.

The second question, that of whether evaporation of carbon atoms as such takes place at all, cannot be answered on the basis of the present evidence. The results of Chupka and Inghram[78] show

that C_3 is a species of major importance, and the very recently reported mass spectrometric study by Honig[229a] suggests that the production of C is closely linked to that of C_3. Application of the ideas of Herzberg, Herzfeld, and Teller[218] to the evaporation of C_3 from a graphite lattice gives the result that a similar effect to that predicted for atomic carbon, though not so pronounced, might be expected. Here the successive removal of C_3 molecules from the edge of a graphite plane requires the alternate rupture of three bonds and two bonds, if one type of edge is considered, or the rupture of two sets of three bonds and two sets of two bonds per pair of molecules, if the other type of edge is considered.

If the foregoing arguments are valid, one would expect that attempts to measure the equilibrium vapour pressure of graphite using the Knudsen effusion method would give low results, and consequently high results for the heat of vaporization, unless the ratio of the internal area of the Knudsen cell to the area of the hole were very large. This is because of the expected very low 'accommodation coefficient' for the evaporation of carbon atoms from a graphite surface under non-equilibrium conditions. On the other hand, one would not observe a low accommodation coefficient for the condensation of carbon atoms on graphite. In 1948, Brewer, Gilles, and Jenkins[51] reported measurements of the amount of carbon volatilized from a Knudsen cell at high temperatures, from which they concluded that $L_C = 170{\cdot}4$ kcal mole^{-1}. Their experimental results yielded values lying around this figure, apart from those given by the first two runs, which were lower (155 and 162 kcal) by a fairly small amount attributed by the authors to the presence of small residual amounts of more volatile tars. The amount of carbon volatilized was burned in a micro-combustion apparatus and determined as carbon dioxide. Two different surface area–hole area ratios, 250 : 1 and 600 : 1, were used, similar results being obtained with each. It was concluded from this that the accommodation coefficient must be greater than 0·004, and comparison of their results with those of Marshall and Norton suggested a value of about 0·3 for this coefficient. These workers also measured spectroscopically the partial pressure of C_2 in equilibrium, and concluded that there was less than 1 per cent of C_2 present at a temperature as high as 3,500° K. The mass spectrometric results of Chupka and Inghram show that this last conclusion is probably in error, and it has been suggested by Norrish, Porter, and Thrush[372] that the ground state of the C_2 molecule has not been correctly identified. The suggestion that much more C_2 is present than was estimated by Brewer, Gilles, and Jenkins has also

been made independently by Waelbroek[542]. The low apparent vapour pressure of carbon and consequently high heat of vaporization is not affected by the proportion of C_2. In an attempt to clarify the situation Doehaerd, Goldfinger, and Waelbroek[114] experimented with a much wider range of surface area–hole size ratios in a Knudsen cell than had been used by Brewer. They found that the apparent vapour pressure increased with decreasing hole size, and that their results lead to $L_C = 141{\cdot}9$ kcal. They obtained the same results as did Brewer if they used the same surface area–hole area ratio, and conclude that the accommodation coefficient for carbon is very small, possibly less than 10^{-3}. They measured the amount of carbon vaporized by measuring the optical density of a carbon deposit on a glass plate. Brewer has suggested that there is a logical inconsistency in their results, in that they lead to a very low accommodation coefficient for carbon of which no account is taken in determining the amount of carbon deposited on the plate. This, however, does not involve logical inconsistency if the views of Herzberg, Herzfeld, and Teller are correct, and indeed the above-mentioned experiments do much to vindicate at least their qualitative correctness.

The position is still not completely clear, because direct evidence on the molecular species effusing from a Knudsen cell at equilibrium is not available. It is the present author's opinion, however, that the direct measurements seem to favour a value of about 140 kcal.

(*b*) *Indirect methods.* (*i*) Carbon monoxide. The heat of formation of carbon monoxide from its atoms in their standard states is well known, and so is the heat of formation of atomic from molecular oxygen. Thus if the energy of dissociation of carbon monoxide to gaseous carbon and oxygen atoms in their ground states were known, the heat of formation of atomic carbon could be established. Unfortunately $D(CO)$ is still controversial. An account of the present position follows.

Electron impact measurements on the dissociation of CO have been most detailed, and an account of the work is given in Section 5.2. They lead to $D(CO) = 9{\cdot}6 \pm 0{\cdot}2$ eV, whence $L_C = 136 \pm 4$ kcal, and as far as can be seen do not admit of any other interpretation. Gaydon's criticism of them is also discussed in Section 5.2.

Spectroscopic evidence depends largely on predissociations and is difficult to interpret. It has been discussed at length by Gaydon[166] and by Herzberg[217], and from it four values of $D(CO)$ can be obtained: 11·11, 9·85, 9·61, and 9·14 eV, leading to $L_C = 170{\cdot}4$, $141{\cdot}3$, $135{\cdot}8$, and $125{\cdot}0$ kcal respectively[166]. The first of these values is preferred by Gaydon, the last by Herzberg. None

of them offers a completely satisfactory explanation of all the observed features of the spectrum, but presumably one of them must be correct. Pauling and Sheehan[384] have made a suggestion which at least partially reconciles Gaydon's preference for $D(CO) = 11{\cdot}11$ with a lower value. One of Gaydon's reasons for advancing this high value is that it is obtained by a Birge-Sponer extrapolation of the vibrational levels of the ground state. Pauling postulates that the linear Birge-Sponer extrapolation leads to the dissociation energy of the atoms in their 'valence states', and that the true dissociation energy is less than this by an amount equal to the promotional energy of the atoms from their ground states to the valence states. The departure from linearity of a Birge-Sponer extrapolation at large vibrational energies is an indication that the electronic state of the combined atoms is changing. An estimate of the valence states of the atoms in carbon monoxide and comparison with CN leads to $D(CO) = 9{\cdot}77$ eV and $L_C = 140$ kcal. Long[314] has pointed out an inconsistency in Pauling and Sheehan's argument, and shows that more detailed consideration of valence states leads to $D(CO) = 9{\cdot}14$ eV. They agree that the high value is excluded.

Decomposition of carbon monoxide takes place when it is exposed to radiation of wavelength 1,295 Å, but not when exposed to 1,470 Å[150]. Herzberg[215] has concluded from this that $D(CO) \leqslant 9{\cdot}57$ eV, but Gaydon[166] has pointed out that when vibrational and rotational energy are taken into account the upper limit may be as high as 10·1 eV, and further that it is not established that photodissociation is the primary act in the reaction.

Thus evidence from the dissociation energy of carbon monoxide obtained spectroscopically can be used to support either of the values obtained by direct measurement of the heat of vaporization of carbon, whereas the electron impact results are compatible only with the lower.

(*ii*) Methane and its derivatives. Measurement of the appearance potential of C^+ from CH_3X using the electron impact method has been used to give information about the heat of atomization of carbon[48]. If ΔH_f is the heat of the following reaction:

$$C_{\text{graphite}} + \tfrac{3}{2}H_2 + \tfrac{1}{2}X_2 = CH_3X$$

then

$$D(C-3H-X) = \tfrac{3}{2}D(H_2) + \tfrac{1}{2}D(X_2) + L_C - \Delta H_f$$

where $D(C-3H-X)$ is the energy required to atomize CH_3X completely. Now if, in the mass spectrometer, the production of C^+ is accompanied by the production of the other atoms only, then

$A(C^+) = D(C-3H-X) + I(C^+)$ + translational + excitational energy, where $A(C^+)$ is the appearance potential of C^+ and I is its ionization potential. The amount of translational and excitational energy will in general not be known, but it is likely to vary as the atom X varies. Substituting for $D(C-3H-X)$ in the expression for $A(C^+)$ allows one to estimate an upper limit to L_C from measured $A(C^+)$ for various compounds, and Branson and Smith found the results given in *Table 8.2.2.6.1*. Their value of $A(C^+)$ from methane

Table 8.2.2.6.1

Compound	$A(C^+)$ V	ΔH_f°(C; gas) kcal
CH_4	26·9 ± 0·2	≤139 ± 5
CH_3Cl	26·0 ± 0·3	≤137 ± 7
CH_3Br	25·4 ± 0·4	≤140 ± 10
CH_3I	24·4 ± 0·4	≤136 ± 10

is in fair agreement with the value obtained by McDowell and Warren[331], who deduce $\Delta H_f^\circ(C; gas) \sim 120$–$140$ kcal from their measurements on methane. It can be seen from the ionization efficiency curve for C^+ reproduced in their paper that the precise determination of $A(C^+)$ is not easy, and a fairly large uncertainty in the final result must be allowed. They obtain a difference of 1 eV for $A(C^+)$ in two different interpretations of the curve, corresponding to the uncertainty 120~140 kcal for the heat of atomization of carbon. It is thus possible that Branson and Smith have overestimated the accuracy of their results.

There is an interpretation of the results which would allow us to obtain the high value of the heat of atomization of carbon, although it is rather a strained one. If the dissociative ionization process yields C^+, H_2, H, and X, instead of C^+, 3H, and X, as originally assumed, the derived upper limit for the heat of atomization of carbon is increased by $D(H_2)$ or about 103 kcal, thus becoming $\Delta H_f^\circ(C; gas) \leq 240$ kcal. This allows any of the presently canvassed values for this quantity, if the appropriate amount of kinetic or excitational energy is assumed. This is 3 eV for $L_C = 170$ kcal, and correspondingly more for other estimates. It seems unlikely that this explanation is correct, particularly in view of McDowell's work, but the possibility exists.

Another method of obtaining L_C from methane would be to determine $D(CH_3-H)$, $D(CH_2-H)$, $D(CH-H)$ and $D(C-H)$, which would give the heat of atomization of methane and hence the

heat of atomization of carbon. Only the first and last of these quantities are known with certainty, but we may deduce from them and established thermochemistry that $D(CH_2-H)+D(CH-H)$ must be 211, 182, 177, and 166 kcal, corresponding to L_C 170, 141, 136, and 125 respectively[463]. $D(CH_2-H)+D(CH-H)$ may be deduced from McDowell and Warren's value for $A(CH^+)$ in methane to be ~160 kcal, but this is subject to considerable uncertainty, because of the difficulty of measuring A for ions of low relative intensity. Other workers have found a value for $A(CH^+)$ higher than theirs by up to 2 eV, corresponding to values of $D(CH_2-H)+D(CH-H)$ of up to 180 kcal. The high value of L_C seems to be excluded by this evidence. Laidler and Casey[287] have assumed $L_C=170$ kcal and have argued from $D(CH_2-H)<87$ kcal, as deduced from experiments of Bawn and Dunning on the reaction between sodium vapour and methylene chloride[26], that $D(CH-H)$ is greater than 125 kcal. They have given arguments to suggest that this is plausible. This result is difficult to reconcile with electron impact processes in methane, and also with the electron impact results for methyl cyanide[332]. Kistiakowsky and Rosenberg[270] deduced $D(CH_2-H)>71$ kcal from a study of the mechanism of the photochemical decomposition of ketene, the primary step in which is the formation of methylene and carbon monoxide. They concluded that $D(CH_2-H)$ is probably about 80 kcal, and if they are correct, then $D(CH-H)$ must be greater than 130 kcal, if $L_C=170$ kcal, a result which of course is even more difficult to fit to the electron impact evidence.

(*iii*) Other indirect evidence. The heat of atomization of carbon is linked with that of nitrogen, the heat of formation and dissociation of cyanogen and $D(CN)$ by a thermochemical cycle[313, 462]. Many of these quantities are not certainly known, and arguments using them are therefore less direct than the present author considers desirable. Long prefers a value of about 130 kcal on this basis[313]. Indirect evidence on $D(CO)$ is that adduced from gaseous detonations by Kistiakowsky[268] discussed earlier in Section 3.5. This leads to $D(CO)=11{\cdot}11$ eV, and consequently to $L_C=170$ kcal. This again depends on the reliability of a large amount of other information.

Another kind of indirect evidence is that provided by the way in which bond energies calculated on various assumptions about L_C fit into schemes connecting bond energy with length and other properties. This type of evidence seems to the present author easily to lead to circular arguments, and it will not be discussed further here.

Taking all the above evidence into account, it seems to the author that L_C is about 140 kcal, corresponding to a spectroscopic value of $D(CO)$ of 9·85 or 9·61 eV. Allowing for the possible correctness of either of these possibilities, it seems fairly safe to conclude that $L_C = 138 \pm 3$ kcal, and in view of the remaining uncertainty, it seems reasonable to put $\Delta H_f^\circ(C;\ gas)_{25^\circ C} \sim 138$ kcal. It is fair to summarize the main objections to this point of view, which are Brewer's results using a small variation of hole size in the Knudsen method of direct determination, Kistiakowsky's detonation determination of $D(CO)$, and the fact that 9·61 and 9·85 eV, though there is some spectroscopic evidence in their favour, are not on the whole so well supported by the spectroscopic evidence as 9·14 and 11·11 eV for $D(CO)$. More or less plausible counter-objections can be raised against these however, whereas the author has not seen any satisfactory objection to the electron impact results on $D(CO)$, nor has he been able to think of any himself. The main need at present is not to provide a new method of determining L_C, but to show why some of the apparently sound methods used up to now do not in fact give the true value of L_C.

8.2.2.7. *Nitrogen*—The standard state of nitrogen is the diatomic molecular gas, and the heat of atomization of nitrogen is thus $\frac{1}{2}D(N_2)$. The direct spectroscopic determination of $D(N_2)$, like that of $D(CO)$ depends upon predissociations which are difficult to interpret. There are two possible values, the higher 9·76 eV, being favoured by Gaydon [166], and the lower 7·38 eV, by Herzberg [217]. The electron impact measurements have been discussed in detail by H. D. Hagstrum [198]; only his conclusions are presented here. The type of evidence is the same as discussed for CO in Section 5.2. Production of N^+ from N_2 allows for $D(N_2)$ the values 9·8, 7·9, 7·4 eV, and other lower values which may be ruled out from spectroscopic considerations, depending upon the (unknown) state of excitation of the nitrogen atoms obtained. The position is analogous to that in the spectroscopic work where the choice of the values 9·76 and 7·38 depends upon the assumed state of excitation of the products from the well established predissociation at 12·145 eV. Indirect evidence must therefore be used, and the molecule NO, the heat of formation of which is known and has recently been confirmed [277], is the obvious source. Since we know $D(O_2)$, we can determine $D(N_2)$ from $D(NO)$. Unfortunately D(NO) is not certainly known from spectroscopic measurements. The high value of $D(N_2)$ corresponds to $D(NO) = 6{\cdot}49$ eV, the low value to 5·29 eV, but although some of the spectroscopic evidence appears to favour the higher value for $D(NO)$ [166] this interpretation

has been challenged[217]. The electron impact evidence is more compelling. Consideration of a variety of dissociative ionization processes in NO leads Hagstrum[198] to the conclusion that $D(NO) = 5{\cdot}8$ eV. Any interpretation of the electron impact results to favour a value of 6·5 eV is extremely forced, and implies that the methods of detection of kinetic energy in the products are very much less sensitive than they appear to be. Thus the electron impact results give $D(N_2) = 7{\cdot}38$ eV, and this seems to settle the matter. The only other simple relevant molecule from which conclusions about $D(N_2)$ may be drawn is CN. Unfortunately the value of the heat of atomization of carbon is required, and this is itself uncertain. Further, the dissociation energy of CN cannot itself be determined certainly from spectroscopic evidence. The adoption of the lower value of $D(N_2)$ means, however, that the value of $D(CN)$ must be much less than that obtained by a Birge-Sponer extrapolation.

$D(N_2)$ has also been determined by the flame and by the detonation method, and the experiments have been described and discussed in Section 3.5. Both measurements favour the higher value, as does the hot wire method[151]. Although these results are disturbing, it is possible to advance more or less plausible reasons for doubting them (*see* Section 3.5), whereas it does not appear possible on the present evidence to deny the validity of the electron impact results. The author has therefore chosen $D(N_2) = 7{\cdot}38$ eV, or $\Delta H_f^\circ(N)_{25^\circ C} = 85{\cdot}57$ kcal[529].

The author confesses that he makes this choice with some reluctance, because he thinks that $D(CO)$ and $D(N_2)$ should be close together. Since $D(CO) = 9{\cdot}85$ or 9·61 eV, $D(N_2) = 9{\cdot}76$ would be a very plausible value. However, it is the policy in this book to stick as closely as possible to what appear to be the least easily controvertible experimental results, and so $D(N_2)$ is provisionally taken as the lower value.

8.2.2.8. *Oxygen*—The standard state of oxygen is the diatomic molecular gas, and its heat of atomization is therefore $\frac{1}{2}D(O_2)$. Here the spectroscopic dissociation energy is derived from the convergence of a series of absorption bands (Schumann-Runge bands) to a very clear limit followed by a continuum. The convergence limit corresponds to 7·047 eV. There is no ambiguity in the choice of the states of the oxygen atoms produced: the products of the dissociation must be $O(^3P)$ and $O(^1D)$ whence $D(O_2) = 5{\cdot}080$ eV, and $\Delta H_f^\circ(O;\ g)$ at $25^\circ C = 59{\cdot}16$[529].*

* A very recent revision of $D_0^\circ(O_2)$ to $5{\cdot}114_8 \pm 0{\cdot}002$ eV (117·96 kcal)[58a] was not available in time for general incorporation in this book.

8.2.2.9. *Fluorine*—The standard state of fluorine is the diatomic molecular gas F_2, so that the heat of atomization of fluorine is $\frac{1}{2}D(F_2)$. $D(F_2)$ has been determined by direct measurement of the equilibrium pressure [116] leading to 37·4 kcal at 25° C, by the effusion method [575] leading to 39·9 kcal, and, less directly, by the explosion method, using a hydrogen–fluorine mixture [568], leading to37 kcal. The excellence of the agreement of these three thermal measurements leaves little doubt that the correct value is about 37 kcal.

For a long time, however, the value $D(F_2) = 63{\cdot}5$ kcal [557] was accepted. This was based on spectroscopic data for fluorine and the other halogens. The absorption spectrum of fluorine is continuous so that $D(F_2)$ cannot be obtained from band convergence limits. The dissociation energies of the other halogens can be so obtained. Therefore the values of λ_m, the wavelength at which continuous absorption shows a maximum, were listed for all four halogens. For the halogens other than fluorine, λ_c, the wavelength of the convergence limit, was known, and a plot of $\lambda_c - \lambda_m$ against atomic weight was found to give a very good straight line which was extrapolated to give λ_c for fluorine and $D(F_2)$. Clearly this method is likely to be unreliable, and direct observation on the spectrum of ClF, leading to $D(Cl-F)$ combined with the heat of formation of ClF, led to a much lower estimate of $D(F_2)$ [544]. The heat of formation of ClF, however, was not certainly known, and further work was required. A detailed account of this work, with references, together with a consideration of other evidence up to the end of 1949, has been given by Evans, Warhurst, and Whittle [148], who concluded that the most probable value was 37 kcal. A less direct spectroscopic attack on the problem has been made by Barrow and Caunt [17], who obtain upper limits for the dissociation energies of the twelve potassium, rubidium, and caesium halides, and combine these results with thermochemical information about these molecules to obtain $D(F_2) = 37{\cdot}6 \pm 3{\cdot}5$ kcal, at 25° C.

It remains to point out that there is some evidence in conflict with the low value. Hot wire measurements of thermal conductivity [160] apparently do not admit values of $D(F_2)$ less than 45 kcal, and measurements of flame temperature in the stoichiometric hydrogen–fluorine flame also lead to a high value [5]. In view of the weight of evidence for the low value, these results can only serve to cast doubt on the methods by which they were obtained. In particular the disagreement between the results from the hydrogen–fluorine flame and the hydrogen–fluorine explosion methods, and the probable correctness of the latter, reflects directly on the flame method, because similar subsidiary data are required in each case.

8.2.2.11. *Sodium*—The heat of vaporization of sodium to sodium atoms is determined from a large amount of concordant vapour pressure data, which according to the N.B.S.[529] lead to $\Delta H_f^\circ(\mathrm{Na;\ g})_{25^\circ\mathrm{C}} = 25{\cdot}98$ kcal. The data are reviewed by Gordon[184] and Kelley[259].

8.2.2.12. *Magnesium*—Vapour pressure data reviewed by Kelley[259] lead to $\Delta H_f^\circ(\mathrm{Mg;\ g})_{25^\circ\mathrm{C}} = 35{\cdot}9$ kcal.

8.2.2.13. *Aluminium*—Vapour pressure data on aluminium have been given by Baur and Brunner[25], which lead to a boiling point of 2,543° K. Kelley[259] took a weighted mean value of 2,330° K from two earlier results of 2,073 and 2,473° K, and deduced $\Delta H_{25^\circ\mathrm{C}}$ for vaporization of solid aluminium to be 67·50 kcal. Long and Norrish[319] deduce 84·4 kcal by second law methods based on the work of Baur and Brunner[25] as reviewed by Ditchburn and Gilmour[113]. The N.B.S. choose $\Delta H_f^\circ(\mathrm{Al;\ g})_{25^\circ\mathrm{C}} = 75{\cdot}0$ kcal[529], which appears to be a further weighted mean of all these results, although they also refer to unpublished work of L. Brewer. We adopt this value in default of better.

8.2.2.14. *Silicon*—A detailed discussion of the data on the vaporization of silicon has been given by Baughan[24], who gives the value $\Delta H_f^\circ(\mathrm{Si;\ g})_{25^\circ\mathrm{C}} = 89{\cdot}9$ kcal. This is close to the value given by the N.B.S.[529] on the basis of Baur and Brunner's work, and that the true value lies between 85 and 90 kcal is well established.

A much higher value, 102 kcal, has been suggested on the basis of a very indirect argument by Emeléus, Maddock, and Reid[145], and by Skinner[452], but the evidence is not compelling.

8.2.2.15. *Phosphorus*—The heat of formation of phosphorus atoms is deduced from the following thermochemical cycle:

$$\begin{aligned}
4\mathrm{P(c,\ yellow)} &\rightarrow \mathrm{P_4(g)} \quad \Delta H_1 \\
\mathrm{P_4(g)} &\rightarrow 2\mathrm{P_2(g)} \quad \Delta H_2 \\
\mathrm{P_2(g)} &\rightarrow 2\mathrm{P(g)} \quad \Delta H_3 = D(\mathrm{P_2}) \\
\Delta H_f(\mathrm{P;\ g}) &= \tfrac{1}{4}(\Delta H_1 + \Delta H_2 + 2\Delta H_3)
\end{aligned}$$

The literature on these reactions has been discussed by Stevenson and Yost[479]. From vapour pressure data $\Delta H_{1\ 25^\circ\mathrm{C}}$ is deduced to be 13·20 kcal, which is in agreement with Kelley's estimate of 13·13 kcal[259]. ΔH_2° at 0° K is deduced to be 53·61 kcal from molecular data and the equilibrium measurements of Stock *et al.*[481] from which $\Delta H_{2\ 25^\circ\mathrm{C}} = 54{\cdot}5$ kcal. The same equilibrium was measured by Preuner and Brockmöller[398], whose results lead to a value of $\Delta H_{\circ 2}^\circ$ which drifts badly with temperature, and which may therefore be disregarded. $D(\mathrm{P_2})$ has been determined

spectroscopically, and Herzberg[217] gives the value 5·031 eV, or 116·0 kcal, whence $\Delta H_{3\ 25°C} = 116·8$, although Stevenson and Yost give 5·008 eV. Thus $\Delta H_f^\circ(\mathrm{P};\ g)_{25°C} = 75·3$ kcal. The N.B.S.[529] give 75·18 on the basis of the very slightly lower value of $D(P_2)$.

8.2.2.16. *Sulphur*—The heat of formation of atomic sulphur is not certainly known. The most satisfactory route to it is via the processes

$$\mathrm{S(rhombic)} \rightarrow \tfrac{1}{2}\mathrm{S_2(g)} \quad \Delta H_1$$
$$\tfrac{1}{2}\mathrm{S_2(g)} \rightarrow \mathrm{S(g)} \quad \Delta H_2 = \tfrac{1}{2}D(\mathrm{S_2})$$
$$\Delta H_f^\circ(\mathrm{S};\ g) = \Delta H_1 + \Delta H_2$$

The vapour pressure of sulphur in the temperature region in which S_2 is an important species in the vapour is accurately known (*see* Kelley[259] for references) and Lewis and Randall[304] have deduced $\Delta H_{1\ 25°C} = 14·85$ kcal. Kelley has obtained a similar result. $D(S_2)$ is, however, controversial. The spectroscopic data admit 4·4, 3·6, or 3·3 eV[166].

Goldfinger *et al.*[181] have pointed out that if dissociation at 4·4 eV took place to S(^{3}P) and S(^{1}D), instead of to the normal(^{3}P), the value of 3·3 eV would be obtained, and they contended that this value is in much better agreement with the high temperature vapour density data than is the higher. They refer to the vapour density data of Nernst[364] and of von Wartenberg[553]. Bichowsky and Rossini[38] deduced $D(S_2) = 48$ kcal or 2·1 eV, from Nernst's results, which is clearly impossible to reconcile with any of the spectroscopic values. Von Wartenberg reports values of 42, 50, and 57 for the average molecular weight of the gas produced from 0·18, 0·33, and 0·48 mg sulphur respectively, at a temperature of 2,343° K. These results are not compatible with the view that the only molecular species present are S and S_2, because the equilibrium 'constant' calculated from them on this assumption is far from constant. Thus the internal evidence suggests that the results are rather rough, and von Wartenberg himself deduces $D(S_2) = 90$ kcal. In an earlier paper dealing with vapour density of silver using the same method von Wartenberg[552] publishes curves of vapour pressure against time as the substance to be vaporized is dropped into his apparatus, showing the uncertainty of the maximum pressure reached. These do not inspire confidence. A seemingly plausible extrapolation to maximum pressure gave the result that the average molecular weight of silver vapour was less than the atomic weight. An earlier investigation[39] of the vapour density of sulphur vapour at 1,992° K gave a value within 2 per cent of the theoretical for S_2.

This disagreement among the vapour density results makes it seem unreasonable to use this information to deduce $D(S_2)$ [352], and the spectroscopic possibilities remain, leading to $\Delta H_f^\circ(S;\ g)$ values of 53, 56, and 66 respectively. The lowest value is favoured by the N.B.S.[529], the middle value corresponds to the $D(S_2)$ value favoured by Herzberg[217], and the highest to the $D(S_2)$ value favoured by Gaydon[166], and also adopted by Bichowsky and Rossini[38].

Another approach may be through the cycle involving SH:

$$\begin{aligned} S(\text{rhombic}) + \tfrac{1}{2}H_2(g) &\rightarrow SH(g) && \Delta H_3 \\ SH &\rightarrow S(g) + H(g) && \Delta H_4 = D(SH) \\ H(g) &\rightarrow \tfrac{1}{2}H_2(g) && \Delta H_5 \\ \Delta H_f^\circ(S;\ g) &= \Delta H_3 + \Delta H_4 + \Delta H_5 \end{aligned}$$

ΔH_5 is of course well known, and values have been suggested for ΔH_3 and ΔH_4. ΔH_3 is the heat of formation of the SH radical, and this has been investigated using electron impact methods by Franklin and Lumpkin[161]. They measured the appearance potential of some alkyl ions from mercaptans, the reactions being

$$RSH + e \rightarrow R^+ + SH + 2e$$

With the usual assumption of little kinetic energy, these appearance potential values may be combined with the known heats of formation of the mercaptans[16] and of the gaseous alkyl ions[477, 478] to give the heat of formation of SH. Their results for ΔH_3 are 36·9, 44·4, and 33·9 kcal, derived from ethyl, *n*-propyl, and *t*-butyl mercaptan respectively, and they adopt the value 38·4 kcal, although the figure after the decimal point would appear to be meaningless. In view of the fact that strictly speaking these are upper limits and the discrepancies may be due to real kinetic energy effects, it would perhaps be better to choose 34 kcal for ΔH_3. Porter[395] has described the absorption spectrum of SH, and deduced $D(SH)$ to be 85 ± 5 kcal. This value is obtained by a linear Birge-Sponer extrapolation for the upper state, the products from which are identified by analogy with OH. Also by analogy with OH, it is assumed that the linear extrapolation gives a result 25 per cent too high. Under these circumstances Porter's estimate of the error seems perhaps a little optimistic. It is, however, consistent with a more detailed analysis of the spectrum by Ramsay[409]. Combining these figures with the known value for ΔH_5, we obtain 67 kcal for the heat of formation of atomic sulphur, in agreement with the high value for $D(S_2)$ (*see*, for example, Friedman[162]). Similar

thermochemical considerations for SnS lead to the same result[18]. We therefore follow Bichowsky and Rossini[38] and put $\Delta H_f^\circ(S; g)_{25^\circ C} = 66{\cdot}3$ kcal.

8.2.2.17. *Chlorine*—The dissociation energy of chlorine has been accurately established spectroscopically using a band convergence limit[166, 217]. If $D(Cl_2) = 2{\cdot}476$ eV, $\Delta H_f(Cl; g)_{25^\circ C}$ is 28·94 kcal.

8.2.2.19. *Potassium*—There is a large amount of information, reviewed by Kelley[259], on the vapour pressure of potassium. He deduces $\Delta H_f^\circ(K; g)_{25^\circ C} = 21{\cdot}51$ kcal, and this value is adopted by the N.B.S.[529]. Gordon[184], considering the same data, gave an equation for the vapour pressure which leads to a value of 22·0 kcal. The accurate low temperature data of Neumann and Völker[366], which should perhaps be given most weight, lead to 21·4 kcal. Other assessments of the data have led to lower values[38], so the significance of the figure after the decimal point is doubtful.

8.2.2.20. *Calcium*—Kelley[259], reviewing the literature on the vapour pressure measurements, gave $\Delta H_f^\circ(Ca; g)_{25^\circ C} = 42{\cdot}6$ kcal, while Bichowsky and Rossini[38] give 47·8. The most recent determination, that of Rudberg[434] using the effusion method, leads to 45·3. The N.B.S.[529] choose 46·04 kcal, and a value of 46 is probably good to within ± 3 kcal.

8.2.2.21. *Scandium*—There appears to be no direct experimental work on the heat of atomization of scandium. Bichowsky and Rossini[38] 'estimate' 70 kcal, and the N.B.S.[529] give 93 kcal, referring to unpublished data of L. Brewer.

8.2.2.22. *Titanium*—Carpenter and Mair[66] have measured the vapour pressure of titanium by the rate of evaporation method. They deduce $\Delta H_{25^\circ C} = 112{\cdot}6$ kcal from third law considerations, and 114·7 kcal from the dependence of vapour pressure on temperature (second law plot). This is good agreement, and the value must be taken as fairly well established. Edwards, Johnston, and Ditmars[140], using the same technique, obtained slightly lower vapour pressures, perhaps because of a slight discrepancy in the two temperature scales, but obtained $\Delta H_0^\circ = 112{\cdot}76$ kcal, in good agreement with Carpenter and Mair.

8.2.2.23. *Vanadium*—Edwards, Johnston, and Blackburn[137] measured the vapour pressure of vanadium and deduced ΔH_0° for vaporization to be 121·95, from which we may put $\Delta H_f^\circ(V; g)_{25^\circ C} = 122$ kcal.

8.2.2.24. *Chromium*—Speiser, Johnston, and Blackburn[460] measured the vapour pressure of chromium using the rate of evaporation technique and deduced $\Delta H_0^\circ = 93{\cdot}50 \pm 0{\cdot}18$ kcal. Gulbransen and Andrew[194], using the same method, obtained

$93{\cdot}9 \pm 0{\cdot}2$ kcal. The value seems well established; we take $\Delta H_f^\circ(\mathrm{Cr;\ g})_{25^\circ\mathrm{C}} = 94{\cdot}0$ kcal.

8.2.2.25. *Manganese*—No very reliable vapour pressure data on manganese appear to be available. Kelley *et al.*[260] have measured the thermodynamic properties of manganese, and combine them with such vapour pressure data as are available to give the heat of vaporization. The N.B.S.[529] on this basis adopt $\Delta H_f^\circ(\mathrm{Mn;\ g})_{25^\circ\mathrm{C}} = 68{\cdot}34$ kcal. The accuracy of this result is doubtful.

8.2.2.26. *Iron*—The most recent determination of the vapour pressure of iron is by Edwards, Johnston, and Ditmars[139]. They used the rate of vaporization technique, and deduced from their results $\Delta H_0^\circ = 99{\cdot}21$ kcal. The same method has been used by Marshall, Dornte, and Norton[339] and by Jones, Langmuir, and Mackay[254]. The results of the former lead to $\Delta H_0^\circ = 96{\cdot}03$ kcal, and those of the latter to 96·52 kcal, which is the value used by Kelley[259]. The most recent determination gives results for the vapour pressures about half those given by the other two. The value of 99 kcal for $\Delta H_f^\circ(\mathrm{Fe;\ g})_{25^\circ\mathrm{C}}$ which is given here may therefore be a little high.

8.2.2.27. *Cobalt*—Edwards, Johnston, and Ditmars[139] give $\Delta H_0^\circ = 101{\cdot}63$ for the vaporization of cobalt, using the rate of evaporation method. We take $\Delta H_f^\circ(\mathrm{Co;\ g})_{25^\circ\mathrm{C}} = 102$ kcal.

8.2.2.28. *Nickel*—The most recent measurements of the vapour pressure of nickel are those of Jones, Langmuir, and Mackay[254], Bryce[61], and Johnston and Marshall[251]. All these used the rate of evaporation technique, and the results for the vapour pressure get lower, and those for ΔH_0° higher, in the order given. The earliest lead to $\Delta H_0^\circ = 98{\cdot}13$ kcal, the latest to 101·14 kcal. A value for $\Delta H_f^\circ(\mathrm{Ni;\ g})_{25^\circ\mathrm{C}}$ of 101 kcal seems indicated.

8.2.2.29. *Copper*—The vapour pressure of copper has been measured by many workers (*see* Kelley[259] for earlier references). The most recent are those of Marshall, Dornte, and Norton[339], Hersh[214], and Edwards, Johnston, and Ditmars[140] which lead to $\Delta H_0^\circ = 81{\cdot}08$, 81·09, and 80·29 kcal respectively. On the basis of Harteck's results[204], Kelley[259] gave 81·73 kcal. A value of 81 kcal for $\Delta H_f^\circ(\mathrm{Cu;\ g})_{25^\circ\mathrm{C}}$ cannot be much in error.

8.2.2.30. *Zinc*—Kelley[259] gives 31·19 kcal for $\Delta H_{25^\circ\mathrm{C}}$ for the vaporization of zinc, on the basis of a fairly good collection of vapour pressure data.

8.2.2.31. *Gallium*—Speiser and Johnston[459], on the basis of vapour pressure measurements, give ΔH_0° for the vaporization of gallium as 65·6 kcal, whence $\Delta H_f^\circ(\mathrm{Ga;\ g})_{25^\circ\mathrm{C}} = 65$ kcal. Earlier

data of Harteck[204] which are irregular and lead to a higher result may have been obtained with less pure gallium.

8.2.2.32. *Germanium*—Baughan[24] has considered the vapour pressure data, and gives $\Delta H_f^\circ(\mathrm{Ge};\ g) = 89 \pm 4$ kcal.

8.2.2.33. *Arsenic*—The heat of formation of gaseous arsenic atoms is deduced from the following cycle.

$$\begin{aligned} 4\mathrm{As(solid)} &\rightarrow \mathrm{As_4(g)} && \Delta H_1 \\ \mathrm{As_4(g)} &\rightarrow 2\mathrm{As_2(g)} && \Delta H_2 \\ 2\mathrm{As_2(g)} &\rightarrow 4\mathrm{As(g)} && \Delta H_3 = 2D(\mathrm{As_2}) \\ \mathrm{As(solid)} &\rightarrow \mathrm{As(g)} = \tfrac{1}{4}(\Delta H_1 + \Delta H_2 + \Delta H_3) = \Delta H_f(\mathrm{As};\ g) \end{aligned}$$

This is the same cycle as was used for phosphorus. Below 800° K the vapour is almost entirely As_4 and there are a large number of vapour pressure data. Kelley[259] deduces for ΔH_1, 31 kcal. Vapour density data of Preuner and Brockmöller[398] lead to $\Delta H_2 \sim 21$ kcal[38], and also to $D(As_2) \sim 35$ kcal. The last value is almost certainly wrong, because there is good spectroscopic evidence for $D(As_2)$ about 3·96 eV, or 91 kcal[166, 217]. Thus the situation is much the same as for phosphorus, except that for arsenic we have no more reliable data than those of Preuner and Brockmöller for ΔH_2. Using the vapour density data for ΔH_2 and the spectroscopic for ΔH_3, we have $\Delta H_f(\mathrm{As};\ g)_{25^\circ C} = 59$ kcal. The N.B.S.[529] give 60·64 kcal on the basis of the same evidence. In view of the facts that similar evidence did not give the correct results for phosphorus, and that the vapour density measurements at the highest temperature are in disagreement with the spectroscopic result, ΔH_2 must be considered doubtful, possibly low. Thus our value for $\Delta H_f(\mathrm{As})$ is itself doubtful. More work on the vapour density would clearly be useful.

8.2.2.34. *Selenium*—The heat of formation of atomic selenium depends upon the heat of vaporization to Se_2 and $D(Se_2)$. Kelley[259], using Preuner and Brockmöller's data on the vapour density[398], gives $\Delta H_{25^\circ C}$ for $2\mathrm{Se(solid)} \rightarrow \mathrm{Se_2(g)}$ as 32·9 kcal. Recent data obtained by Brooks[60] are in disagreement, and suggest a value lower by about 10 kcal. There is some argument about $D(Se_2)$, but it is certain that the value of 92 kcal, estimated by Bichowsky and Rossini[38], is much too high. Gaydon[166] favours 65 kcal, whence $\Delta H_f^\circ(\mathrm{Se};\ g) = 49$ kcal, in agreement with the value adopted by the N.B.S.[529].

As for S_2, Goldfinger *et al.*[181] compare the spectroscopic value with the thermochemical value derived from von Wartenberg's vapour density measurements, which according to them lead to

62 or 71 kcal, depending on whether the ground state is triplet or singlet. This result is, however, very doubtful (*see* Section 8.2.2.16).

8.2.2.35. *Bromine*—The dissociation energy of bromine has been well established spectroscopically by a band convergence limit [166, 217]. We follow the N.B.S. in putting $\Delta H_f^\circ(\mathrm{Br};\ g)_{25^\circ C} = 26{\cdot}71$ kcal [529].

8.2.2.37. *Rubidium*—Kelley [259] has derived $\Delta H_{25^\circ C}$ for the vaporization of rubidium to be 20·51 kcal, from two concordant sets of vapour pressure measurements.

8.2.2.38. *Strontium*—Kelley [259], using vapour pressure data, gives $\Delta H_{25^\circ C} = 37{\cdot}05$ kcal for $\mathrm{Sr}(l) \rightarrow \mathrm{Sr}(g)$, from which the N.B.S. obtain 39·2 for the heat of vaporization from the solid [529].

8.2.2.39. *Yttrium*—There appears to be no published information on the heat of formation of yttrium. The N.B.S. [529] give 103 kcal, referring to unpublished data of Brewer *et al.*

8.2.2.40. *Zirconium*—Skinner, Edwards, and Johnston [451] give ΔH_0° for vaporization of zirconium as 142·15 kcal. We take $\Delta H_f^\circ(\mathrm{Zr};\ g)_{25^\circ C} = 142$ kcal. The N.B.S. [529] value for this quantity is 125 kcal, from unpublished data of Brewer *et al.* Bichowsky and Rossini [38] estimated 110 kcal.

8.2.2.41. *Niobium* (*Columbium*)—From measurement of the rate of vaporization of niobium filament [411], the N.B.S. [529] derive $\Delta H_f^\circ(\mathrm{Nb};\ g)_{25^\circ C} = 184{\cdot}5$ kcal. Only three determinations were made, so the reliability may not be very high.

8.2.2.42. *Molybdenum*—Kelley [259] gives $\Delta H_{25^\circ C}$ for Mo(solid) → Mo(g) as 155·5 kcal. Recent measurements by Edwards, Johnston, and Blackburn give the same result [138].

8.2.2.43–46.—There appears to be no published evidence about the heat of atomization of elements 43–46, although estimates of unknown reliability have been made for ruthenium, rhodium, and palladium [529].

8.2.2.47. *Silver*—Kelley [259] reviewed the vapour pressure data, which are discordant, and using the results of Harteck [204] deduced $\Delta H_{25^\circ C}$ for the vaporization of solid silver to be 69·1 kcal, but the reliability of this is doubtful. Schadel and Birchenall [441] measured the vapour pressure by the Knudsen method using radioactive Ag^{110} as tracer, and obtained for the heat of sublimation in the range 750–1000° K, 64·1 ± 0·7 kcal. Long [317] deduces $\Delta H_f^\circ(\mathrm{Ag};\ g)_{25^\circ C} = 67{\cdot}8$ from their results. Using the values for specific heats given by Kelley [259] the present author finds 65·2 kcal.

8.2.2.48. *Cadmium*—Kelley [259] has reviewed the vapour pressure data of several investigators, most of which are concordant, and

deduced $\Delta H_{25°C} = 26{\cdot}8$, which is close to the value adopted by the N.B.S.[529]. The N.B.S.[529] also refer to Richnow[419], who obtained 32 kcal using a calorimeter furnace. He also obtained values high by a similar amount for zinc and magnesium.

8.2.2.49. *Indium*—There does not appear to be an experimental value for indium. The N.B.S. tables[529] give a 'calculated' figure.

8.2.2.50 *Tin*—The vapour pressure data for tin are very discordant. Kelley[259] does not consider it possible to derive a value for the heat of vaporization to Sn atoms. Baughan[24] obtains a third law value of 62·4 kcal for ΔH_f°, which is supported by all the data except those of Harteck[204]. Since the publication of Baughan's review, Brewer and Porter[54] have reported new results obtained by the Knudsen method, which are in agreement with those of Harteck and lead to $\Delta H_0^\circ = 70 \pm 2$ kcal. They suggest that the higher values for the vapour pressure, corresponding to lower values of ΔH_0°, obtained by other workers were due to contamination of the tin with oxygen. We take 70 kcal for the heat of atomization of tin, but with some misgivings. Other estimates have ranged from 51[319] to 78[38].

8.2.2.51. *Antimony*—The vapour pressure data on antimony are very discordant[259], and there is considerable confusion regarding the species present in the gas phase. Measurements by Biltz and Meyer[39] show the gas density near the boiling point to be a little greater than that corresponding to Sb_2. Bichowsky and Rossini[38] take this to mean that the heat of vaporization near the boiling point is the heat of formation of $Sb_2(g)$ from Sb(l), and deduce $\Delta H_f^\circ(Sb_2)$ as 52 kcal at 18° C. This interpretation is doubtful, but using it we require $D(Sb_2)$ to deduce the heat of formation of Sb gas. Spectroscopic evidence on Sb_2 is discussed by Gaydon[166] and Herzberg[217]. A Birge-Sponer extrapolation leads to $D(Sb_2) = 3{\cdot}7$ eV, and Gaydon considers that this is likely to be too high. He gives $3{\cdot}0 \pm 0{\cdot}5$ eV, or 69 ± 11 kcal. Combining this with Bichowsky and Rossini's datum[38], we have $\Delta H_f(Sb; g)_{25°C} = 61$ kcal, which is likely to be correct to within, say ± 15 kcal. This is presumably the evidence which leads the N.B.S. to the value 60·8 kcal[529]. Bichowsky and Rossini's value of 40 kcal[38] is based on an estimated value of 1·17 eV for $D(Sb_2)$, which is almost certainly too low.

8.2.2.52. *Tellurium*—Kelley[259] quotes some data on the vapour pressure of liquid tellurium, but states that the composition of the vapour is uncertain. It has since been shown by Niwa[371] that tellurium vapour at a few hundred degrees is composed of diatomic molecules. The N.B.S.[529] derive from this $\Delta H_f(Te_2; g) = 41$ kcal,

which is slightly higher than the value which may be deduced from the vapour pressure equation given by Kelley. On the other hand, recent results by Brooks[60] suggest a lower value. $D(Te_2)$ is required in order to obtain $\Delta H_f(Te; g)$. Herzberg[217] gives $D(Te_2) \lesssim 3{\cdot}18$ eV, and Gaydon[166] gives 2·3 eV, or 53 kcal. Taking Gaydon's result yields $\Delta H_f(Te; g)_{25^\circ C} = 48$ kcal, but the figure is uncertain by at least half the uncertainty in the value for $D(Te_2)$, which Gaydon puts at 5 kcal.

8.2.2.53. *Iodine*—The dissociation energy of gaseous I_2 is very accurately known both from thermal and spectroscopic measurements (Section 3.2). This is combined with the heat of vaporization of iodine[529] to give $\Delta H_f^\circ(I; g)_{25^\circ C} = 25{\cdot}48$ kcal.

8.2.2.55. *Caesium*—Kelley[259] deduces from concordant vapour pressure measurements that $\Delta H_{25^\circ C}$ for vaporization of solid caesium is 18·83 kcal.

8.2.2.56. *Barium*—Kelley[259] gives $\Delta H_{25^\circ C}$ for the vaporization of liquid Ba as 39·75 kcal, deduced from the vapour pressure data of Hartmann and Scheider[207]. The subsequent measurements by Rudberg and Lempert[435], which were carried out at lower temperatures, yield a second law value of 40·9 kcal at about 1,000° K, which gives, with the use of Kelley's values for the specific heats, 39·1 kcal at 25° C. The N.B.S. give for the vaporization of the solid 41·96 kcal, which presumably depends on a heat of fusion estimated from the melting point of 704° C[225]. Therefore 42 kcal seems a fair estimate of $\Delta H_f^\circ(Ba; g)_{25^\circ C}$.

8.2.2.57–72.—There appear to be no published experimental values of the heats of atomization of the rare earths, or of hafnium.

8.2.2.73. *Tantalum*—There are three determinations of ΔH_0° for the vaporization of tantalum, all made using the rate of evaporation method. Two are in exact agreement at 185·5 kcal[136, 291], the third, which was intermediate in time, is 181·2 kcal[156]. The higher value seems preferable.

8.2.2.74. *Tungsten*—Kelley[259] gives 202·7 for $\Delta H_{25^\circ C}$ for the vaporization of tungsten.

8.2.2.75–77.—The N.B.S.[529] give 189, 174, and 165 respectively for the heats of atomization of rhenium, osmium, and iridium respectively, referring to unpublished data of Brewer *et al.*

8.2.2.78. *Platinum*—Kelley[259] has used the experimental data given by Jones, Langmuir, and Mackay[254] on the rate of evaporation of platinum filaments to deduce 124·4 kcal for $\Delta H_{25^\circ C}$. The data are not very concordant and the N.B.S. deduces 121·6 kcal[529].

8.2.2.79. *Gold*—Kelley[259] deduced $\Delta H_{25^\circ C} = 90{\cdot}49$ kcal for the vaporization of solid gold from the vapour pressure measurements

of Harteck[204], who used the Knudsen effusion method. The N.B.S.[529] give some weight to other determinations, and deduce 82·29 kcal. The position was re-examined by Hall[200], who also used the Knudsen method, but with particular precautions against error. He determined the amount of gold effusing by using radioactive Au^{198} as tracer. The hole area–surface area of cell ratio was varied by a factor of two and it was shown that the vapour pressure was unaffected by this variation (*see*, however, Section 8.2.2.6). A molybdenum plate was placed in the evacuated chamber near the aluminium collector plate in such a position that gold atoms could only strike it after reflection from the collector plate. No gold was detected on the molybdenum plate, giving a check that the condensation coefficient was near unity. He deduced $\Delta H_0^\circ = 84{\cdot}6 \pm 0{\cdot}8$ kcal from the results. This corresponds to 84·4 kcal at 298·1° K. Hall has suggested that Harteck's vapour pressures are too low because he used too large a hole in his Knudsen cell.

8.2.2.80. *Mercury*—Busey and Giauque[65] give the heat of evaporation of mercury as 14·65 kcal at 25° C. This differs only very slightly from the previously accepted value.

8.2.2.81. *Thallium*—The vapour pressure data on thallium are in considerable disagreement with one another[259]. Kelley[259] gives $\Delta H_{25^\circ C}$ for vaporization of solid thallium as 42·78 kcal, but the reliability of this is doubtful.

8.2.2.82. *Lead*—The vapour pressure data for lead are not at all concordant. Kelley[259] chooses those which lead to $\Delta H_{25^\circ C}$ for vaporization of solid lead = 46·39 kcal, a figure of doubtful reliability.

8.2.2.83. *Bismuth*—According to Kelley[259], the vapour pressure data on bismuth show wide disagreement, and there is considerable uncertainty concerning the molecular species present in the gas. Bichowsky and Rossini[36] deduced $\Delta H_f(Bi_2; g) = 76{\cdot}2$ kcal from the vapour pressure measurements, and this, with the value $D(Bi_2) = 18{\cdot}5$ kcal, leads to $\Delta H_f(Bi; g)_{25^\circ C} = 47{\cdot}8$ kcal. However, this value of $D(Bi_2)$ appears to be much too low. The spectroscopic evidence leads to 1·7 eV, or 39 kcal[166]. If we take Kelley's empirical vapour pressure equation, for the liquid, assume it refers to Bi_2 and convert to the solid using the heat of fusion given by Bichowsky and Rossini, we deduce $\Delta H_f(Bi_2; g) = 77{\cdot}0$, in good agreement with the earlier value. Hence $\Delta H_f(Bi; g) = 58{\cdot}5$ kcal. The N.B.S.[529] consider that $\Delta H_f(Bi_2; g) = 59{\cdot}4$ kcal, whence $\Delta H_f(Bi; g) = 49{\cdot}7$ kcal. This figure is of doubtful reliability.

8.2.2.92. *Uranium*—The N.B.S.[529] give $\Delta H_f(U; g) = 125$ kcal, referring to two sets of unpublished results.

9

NUMERICAL VALUES OF BOND DISSOCIATION ENERGIES

NUMERICAL values for a number of bond dissociation energies are given in this chapter. It is intended to be complete as far as directly determined dissociation energies are concerned; some dissociation energies deduced thermochemically from heats of formation of radicals or atoms are included, often for purposes of comparison with directly determined values, but the list is not intended to be exhaustive or critical in this respect, and the reader can supply the missing values by simple arithmetic. Often older or less reliable estimates of dissociation energies are not discussed.

Three important compilations of data give dissociation energies; the books of Herzberg and of Gaydon in particular give values for the dissociation energies of diatomic molecules, and the review by Szwarc deals with dissociation energies in polyatomic molecules. For this reason the present author does not feel obliged to give a detailed discussion of all the values, and references to all the original literature cited by these authors are not given. Full references for values which do not appear in these compilations are, of course, given.

The arrangement in the following section is in order of increasing atomic number. Thus bonds involving hydrogen are treated first, again in order of increasing atomic number of the other elements, *e.g.* Section 9.1.6 deals with C – H bonds. Then again C – H bonds in which only H is attached to carbon are treated first, and so on in order of increasing atomic number of substituent. The numerals following 9, the chapter number, are the atomic numbers themselves, so that, for example, 9.1.3 follows 9.1.1 because the He – H bond is not treated. The D values given are D_0°, *i.e.* they refer to the zero*th* vibrational level at 0° K. In many cases fairly arbitrary corrections have been made to obtain this figure, but they are always small.

9.1.1. $D(H_2)$

See Section 8.2.2.1. $D(H_2) = 4{\cdot}4763$ eV.

9.1.3. D(LiH)

$2{\cdot}5 \pm 0{\cdot}2$ eV [166, 217].

9.1.4. D(BeH)

$2{\cdot}3 \pm 0{\cdot}3$ [166, 217].

9.1.5. D(BH)

Gaydon [166] gives $D(B-H)$ in the diatomic molecule as $3{\cdot}0 \pm 0{\cdot}4$ eV, Herzberg [217] an upper limit of 3·51 eV. Nothing appears to be known about $D(B-H)$ in polyatomic molecules.

9.1.6. $D(C-H)$ *Diatomic Molecule*

Herzberg [217] and Gaydon [166] both give 3·47 eV, or 80 kcal. This is based on a predissociation. Glockler [176] has suggested that this may in fact be a perturbation and gives $D(C-H) = 4{\cdot}00$ eV (92·2 kcal). This value is based on the extrapolation of an average bond energy against bond length curve for C – H bonds, with the assumption of the high value of L_C (*see* Section 8.2.2.6). Glockler also prefers this value because it fits better into the sequence HF, OH, NH, and CH. This argument loses its attraction when it is realized that D(NH) itself is doubtful. Moreover there appears to be no doubt that the predissociation is strong and real and not of the type which could be confused with a perturbation [165], and there is also good evidence that the ground state has been correctly identified [396].

9.1.6. $D(CH-H)$

There is no very reliable value for $D(CH-H)$ in methylene. The electron impact experiments of McDowell and Warren [331] give $3{\cdot}4 \pm 0{\cdot}3$ eV (78 kcal). Their work leads to a value of $L_C = 120 - 140$ kcal (*see* Section 8.2.2.6). Another consideration of the electron impact data [153] leads to 88 kcal for $D(CH-H)$, whence $L_C = 139$ kcal. Possibly the best method of obtaining $D(CH-H)$ is to decide upon L_C, $D(C-H)$, $D(CH_2-H)$, and $D(CH_3-H)$. These data, together with $D(H_2)$ and $\Delta H_f(CH_4)$, can be used to deduce $D(CH-H)$. If we accept $D(CH)$ and $D(CH_3-H)$ to be 80 and 101 kcal respectively, and take $L_C = 138$ kcal (Section 8.2.2.6), we deduce $D(CH_2-H) + D(CH-H) = 179$ kcal. Evidence on $D(CH_2-H)$ suggests $D(CH-H) \sim 92$ kcal, but this is by no means certain.

9.1.6. $D(CH_2-H)$

An upper limit for $D(CH_2-H)$ has been deduced by Laidler and Casey [287] on the basis of the work by Bawn and Dunning [26] on the

reaction between sodium vapour and methylene chloride. The suggested mechanism for the chemiluminescence reaction is:

1. $Na + CH_2Cl_2 \rightarrow NaCl + CH_2Cl$
2. $Na + CH_2Cl \rightarrow NaCl^* + CH_2$
3. $NaCl^* + Na \rightarrow NaCl + Na^*$

Here $NaCl^*$ is vibrationally excited and Na^* electronically excited. The sodium excitation requires 48·3 kcal, so that reactions 1 and 2, with formation of normal NaCl, must jointly be exothermic by this amount, so that for

$$2Na(g) + CH_2Cl_2(g) \rightarrow 2NaCl(g) + CH_2$$
$$-\Delta H > 48{\cdot}3 \text{ kcal}$$

The heats of formation of all these compounds except methylene are known, so we may deduce $\Delta H_f(CH_2)$ and hence, if we put $D(CH_3 - H) = 101$ kcal, $D(CH_2 - H) \leqslant 87$ kcal. The uncertainties in the subsidiary thermochemical data are such that if we use the data given by the N.B.S.[529], instead of those used by Laidler and Casey, we find $D(CH_2 - H) \lesssim 90$ kcal.

A lower limit for $D(CH_2 - H)$ has been given by Kistiakowsky and Rosenberg[270]. The basis is a not very well established mechanism for the photolysis of ketene, together with the assumption that ΔH for $CH_3 . CH_2 . CH_3 \rightarrow CH_2 . CH_2 . CH_2 + 2H$ is twice that for $CH_3 . CH_3 \rightarrow CH_3 . CH_2 + H$. In any case $D(CH_3 . CH_2 - H)$ is not as well established as we might wish, so that the total uncertainty of this estimate must be quite large, say $D(CH_2 - H) > 71 \pm 10$ kcal. Thus the kinetic evidence would place $D(CH_2 - H)$ between 80 and 90 kcal.

McDowell and Warren[331] deduce $D(CH_2 - H) \leqslant 3{\cdot}45 \pm 0{\cdot}2$ eV, or 80 kcal, from their measurements of the appearance potential of CH_2^+ from methane. There is, however, some uncertainty in the measurements of this appearance potential because of the low relative abundance of CH_2^+. McDowell and Warren themselves say that it has the value $15{\cdot}30 \pm 0{\cdot}5$ eV, which suggests that the error limit assigned by them to $D(CH_2 - H)$ is too small. There are also some indications that 15·3 eV is too low for $A(CH_2^+)$. The ionization efficiency curve for CH_2^+ shows a second break at a point given by McDowell and Warren as $20{\cdot}1 \pm 0{\cdot}1$ eV. Now it is assumed that this corresponds to the production of CH_2^+ along with two hydrogen atoms, instead of along with a hydrogen molecule. The energies for the two processes should therefore differ by

$D(H_2)$ or 4·48 eV. If the upper value is correct the lower should be about 15·6 eV, corresponding to $D(CH_2-H)=3{\cdot}75$ eV, or 86 kcal. Furthermore, Smith[457] obtained $A(CH_2^+)$ from methane as 15·8 eV, which would increase $D(CH_2-H)$ to 3·95 eV, or 91 kcal. If this value is used, together with McDowell and Warren's data on methyl cyanide[332], we obtain $D(H-CN)-D(CH_3-CN)=0{\cdot}3$ eV, whereas if we take $A(CH_2^+)$ in methane as 15·3 eV, we deduce $D(H-CN)-D(CH_3CN)=-0{\cdot}2$ eV, which disagrees with thermochemical evidence[474]. This is evidence for believing that McDowell and Warren's value for $A(CH_2^+)$ in methane is decidedly too low, and therefore that $D(CH_2-H)$ is about 10 kcal higher than they derive it to be. Thus a value of 86–90 kcal for $D(CH_2-H)$ appears to accord best with the evidence.*

9.1.6. $D(CH_3-H)$

The electron impact method has been used in several different ways to determine $D(CH_3-H)$. The results have been reviewed by Stevenson[473], *Table 9.1.6.1* being taken from his paper.

Table 9.1.6.1

Method	*Process*	$D(CH_3-H)$ eV
Direct electron impact* (*see* Section 5.24)	$CH_3 \rightarrow CH_3^+ + e^-$ *with*	4·44 ± 0·2
	$CH_4 \rightarrow CH_3^+ + H + e^-$	4·48 ± 0·4
	$CH_3OH \rightarrow CH_3^+ + OH + e^-$	
Indirect electron impact* (*see* Section 5.24)	$C_2H_6 \rightarrow C_2H_5^+ + H + e^-$ *with* $C_3H_8 \rightarrow C_2H_5^+ + CH_3 + e$	4·38 ± 0·2
	$C_3H_8 \rightarrow C_3H_7^+ + H + e^-$ *with* *iso* $C_4H_{10} \rightarrow C_3H_7^+ + CH_3 + e^-$	4·34 ± 0·2
	$C_3H_6 \rightarrow C_3H_5^+ + H + e^-$ *with* *iso* $C_4H_8 \rightarrow C_3H_5^+ + CH_3 + e^-$	4·48 ± 0·2
	$n\text{-}C_3H_7Cl \rightarrow C_3H_7^+ + Cl + e$ *with* $n\text{-}C_4H_{10} \rightarrow C_3H_7^+ + CH_3 + e^-$	4·42 ± 0·2
	$CH_3OH \rightarrow CH_2OH^+ + H + e^-$ *with* $C_2H_5OH \rightarrow CH_2OH^+ + CH_3 + e^-$	4·42 ± 0·2

* Electron impact average = 4·42 ± 0·04 eV = 102 kcal.

The photobromination of methane has already been discussed (Section 4.1), a value of 101 kcal for $D(CH_3-H)$ at 0° K being obtained[11]. Szwarc[494] obtained 103 ± 3 from the pyrolysis of ethyl benzene, to give methyl and benzyl radicals. The pyrolysis

* On the other hand, a very recent measurement of the appearance potential of CH_2^+ from methyl radicals confirms McDowell and Warren's estimate[544].

of methyl iodide leads to 103 kcal, though the method is of doubtful validity (*see* Sections 4.2 and 9.6.53). A value of 101–102 kcal seems to be well established.

9.1.6. $D(HC:C-H)$

It has been shown that acetylene when submitted to a high frequency electric discharge yields some diacetylene[75]. The action of ultra-violet radiation of wavelength 2,378–2,100 Å on acetylene also produced diacetylene, and Cherton[76] considered that the primary step must be the photodissociation of acetylene to C_2H and H. At sufficient pressure the absorption spectrum of acetylene shows a continuous absorption in this region superimposed in the band structure. This gives an upper limit of 121 kcal to $D(HC:C-H)$.

The mercury photosensitized polymerization of acetylene has been studied by Steacie and LeRoy[433]. They investigated the effect of nitric oxide on the reaction, and deduced that it proceeds at least partially by a free radical mechanism. If this is so, the reaction must be

$$\begin{aligned} Hg(^3P_1) + C_2H_2 &\rightarrow C_2H + H + Hg(^1S_0) \\ &\rightarrow C_2H + HgH \end{aligned}$$

or

$$\rightarrow HgC_2H + H$$

The first reaction is only possible if $D(CH)$ in acetylene $<112{\cdot}2$ kcal. If HgH is formed directly in the primary step the upper limit to $D(CH)$ is raised to 120·7 kcal. The reaction of deuterium atoms with acetylene may provide additional evidence. Geib and Steacie[168] found the activation energy to be <5 kcal. There are two possible mechanisms:

1. $D + C_2H_2 \rightarrow C_2H_2D$
   $D + C_2H_2D \rightarrow C_2HD + HD$
2. $D + C_2H_2 \rightarrow C_2H + HD$
   $D + C_2H \rightarrow C_2HD$

If the observed activation energy corresponds to that of the primary step of the second mechanism, $D(CH)<108$ kcal. Unfortunately there is no way of telling which is correct.

Laidler[286] has given a value of 104 kcal for $D(CH)$ in acetylene, which has been quoted elsewhere[99]. This is taken from Steacie's book[467], and is an average value for the two CH bonds in acetylene,

which depends on standard thermochemical data, plus L_C, $D(CH)$ and $D(C_2)$. Under these circumstances it can hardly be taken very seriously.

Thus we know fairly reliably that 121 kcal is an upper limit to $D(HC:C-H)$, but it is not possible to say how much lower than 121 kcal the true value is. The other quoted value, 104, can be disregarded.

9.1.6. $D(H_2C:CH-H)$

Electron impact measurements and the study of photosensitized reactions both provide values for $D(CH)$ in ethylene. Indeed, electron impact work, perhaps overgenerously, provides two values, which differ by 30 kcal!

The original electron impact work is due to Stevenson[471]. He determined the appearance potential of various ions from 1-butene and found in particular that $A(C_2H_5^+)$ was $11{\cdot}97 \pm 0{\cdot}1$ eV. This was combined with other appearance potential and thermochemical data as follows:

1.	$C_4H_8 \rightarrow C_2H_5^+ + C_2H_3 + e^-$	$\Delta H \leqslant 11{\cdot}97$ eV
2.	$e^- + H + C_2H_5^+ \rightarrow C_2H_6$	$-\leqslant 12{\cdot}84$
3.	$C_2H_6 \rightarrow C_2H_4 + H_2$	$1{\cdot}42$
4.	$2C_2H_4 \rightarrow C_4H_8$	$-1{\cdot}07$
5.	$H_2 \rightarrow 2H$	$4{\cdot}48$

therefore

$$C_2H_4 \rightarrow C_2H_3 + H \qquad \Delta H = 3{\cdot}96 \text{ eV} = 91{\cdot}5 \text{ kcal}$$

The thermochemical data used is all accurate to better than 0·01 eV, so that the only possibility of error lies in the interpretation of the electron impact results. The appearance potential of $C_2H_5^+$ in the butene mass spectrum sets an upper limit to ΔH_1, and this was considered by Stevenson to be accurate to within $\pm 0{\cdot}1$ eV. Similarly the appearance potential of $C_2H_5^+$ in the ethane spectrum gives a lower limit to ΔH_2. This appearance potential may be combined with the known ionization potential of the ethyl radical to give an upper limit to $D(C_2H_5-H)$. Now $I(C_2H_5)$ is $8{\cdot}60 \pm 0{\cdot}1$ eV[223], whence $D(C_2H_5-H) < 4{\cdot}24$ eV, or $\sim$98 kcal. There are some indications that this may be about 4 kcal too high, though there is other evidence that it is likely to be about right (*see* ethane, C_2H_5-H). If it is 4 kcal high, then this would put $D(C_2H_3-H)$ up by 4 kcal. Thus about 96 kcal appears to be the highest value allowed by this electron impact work for ethylene.

There are indications that the vinyl ion behaves unusually in that there appears to be an activation energy for the combination of vinyl ions and hydrogen atoms. Stevenson mentions that the appearance potential of $C_2H_3^+$ in ethane, 15·2 eV, together with the heat of hydrogenation of ethylene, 1·2 eV, leads to an estimate of 13·8 eV for the appearance potential of $C_2H_3^+$ in ethylene. However, he pointed out that the appearance potential of $C_2H_3^+$ in ethylene has been directly measured to be 14·2 eV[281]. This suggests that the products of this dissociative ionization process in ethylene have a kinetic energy of 0·4 eV. A possible interpretation of this is that there is an activation energy for the recombination process. Good confirmation of Stevenson's result comes from the ethyl ion appearance potentials in *cis*- and *trans*-2-butene, measured by Dibeler[110]. These are 12·2 and 12·4 eV respectively, leading to a mean value of $D(C_2H_3 - H)$ of 96 kcal, using the same methods as Stevenson.

Recently, however, Field[154] has cast doubt on some of Stevenson's results, and given new evidence which leads to $D(C_2H_3 - H) = 122$ kcal. Field measured the appearance potential of the ethyl ion in 1-butene to be $13{\cdot}30 \pm 0{\cdot}2$ eV, or 1·3 eV greater than Stevenson's value. Similarly, for the appearance potential of the vinyl ion in 1-butene, Field obtained $14{\cdot}96 \pm 0{\cdot}1$ compared with Stevenson's value of $13{\cdot}6 \pm 0{\cdot}3$ eV, an increase of 1·4 eV. If Field's value for $A(C_2H_5^+)$ in 1-butene is correct, then $D(C_2H_3 - H) = 122$ kcal follows. The same value, within 2 kcal, is obtained from the appearance potential of the methyl ion in propylene and the tertiary butyl ion from 3 : 3-dimethyl-1-butene.

The discrepancy can hardly be resolved without further work, and until this is forthcoming, the present author tends to the view that $D(C_2H_3 - H) = 96$ kcal, depending on Dibeler's result, is the most likely. It is possible that there is an activation energy for radical recombinations involving vinyl radicals in general, though this conclusion is somewhat speculative. If it is correct, it means that kinetic results on $D(C_2H_3 - H)$ must be interpreted with caution.

The photosensitized reactions of ethylene have been discussed by Laidler[286] and by Steacie[467]. If A* is an excited metal atom, there are two possible types of reaction:

1. $A^* + RH_2 \rightarrow A + RH + H$

2. $A^* + RH_2 \rightarrow A + RH_2^*$

involving bond breaking or molecular excitation. 1 may also

take place with the formation of the metallic hydride, AH, in the primary step

1a. $A^* + RH_2 \rightarrow AH + RH$

If 1a takes place, the reaction will occur without activation energy if the excitation energy of A^* plus the heat evolved on formation of the hydride from atoms is at least as great as the bond strength RH – H. If reaction 1 takes place, then the excitation energy alone must be greater than the bond strength. The experimental results for ethylene are summarized by Steacie in the following table. The D(AH) values are those used by Steacie[467], and some differ slightly, though probably not significantly, from those given elsewhere in the present tables.

Table 9.1.6.2.

Sensitizer	*Excitation energy* kcal	D(AH) kcal	*Total energy* kcal	*Result*
Na(^{2}P)	48·3	51·6	99·9	*No reaction*
Cd($^3P_1$)	87·3	15·5	102·8	*Slow reaction*
Zn($^3P_1$)	92·5	23·1	115·6	*Slow reaction*
Hg($^3P_1$)	112·2	8·5	120·7	*Fast; much* C_2H_2 *formed*
Cd($^1P_1$)	124·4	15·5	139·9	*Fast; little* C_2H_2 *formed*
Zn($^1P_1$)	133·4	23·1	156 5	*Fast; no* C_2H_2

Laidler[286] considers that the slow reactions are of type 1a. Ethylene strongly quenches excited Na, but no reaction occurs, whereas a slow reaction occurs with Cd(^{3}P), and Laidler deduces $99{\cdot}9 < D(C_2H_3 - H) < 102{\cdot}8$ kcal. Although his argument, if the mechanism is correct, certainly leads to $D(C_2H_3 - H) < 102{\cdot}8$ kcal, it is not possible to say, without a more detailed specification of the transition state, that the lack of reaction with excited Na definitely corresponds to a lower limit for $D(C_2H_3 - H)$. A potential maximum in the dissociation process, corresponding to an activation energy for the reverse reaction, would upset this deduction. If this is so, then $D(C_2H_3 - H) < 103$ kcal in agreement with Stevenson's electron impact result. There is no direct kinetic evidence on the activation energy for the reaction

$$H + C_2H_3 \rightarrow C_2H_4$$

but Steacie[467] remarks that it is surprising that ethylene is not

formed via this reaction when hydrogen atoms, produced by the discharge tube method, react with acetylene. This may be taken as suggesting that it does have an activation energy.

There remains the possibility that the results of the photosensitized reactions may not be relevant to $D(C_2H_3+H)$ because of the preferred occurrence of reaction 2. If the fast reaction corresponded to vinyl radical formation, then $D(C_2H_3-H)<121$ kcal, which fits better with Field's electron impact work.

9.1.6. $D(C_2H_5-H)$

The electron impact measurements on $D(C_2H_5-H)$ by the indirect method[470] yield $96\pm4{\cdot}5$ kcal. Stevenson remarked that this was, within the accuracy of the method, indistinguishable from $D(CH_3-H)$, but there is much other evidence to confirm that $D(C_2H_5-H)$ is several kcal less than $D(CH_3-H)$. The direct electron impact method gives about 98 kcal (*see* C_2H_3-H). The pyrolysis of *n*-propyl benzene has been studied by Leigh and Szwarc[296]. The primary step has been shown to be the formation of ethyl radicals and benzyl radicals. The heat of formation of the benzyl radical is known from the pyrolysis of toluene. Thus the heat of formation of the ethyl radical can be deduced from this information, together with standard thermochemical results. Leigh and Szwarc give $\Delta H_f(C_2H_5)=22$ kcal, and $D(C_2H_5-H)=94\pm4$ kcal, confirming the indirect electron impact work.

The work on the photobromination of methane and ethane, as originally interpreted, gave $D(CH_3-H)-D(C_2H_5-H)=3$ kcal. These values are based on the activation energies of the reactions

$$1.\ Br+CH_4 \underset{2{\cdot}0}{\overset{17{\cdot}8}{\rightleftharpoons}} CH_3+HBr$$

$$2.\ Br+C_2H_6 \underset{0{\cdot}8}{\overset{13{\cdot}3}{\rightleftharpoons}} C_2H_5+HBr$$

Trotman-Dickenson[528] has pointed out that the activation energies of the two forward reactions and the reverse of reaction 1 are likely to be fairly accurate, but that it is improbable that the reaction of an ethyl radical with hydrogen bromide should have a lower activation energy than the reaction of a methyl radical. The evidence in favour of an activation energy of 0·8 kcal is not

compelling. Accordingly he suggested that the photobromination should be interpreted as giving:

$D(CH_3-H)=102\pm1$ kcal (at 298° K), 101 kcal (at 0° K) and $D(CH_3-H)-D(C_2H_5-H)\geqslant4{\cdot}5$ kcal

This is more in line with the electron impact results and with the results from the pyroloysis of *n*-propyl benzene. Stevenson[475] has since stated that the electron impact work already quoted together with some unpublished results leads to $D(CH_3-H)-D(C_2H_5-H)=5{\cdot}1\pm0{\cdot}7$ kcal. Evidence from the pyrolysis of iodides, though possibly not very reliable, gives 6 kcal for this quantity. Accordingly a value of ~96 kcal for $D(C_2H_5-H)$ can be adopted with fair confidence. This is a little lower than the value commonly adopted until recently.

9.1.6. $D(n\text{-}C_3H_7-H)$

The evidence on $D(CH)$ in *n*-propane is threefold. The pyrolysis of *n*-propyl iodide gives ~95 kcal, but this may well not be reliable. Leigh and Szwarc[297] have studied the pyrolysis of *n*-butyl benzene, which yields *n*-propyl and benzyl in the primary step. Using thermochemical data, and $D(CH)$ in toluene, they obtain $D(n\text{-}C_3H_7-H)\sim100$ kcal. The evidence of the two pyrolysis reactions, those of *n*-propyl and *n*-butyl benzene, strongly suggests that $D(n\text{-}C_3H_7-H)>D(C_2H_5-H)$. It is perhaps a little surprising that the difference between the two $D(CH)$ values should be as great as 6 kcal, but there is no reason to doubt the accuracy of the measurement. It has recently been confirmed by electron impact measurement by Stevenson[476], who finds $D(n\text{-}C_3H_7-H)=4{\cdot}30\pm0{\cdot}04$ eV, or 99·5 kcal.

9.1.6. $D(iso\text{-}C_3H_7-H)$

Electron impact results give 94 ± 2 kcal (4·07 eV) for $D(Me_2CH-H)$[473]. Stevenson found the appearance potentials, $A(C_3H_7^+)$, in the mass spectra of *iso*butane, *iso*pentane and 2 : 3-dimethyl butane, to be $11{\cdot}0_1\pm0{\cdot}1$, $10{\cdot}8_4\pm0{\cdot}1$, and $10{\cdot}79\pm0{\cdot}1$ eV respectively. These values were combined with the following data:

2 : 3-Me_2-butane + CH_4 → *iso*-C_4H_{10} + C_3H_8; $\Delta H^\circ_{298^\circ K}=0{\cdot}18$ eV

2 : 3-Me_2-butane + C_2H_6 → *iso*-C_5H_{12} + C_3H_8; $\Delta H^\circ_{298^\circ K}=0{\cdot}4$ eV

$CH_4 \rightarrow CH_3+H$ $\qquad D=4{\cdot}42$ eV

$C_2H_6 \rightarrow C_2H_5+H$ $\qquad D=4{\cdot}2_0$ eV

to give $D(iso\text{-}C_3H_7\text{–}H) = 4{\cdot}0_7 \pm 0{\cdot}1$ eV, and I ($sec\text{-}C_3H_7$) $= 7{\cdot}4_5 \pm 0{\cdot}1$ eV. These are the mean values obtained by the indirect method from the two separate processes detailed below:

$$\left.\begin{array}{l} iso\text{-}C_4H_{10} \rightarrow C_3H_7^+ + CH_3 + e^- \text{ with} \\ 2:3\text{-}Me_2\text{-butane} \rightarrow C_3H_7 + C_3H_7 + e^- \end{array}\right\} D(C_3H_7 - H) = 4{\cdot}0_2 \text{ eV}$$

$$\left.\begin{array}{l} iso\text{-}C_5H_{12} \rightarrow C_3H_7^+ + C_2H_5 + e^- \text{ with} \\ 2:3\text{-}Me_2\text{-butane} \rightarrow C_3H_7^+ + C_3H_7 + e^- \end{array}\right\} D(C_3H_7 - H) = 4{\cdot}1_1 \text{ eV}$$

The pyrolysis of *iso*propyl iodide gave ~89 kcal, so the agreement is fairly satisfactory considering the nature of the iodide pyrolysis.

9.1.6. $D(n\text{-}C_4H_9 - H)$

Recent electron impact work by Stevenson[476] leads to $D(n\text{-}C_4H_9 - H) = 4{\cdot}3_8 \pm 0{\cdot}1$ eV, or 101 kcal. This is much higher than the not very reliable result of ~94 kcal obtained from the pyrolysis of *n*-butyl iodide.

9.1.6. $D(tert\text{-}C_4H_9 - H)$

Electron impact evidence using the indirect method similar to that obtained for $D(iso\text{-}C_3H_7 - H)$ has been given for D(CH), tertiary, in *iso*butane[473]. The processes used are:

$$\left.\begin{array}{l} neo\text{-}C_5H_{12} \rightarrow \\ \quad C_4H_9^+ + CH_3 + e^- \text{ with} \\ 2:2:3:3\text{-}Me_4\text{-butane} \rightarrow \\ \quad C_4H_9^+ + C_4H_9 + e^- \end{array}\right\} D(tert\text{-}C_4H_9 - H) = 3{\cdot}8_9 \text{ eV}$$

$$\left.\begin{array}{l} 2:2\text{-}Me_2\text{-butane} \rightarrow \\ \quad C_4H_9^+ + C_2H_5 + e^- \text{ with} \\ 2:2:3:3\text{-}Me_4\text{-butane} \rightarrow \\ \quad C_4H_9^+ + C_4H_9 + e^- \end{array}\right\} D(tert\text{-}C_4H_9 - H) = 3{\cdot}8_7 \text{ eV}$$

This leads to a mean value of $3{\cdot}8_8 \pm 0{\cdot}1$ eV, or 89 kcal. The iodide pyrolysis method gives ~86 kcal. The agreement between the more modern results and those obtained by the iodide pyrolysis method is remarkable, considering the objections which may be made to the latter.

9.1.6. $D(neo\text{-}C_5H_{11} + H)$

D(C – H) in *neo*pentane has been obtained as 95·5 kcal at 25° C (94·5 at 0° K) by van Artsdalen from a study of the kinetics of thermal bromination[230].

9.1.6. $D(C_6H_5 - H)$

$D(C - H)$ in benzene has not been determined directly, but has been inserted here for purposes of comparison. It may be derived from the activation energy of the pyrolysis of bromobenzene, which has been shown by Szwarc and Williams[505] to produce phenyl radicals and bromine atoms when the reaction is carried out using the toluene carrier gas technique. $D(C_6H_5 - Br)$ is deduced to be 70·9 kcal, whence $D(C_6H_5 - H) = 101{\cdot}8$ kcal, if the heat of formation of bromobenzene quoted by Szwarc and Williams is known to the required accuracy.

9.1.6. $D(C_6H_5 . CH_2 - H)$

$D(C - H)$ in the methyl group of toluene is much less than most values of $D(C - H)$ because of the great stability of the benzyl radical which is formed (*see* Section 4.2). The pyrolysis of toluene to give benzyl radicals and hydrogen atoms has been carefully studied by Szwarc[493]. The accuracy of the measurement of the activation energy has been discussed again by Szwarc[498], who has pointed out that the results obtained with conversions less than 0·01 per cent are probably not reliable, and that all the data at greater conversions lead to an activation energy of 77·5 kcal. He has also mentioned that subsequent experiments carried out in 1948 by J. S. Roberts and in 1949 by J. Murawski give similar results to those previously obtained. The value $D(C_6H_5 . CH_2 - H) = 77{\cdot}5 \pm 3$ kcal has been confirmed by electron impact measurements[441a]. A much higher value, 89 kcal, has been derived from a study of the bromination of toluene[9b]. The reason for the discrepancy is not at present understood.

9.1.6. $D(CH_3 . C_6H_4 . CH_2 - H)$

The pyrolyses of *o*, *m*, and *p*-xylene have also been studied by Szwarc[493] and values of 75 ± 1, 77 ± 2, and $76 \pm 1{\cdot}5$ respectively were obtained for $D(C - H)$.

9.1.6. $D(C_6H_5 . CHCH_3 - H)$ *etc.*

The following dissociation energies in alkyl substituted benzenes have been obtained by Leigh and Szwarc[298] by the pyrolysis methods: $D(Ph . CHMe - H) = 75$ kcal, $D(Ph . CMe_2 - H) = 74$ kcal, $D(Me . Ph . CHMe - H) = 74$ kcal.

9.1.6 (7). $D(H - CN)$

$D(H - CN)$ can be derived by a somewhat roundabout process from electron impact results on methyl cyanide[333]. A detailed

consideration of the appearance potentials of various ions from methyl cyanide in conjunction with other data leads to the conclusion that $D(CH_3-CN)\sim 4{\cdot}5_2$ eV. From this may be obtained $\Delta H_f(CN)$ and hence $D(H-CN)$, with the result $D(H-CN)=114{\cdot}9$ kcal at 25° C. The figure after the decimal point seems uncalled for, and a value of $D(H-CN)=114$ kcal at 0° K is preferred here. The heat of formation of the CN radical used to obtain $D(H-CN)$, $\Delta H_f^\circ(CN)_{25^\circ C}=92{\cdot}7$ kcal, is in good agreement with that obtained by Long[313] from consideration of thermochemical and photochemical data on various cyanides, 92 kcal, and also with a value obtained by Brewer *et al.* (94 kcal)[56]. Long also refers to a direct spectroscopic measurement of $D(H-CN)$ as 117 kcal. The heat of formation of HCN is probably known to within 1 kcal[38], and thus $D(H-CN)$ is likely to be fairly accurately known. *See also* Section 9.6.6 (7), $D(C_2N_2)$.

9.1.6 (7). $D(C_5H_4NCH_2-H)$

Roberts and Szwarc[422] have determined $D(CH)$ in the methyl groups in α, β, and γ-picoline to be 75, 76, and 77 kcal respectively, using the pyrolysis method.

9.1.6 (8). $D(H-CHO)$

There is no certain value for $D(C-H)$ in formaldehyde. Long and Norrish[318] point out that atomic hydrogen reacts very readily with formaldehyde, removing a hydrogen atom, but does not react with methane. They consider that this shows that the dissociation energy of the first CH bond has a smaller value in formaldehyde than in methane.

The photolysis of formaldehyde has been discussed in detail by Steacie[467]. Gorin[186] investigated the photolysis in presence of iodine, and regarded HI formation as indicating the presence of hydrogen atoms produced by

$$HCHO + h\nu \rightarrow H + CHO$$

At 3,650 Å some hydrogen is formed, indicating that a direct molecular rearrangement to hydrogen and carbon monoxide takes place, but some HI is also formed. Thus the energy available at 3,650Å must be sufficient to break the CH bond, whence $D(H-CHO)<78$ kcal.

9.1.6 (8). $D(H-CO)$

Steacie[467] has discussed the photolysis of acetaldehyde in detail. Gorin[186] has derived a value of 26 ± 2 kcal for the activation energy

of the decomposition of HCO $\rightarrow$ H + CO from his study of the acetaldeyhde photolysis, but his quantitative results have been challenged by other workers. Thus 26 kcal is a doubtful upper limit to D(H – CO).

9.1.6 (9). D(F . C_6H_4 . CH_2 – H)

D(CH) in the methyl group of *o*-, *m*-, and *p*-fluorotoluene has been measured as 78 kcal in each, using the pyrolysis technique [503].

9.1.6 (17). $D(CCl_3 - H)$

Szwarc [497] has deduced $D(CCl_3 - H) = 89 \pm 2$ kcal from the experiments of Braunwarth and Schumaker [50] on the photobromination of chloroform. The mechanism is fairly straightforward, and the activation energy for the forward reaction

1. $\quad Br + CHCl_3 \rightarrow CCl_3 + HBr$

is fairly well established as 10 ± 1 kcal. The activation energy of the reverse reaction, however, is given as 6–7 kcal, and is not so well established [467]. Thus the value of ΔH for the above reaction, $\sim$3 kcal, is perhaps not so certain as Szwarc suggests. As in the bromination of methane, we have

$$\Delta H_1 = D(CCl_3 - H) - D(H - Br)$$

whence $D(CCl_3 - H) \sim 90$ kcal.

9.1.6 (35). $D(CH_2Br - H)$

Kistiakowsky and van Artsdalen [266] have examined the photobromination of methyl bromide. $D(CH_2Br - H) \sim 99$ kcal at 0° K may be deduced from their results.

9.1.7. D(NH)

Gaydon [166] gives $3{\cdot}7 \pm 0{\cdot}5$ eV for D(NH) in the diatomic molecule and the value given by Herzberg lies within these limits. King [264], using a semi-empirical interpolation in the known values for the first-row hydrides, gives $\sim 3{\cdot}4$ eV. He used the value of D(HF) based on the high value of $D(F_2)$, but this had little effect, the interpolation depending mainly on D(OH) and D(CH), both of which are fairly well known. Glockler [176], using an empirical interpolation procedure which also depends mainly on D(CH) and D(OH), derived $3{\cdot}7_4$ eV. He has since [176] advanced a value of 4·2 eV (96·9 kcal). This figure is presumably an interpolation between

CH and OH, using 92·2 kcal for D(CH). This last value has no direct experimental support, and is based on an extrapolation for other CH bonds which itself depends on the value of L_C. Thus it appears that appropriately adjusted empirical interpolation procedures can produce a wide range of values for any given dissociation energy.

9.1.7. $D(NH_2 - H)$

The heat of formation of the NH_2 radical, and hence $D(NH_2 - H)$ from the heat of formation of ammonia and $D(H_2)$, has been derived from the kinetics of the pyrolysis of benzylamine and hydrazine. These results lead to $D(NH_2 - H) = 100$ kcal and 104 ± 2 kcal respectively [495, 496].

9.1.8. D(OH)

Several different methods have been used to determine D(OH) in the diatomic molecule:

(*a*) Direct photodissociation of water vapour.
(*b*) Mercury-sensitized photochemical decomposition of water vapour.
(*c*) Evaluation of the van't Hoff isochore for dissociating water vapour in which the concentration of OH is optically determined.
(*d*) Explosion pressure method.
(*f*) Dissociation of hydrogen peroxide into two OH radicals.
(*g*) Reaction between two OH radicals to give hydrogen and oxygen.

The evidence available up to about 1948 has been reviewed by Edse [134]. He points out that the results obtained by these methods differ among themselves by 5 per cent. In *Table 9.1.8.1* we give some values taken from Edse's tabulation, together with some more recent results. Gaydon has given a less detailed review incorporating some of the more recent evidence, and comes to the same conclusion as Edse: that D(OH) is less accurately known than the experiments on the dissociation of water vapour might suggest.

9.1.8. $D(HO - H)$

Since the heat of formation of water is accurately known, $D(H - OH)$ and D(OH) are directly related. The evidence quoted above is equally relevant to $D(H - OH)$. We have D(OH) $+ D(H - OH) = 219$ kcal, whence $D(H - OH) = 116$ kcal.

Table 9.1.8.1. Dissociation energy of OH *molecule*

Method	D(OH)	*Remarks*
$H_2O + h\nu \rightarrow H + OH^*$	104	*a*
$Hg^* + H_2O \rightarrow Hg + H + OH$	$103{\cdot}8 \pm 1{\cdot}0$	*b*
Dissociation of water vapour	$100{\cdot}4 \pm 0{\cdot}9$	*c*
Explosion method	104 ± 1	*d*
Vibration levels of OH	<111	*e*
H_2O_2 *dissociation*	$102{\cdot}7 \pm 0{\cdot}9$	*f*
Reaction between OH *radicals*	<100	*g*

(*a*) Terenin and Neujmin[513]. *See* Section 9.6.8 (1).

(*b*) Result of Ricchemeier, Senftleben, and Pastorff[420] as corrected by Edse[134]. Edse has discussed the kinetics of the reaction and deduced 104·8 kcal as an upper limit from this work.

(*c*) This is the result of Dwyer and Oldenberg[130]. Edse[134] has suggested that their work is not completely free of objection since a linear relation between absorbing centres and absorption intensity was assumed, but it was not shown that the measurements were in fact made in the region of very weak absorption where this relationship holds. The technique is discussed in more detail in Section 3.2.

(*d*) The explosion method[302] has been discussed in Section 3.5.

(*e*) Gaydon[166] has discussed the OH spectrum. He derives D(OH) $= 4{\cdot}46 \pm 0{\cdot}2$ eV (103 kcal) from the data of Tanaka and Koana[507]. Edse[134] derives 103·9 from the same data. Gaydon has also mentioned the vibrational levels of the ground state given by Meinel[342]. He states that a good Birge-Sponer extrapolation leads to a value of 4·8 eV, and that it would be difficult to bring this down to 4·34 eV.

(*f*) Edse[134] deduces a lower limit of $102{\cdot}7 \pm 0{\cdot}9$ kcal to D(OH) from the work of Urey *et al.*[530] on the photochemical dissociation of hydrogen peroxide.

(*g*) Rodebush *et al.*[425] have discussed the reaction of OH radicals in the gas phase to give H_2 and O_2. The radicals were formed by the glow discharge in water vapour. They deduce D(OH) < 100 kcal, but the reactions occurring under these conditions are complex, and their interpretation has been criticized by Oldenberg[374].

A value of 103 ± 5 kcal, as suggested by Gaydon[166], fits the evidence as well as possible, but there is clearly room for further research.

9.1.9. D(HF)

D(HF) is deduced thermochemically from ΔH_f°(HF), $D(H_2)$, and $D(F_2)$. The first two quantities are well enough known, but there has been some argument about the latter (*see* Section 8.2.2.9). $D(F_2)$ now appears to be reasonably well established as 37 kcal, so D(HF) is 134 kcal or 5·8 eV. This is probably good to within ± 2 kcal. Gaydon[166] gave rather wider limits of $\pm 0{\cdot}2$ eV (5 kcal), because at that time $D(F_2)$ had not been so firmly established.

9.1.11. D(NaH)

$2{\cdot}0_5 \pm 0{\cdot}2$ eV[166, 217].

9.1.12. D(MgH)

$2{\cdot}0 \pm 0{\cdot}5$ eV [166, 217].

9.1.13. D(AlH)

$2{\cdot}9 \pm 0{\cdot}2$ eV [166, 217].

9.1.14 *and* 15

No data on D(Si – H) or D(P – H) in either diatomic or polyatomic molecules appear to be available.

9.1.16. D(SH)

Porter [395] has given a value of 85 ± 5 kcal, about which Gaydon has expressed doubts. A more detailed study by Ramsay [409] gives $92{\cdot}7 > D(\mathrm{SH}) > 66{\cdot}3$ kcal. A knowledge of D(SH) is relevant to the heat of atomization of sulphur (*see* Section 8.2.2.16), and 85 kcal fits fairly well with the highest possible values for $\Delta H_f(\mathrm{S}\,;\,\mathrm{g})$. This is not, however, very strong evidence.

9.1.16. D(H – SH)

As with H_2O, D(H – SH) is thermochemically linked to D(S – H). With the high value of $D(S_2)$, a value of 85 kcal for D(SH) leads to 89 kcal for D(H – SH). Franklin and Lumpkin [161], who use the low value of $D(S_2)$, and hence deduce D(H – SH) = 77 kcal, if D(SH) = 85 kcal, remark that by analogy with H_2O, it seems surprising that the first bond dissociation energy in H_2S should be weaker than the second. They prefer to take D(H – SH) = 95 kcal which follows from their electron impact work, and D(SH) = 67 kcal, which fits the low value of $D(S_2)$, 3·3 eV. This low value of $D(S_2)$ also strikes Franklin and Lumpkin as odd, and on chemical grounds they prefer 101 kcal (4·4 eV) ways. However, their value of 95 kcal for D(H – SH) is equal to the value of 89 mentioned above, within the errors. *See* Section 8.2.2.16, also Friedman [162].

9.1.17. D(HCl)

D(HCl) depends upon well established thermochemistry, $D(H_2)$ and $D(Cl_2)$. It equals 4·43 eV [166, 217].

9.1.19. D(KH)

$1{\cdot}8_6$ eV [166, 217].

9.1.20. D(CaH)

$\leqslant 1{\cdot}7$ eV [166, 217].

9.1.25. D(MnH)

D(MnH) is very uncertain, but probably $<2{\cdot}4$ eV [166, 217].

9.1.28. D(NiH)

Gaydon [166] gives $2{\cdot}6 \pm 0{\cdot}3$ eV, Herzberg [217] $<3{\cdot}1$ eV.

9.1.29. D(CuH)

Gaydon [166] gives $2{\cdot}7 \pm 0{\cdot}5$ eV, Herzberg [217] $<2{\cdot}9$ eV.

9.1.30. D(ZnH)

0·85 eV [166, 217].

9.1.31, 32, 33, 34

There appear to be no data on D(Ga – H), D(Ge – H), D(As – H) and D(Se – H) in either polyatomic or diatomic molecules.

9.1.35. D(HBr)

3·75 eV established as for other halogen acids [166, 217].

9.1.37. D(RbH)

$1{\cdot}7 \pm 0{\cdot}2$ eV according to Gaydon [166], $<1{\cdot}9$ to Herzberg [217].

9.1.38. D(SrH)

Gaydon [166] gives $1{\cdot}65 \pm 0{\cdot}1$ eV, Herzberg [217] $<1{\cdot}68$ eV.

9.1.47. D(AgH)

D(AgH) = 2·5 eV is deduced thermochemically by comparison of the rates of evaporation of silver in He or N_2 and in H_2 [152, 166, 217].

9.1.48. D(CdH)

D(CdH) = 0·678 eV is established spectroscopically by a rapid convergence nearly to a limit [166, 217].

9.1.49. D(InH)

Gaydon [166] gives $2{\cdot}5 \pm 0{\cdot}1$ eV, Herzberg [217] $\leqslant 2{\cdot}48$ eV. This is a molecule where there is a potential maximum [217].

9.1.50. D(SnH)

D(Sn – H) $<3{\cdot}2$ eV [166, 217].

9.1.51, 52

There appear to be no data on D(Sb – H) or on D(Te – H).

9.1.53. D(HI)

Determined as for other halogen acids, $D(HI) = 3{\cdot}056$ eV [166, 217].

9.1.55. D(CsH)

$1{\cdot}8 \pm 0{\cdot}3$ eV [166, 217].

9.1.56. D(BaH)

$1{\cdot}8 \pm 0{\cdot}1$ eV [166, 217].

9.1.79. D(AuH)

3·1 eV [166, 217] based on rate of evaporation measurements (*see* Section 9.1.47).

9.1.80. D(HgH)

0·372 eV [166, 217]. The nature of the binding in HgH and in other monovalent Hg compounds has been discussed by Skinner [453] and by Gowenlock, Polanyi, and Warhurst [190]. The ground state of the mercury atom is zero valent, and excitation to the ^3P state, in which the atom can form two bonds, requires 112 kcal. The large difference between D(RHg – R) and D(R – Hg) the latter of which is only about 6 kcal, suggests that the mercury atom forming a single bond is in the ground state, and therefore that a special explanation for bond formation is required. Gowenlock *et al.* suggest that the bond is predominantly a polarization bond, that is, one held together by Van der Waals forces, stabilized by resonance with an excited covalent structure. This bond is just on the margin of being sufficiently stable to be described as a 'chemical bond' in the usual sense.

9.1.81. D(TlH)

Gaydon [166] gives $D(TlH) = 2{\cdot}0 \pm 0{\cdot}2$ eV, Herzberg [217], $\leqslant 2{\cdot}18$ eV.

9.1.82. D(PbH)

There is some uncertainty about D(Pb – H). Gaydon [166] gives $1{\cdot}8 \pm 0{\cdot}2$, Herzberg [217] $< 1{\cdot}59$ eV.

9.1.83. D(BiH)

$2{\cdot}5 \pm 0{\cdot}3$ eV [166, 217].

9.3.3. $D(Li_2)$

Molecular beam data give 1·03 eV [217, 305]. (*See also* Section 3·6.) Gaydon [166] gives $1{\cdot}10 \pm 0{\cdot}05$ eV, taking spectroscopic data into account.

9.3.9. D(LiF)

Gaydon[166] gives $D(\mathrm{LiF}) = 5{\cdot}95 \pm 0{\cdot}5$ eV, from thermochemical evidence.

9.3.17. D(LiCl)

Gaydon[166] gives $D(\mathrm{LiCl}) = 5{\cdot}0 \pm 0{\cdot}3$ eV from thermochemical evidence.

9.3.35. D(LiBr)

Gaydon[166] gives $4{\cdot}3_5 \pm 0{\cdot}3$ eV from thermochemical evidence.

9·3·53. D(LiI)

Gaydon[166] gives $3{\cdot}5 \pm 0{\cdot}2$ eV from thermochemical data. There is some uncertainty about the heat of sublimation of solid LiI[217].

9.4.8. D(BeO)

The spectroscopic evidence on the diatomic molecule gives a very much lower value of the dissociation energy than does the thermochemical. Gaydon[166] considers that this may be because the ground state is incorrectly identified, and gives $5{\cdot}4 \pm 0{\cdot}7$ eV, being the mean of the flame and thermochemical values. Drummond and Barrow[122] have reconsidered the thermochemical evidence, and give $5{\cdot}5 \pm 0{\cdot}2$ eV. However, since their paper was written, Cosgrove and Snyder[91] have published a new determination of the heat of formation of solid BeO ($\Delta H_f = -143{\cdot}1$ kcal), which differs by 2·9 kcal from the value used by Drummond and Barrow. Their value is consequently reduced to 5·4 eV, the same as that given by Gaydon.

9.4.8. D(Be – OH)

Grossweiner and Seifert[193] observed an increase in the volatility of BeO in the presence of water. This they assumed to be due to the formation of $Be(OH)_2$ in the vapour phase. For the reaction $BeO(s) + H_2O(g) \rightarrow Be(OH)_2$ they obtained $\Delta H^\circ = 41{\cdot}5$ kcal, and thence the average value of D(BeO) in $Be(OH)_2$ as 109 kcal.

9.4.9. D(BeF)

Gaydon[166] gives $D(\mathrm{BeF}) = 4 \pm 1$ eV, Herzberg[217] gives 5·4 eV from linear Birge-Sponer extrapolation. (*See* Section 9.4.17.)

9.4.17. D(BeCl)

The spectroscopic value of D(BeCl) is very doubtful. A Birge-Sponer extrapolation gives 4·3 eV, but Gaydon[166] points out that

for molecules of this nature, in which one atom has a zero-valent ground state, the extrapolation may give too high a value. He suggests $3{\cdot}0 \pm 0{\cdot}5$ eV, or 69 kcal. This value is adopted by Skinner, who sets the uncertainty at ± 15 kcal [453].

9.4.17. $D(\mathrm{ClBe-Cl})$

Skinner [453] has combined Gaydon's estimate of $D(\mathrm{BeCl})$ with the heat of atomization of $BeCl_2(g)$ to give $D(\mathrm{ClBe-Cl}) = 147 \pm 15$ kcal. This gives a very large value for $D(\mathrm{BeCl-Cl}) - D(\mathrm{BeCl})$, which would, of course, be reduced if a higher value for $D(\mathrm{BeCl})$ were chosen. Skinner discusses the significance of this difference.

9.5.5. $D(B_2)$

Gaydon [166] gives $3{\cdot}0 \pm 0{\cdot}5$ eV, Herzberg [217] gives 3·6 eV.

9.5.7. $D(\mathrm{BN})$

Gaydon [166] gives $4{\cdot}0 \pm 0{\cdot}5$ eV for $D(\mathrm{BN})$ from the spectrum. The identification of the ground state of this molecule is uncertain. Herzberg gives 5·0 eV and states that thermochemical evidence due to Satoh leads to $D(\mathrm{BN}) \pm 4{\cdot}93$ eV. The present author has only been able to consult Satoh's paper in abstract [440], from which it appears that he measured the dissociation pressure of solid BN from which we may deduce $-\Delta H_f(\mathrm{BN;\ c}) = 28{\cdot}5$ kcal. The thermochemical derivation of $D(\mathrm{BN})$ from this information requires a knowledge of $\Delta H_f(\mathrm{B;\ g})$, $D(N_2)$, and $\Delta H_f(\mathrm{BN})$, none of which are certainly known. Gaydon's value has been preferred by the N.B.S. [529], who give $\Delta H_f(\mathrm{BN;\ c}) = -32{\cdot}1$ kcal, which is in agreement with the value from Satoh's work. They do not, however, give a reference. Skinner and Smith [455a] give an average value of $D(\mathrm{B-N})$ in $B(NMe_2)_3$.

9.5.8. $D(\mathrm{BO})$

The spectroscopic evidence on $D(\mathrm{BO})$ is not very satisfactory. Gaydon [166] gives $7{\cdot}6 \pm 0{\cdot}4$ eV, Herzberg [217] 9·1 eV. Gaydon quotes thermochemical evidence leading to $8{\cdot}0 \pm 0{\cdot}2$ eV.

9.5.8. $\bar{D}(\mathrm{B-OR})$

Charnley, Skinner, and Smith [74] have deduced the average bond dissociation energy $\bar{D}(\mathrm{B-OR})$ in the esters of boric acid $B(OR)_3$. The heats of formation of four alkyl borates were determined from their heats of hydrolysis. From these, together with some subsidiary data, they found the following values of $\bar{D}(\mathrm{B-O})$ in R_3BO_3 : $\bar{D}(\mathrm{B-O}) = \bar{D}(\mathrm{RO-H}) + x$ kcal, where $x = 4{\cdot}1$, $4{\cdot}3$, $5{\cdot}0_5$

and 5·5 for R = methyl, ethyl, *n*-propyl, and *n*-butyl respectively. Their estimates of $\bar{D}$(RO – H) from other data lead to $\bar{D}$(B – O) in alkyl borates in the range 110 ± 5 kcal. These results require knowledge of the heat of formation of (B; g) about which very little appears to be known (Section 8.2.2.5). They should therefore be accepted with caution.

9.5.9. D(BF)

There is considerable doubt about D(BF). Gaydon[166] gives 8·5 ± 0·5 eV, Herzberg[217] gives 4·3 eV doubtfully. There is no evidence about D(BF) in BF_3 molecule.

9.5.16. D(BS)

Gaydon[166] gives D(BS) = 5·1 ± 0·8 eV, and this appears to be doubtful.

9.5.17. D(B – Cl)

Gaydon[166] gives D(BCl) = 5·1 ± 0·4 eV. A linear Birge-Sponer extrapolation gives 4·2 eV[217], but this is of doubtful validity[166]. The average value of D(BCl) in BCl_3 is ~93 kcal.

9.5.35. D(B – Br)

Gaydon[166] gives 4·2 ± 0·2 eV for D(BBr), Herzberg[217] gives 4·1 eV. The average value of D(BBr) in BBr_3 may be deduced to be 74 kcal, if the N.B.S.[529] value for the heat of vaporization of boron is taken. This suggests that on this basis D(BX) in the diatomic molecule is greater than $\bar{D}$(BX) in BX_3, an argument which favours the higher value for D(BCl).

9.6.6. $D(C_2)$

The dissociation energy of the diatomic molecule C_2 is not known, although much evidence bearing on it exists. Herzberg[217] gives $D(C_2)$ = 3·6 eV, from spectroscopic evidence. Gaydon[166] has criticized this, on the grounds that other explanations for the effect noted by Herzberg are possible. He points out that an extrapolation of the vibrational levels leads to $D(C_2) < 7$ eV, and contends that a value less than 4 eV is not possible on this basis. Brewer, Gilles, and Jenkins[51] have measured the variation in intensity with temperature of the Swan bonds of C_2, and deduce $D(C_2) = 4{\cdot}9_5 \pm 0{\cdot}3$ eV, and this value has been accepted by Gaydon. However, it has been suggested that the ground state of C_2 has not been correctly identified[372] and this evidence may therefore be beside the point. There is evidence[78] to suggest that there is much

more C_2 present in equilibrium with C vapour than calculated by Brewer *et al.*, which suggests a higher valuc of $D(C_2)$. If we assume that Chupka and Inghram's results [78] can be applied to equilibrium conditions, we may deduce $D(C_2) \sim 6{\cdot}2$ eV from their figures for the temperature dependence of the rate of evaporation of C_2 and C. This is in fairly good agreement with the value of 5·9 eV (135·4 kcal) given by Glockler [175] from bond energy–bond length relationships. It is, however, doubtful whether Chupka and Inghram's results do apply to equilibrium conditions (Section 8.2.2.6). If their value of C_2 corresponds to equilibrium with solid graphite, but the pressure of C is low for reasons explained in Section 8.2.2.6, $D(C_2)$ is reduced.

9.6.6 (1). $D(HC{\equiv}CH)$

A figure of <187 kcal for $D(CC)$ in acetylene, due to Price [400], is frequently quoted. Price studied the absorption spectrum of acetylene and deuterated acetylene in the vacuum ultra-violet. He was able to deduce from the amount of the isotopic shifts that the bond systems he observed were probably concerned with the electrons in the CC bond. The absorption bands of acetylene are sharp from 2,300 Å to 1,900 Å, whereas they are very diffuse around 1,500 Å, and even at 1,300 Å they are still slightly diffuse. If it is assumed that this diffuseness is due to predissociation and if it is further assumed that this predissociation takes place to CH radicals in their ground states, then $D(CC) < 187$ kcal. It will be appreciated that such an interpretation is highly speculative, and indeed Price remarks that the only justification for these assumptions is that they lead to a value of $D(CC)$ in acetylene which is roughly what might be expected on other grounds. These other grounds detailed by Price are not very convincing as they depend on estimates of bond energies. Price mentions in addition that such predissociations leading to dissociation to normal products can be detected in many polyatomic molecules, and instances formaldehyde, in which there is a predissociation at 2,750 Å. This leads to $D(CH) \sim 105$ kcal, which is about the value Price expected for the CH bond. It is considerably greater than other estimates of $D(CH)$ in formaldehyde.

We can link $D(CC)$ in acetylene to L_C by a simple thermochemical cycle, since the heat of formation of acetylene is known. It can be shown that $D(CC) = 2L_C - 110$ kcal, or 166 kcal for $L_C = 138$ kcal. This fits in well enough with Price's value, whereas that obtained using $L_C = 170$ is 230 kcal, much greater than Price's. It is doubtful whether this can be taken as support for the predissociation evidence, or for that matter, as confirmatory evidence for $L_C = 138$ kcal.

9.6.6. (1). $D(H_2C{=}CH_2)$

The value for D(CC) in ethylene usually quoted is also due to Price[399] and is no less speculative than that for acetylene. The band spectrum of ethylene at 1,750 Å is diffuse, and Price interprets this as being due to a predissociation to methylene. Thus $D(CC) < 162$ kcal. There is no real evidence that this dissociation takes place. If $L_C = 138$ kcal, we deduce $D(H_2C{=}CH_2) \sim 125$ kcal by obtaining $\Delta H_f(CH_2)$ from $D(CH - H)$ and $D(CH)$.

9.6.6 (1). $D(H_3C - CH_3)$

A direct estimate of D(CC) by Rice and Dooley, using the mirror technique, leads to 80 ± 6 kcal, according to Szwarc[497]. From $D(CH_3 - H) = 101 \pm 1$ kcal at 0° K, and thermochemical data, we deduce $D(CH_3 - CH_3) = 83{\cdot}3 \pm 1$ kcal at 0° K. This can be taken as fairly well established.

9.6.6 (1). $D(CH_2 : CH \,.\, CH_2 - CH_3)$

D(CC) for the 3 : 4 single bond in 1-butene has been determined as 61·5 kcal by Szwarc and Sehon[443].

9.6.6 (1). $D(CH_3 \,.\, CH_2 - CH_2 \,.\, CH_3)$

D(Et – Et) in *n*-butane has been deduced from electron impact measurements to be 77·6 kcal[470]. This depends on the same data as those leading to $D(Et - H) = 96 \pm 4{\cdot}5$ kcal, and is therefore subject to at least that error. D(Et – Et) may of course be deduced thermochemically from D(Et – H).

9.6.6 (1). $D(C_6H_5 \,.\, CH_2 - CH_3)$

Szwarc has obtained $63 \pm 1{\cdot}5$ kcal for $D(Ph \,.\, CH_2 - CH_3)$ from the pyrolysis of ethyl benzene[494]. With the known value of $D(Ph \,.\, CH_2 + H)$ this leads to $D(CH_3 - H) = 103$ kcal, so it is fairly reliable.

9.6.6 (1). $D(C_6H_5 \,.\, CH_2 - C_2H_5)$

Pyrolysis of *n*-propyl benzene gives $D(Ph \,.\, CH_2 - C_2H_5)$ as 57·5 kcal, leading to 94 kcal for D(Et – H) using the known value of $D(Ph \,.\, CH_2 - H)$[296].

9.6.6 (1). $D(C_6H_5 \,.\, CH_2 - C_3H_7)$

Pyrolysis of *n*-butyl benzene gives $D(Ph \,.\, CH_2 - C_3H_7) = 65$ kcal, leading to 100 kcal for $D(n\text{-}Pr - H)$[297].

9.6.6 (1). $D(C_6H_5 . CH(CH_3) - CH_3)$
$D(p\text{-}CH_3 . C_6H_4 . CH(CH_3) - CH_3)$
$D(C_6H_5 . C(CH_3)_2 - CH_3)$

Leigh and Szwarc[298] pyrolysed cumene, *p*-cymene, and *tert*-butyl benzene, by their usual technique, and obtained 61, 60, and 59·5 kcal respectively for the dissociation energies of the weakest C – C bonds. From these they were able to deduce the heats of formation of the corresponding radicals and hence the dissociation energies of the corresponding CH bonds. They noted that the variation in C – H bond strength with substitution, so marked in the series D(Me – H), D(Et – H), D(*iso*-Pr – H), D(*tert*-Bu – H) = 101, 96, 94, 89 kcal respectively, was not found to the same extent in substituted toluenes. They give D(Ph . CH_2 – H), D(Ph . CHMe – H), D(Ph . CMe_2 – H) and D(Me . C_6H_4 . CHMe – H) as 77·5, 75, 74, and 74 kcal respectively.

9.6.6 (1). $D(C_6H_5 . CH_2 - CH_2 . C_6H_5)$

D(CC) in dibenzyl may be derived from the activation energy for the pyrolysis of toluene to be 47 kcal. Horrex and Miles[232] attempted to measure the dissociation of dibenzyl by equilibrium methods, but were unsuccessful. They also report a study of the pyrolysis of dibenzyl at low partial pressures and using fractional decompositions. They obtained a first order rate constant

$$k = 10^{9\cdot3} \exp(-48{,}000/\boldsymbol{R}T) \text{ sec.}^{-1}$$

The temperature independent factor is abnormally low, and so the interpretation of the activation energy as a dissociation energy is very doubtful. It is remarkable how close this activation energy is to the dissociation energy deduced from the toluene pyrolysis.

9.6.6 (1). D(CC) *in solution*

Studies of the dissociation energy of compounds of the hexaaryl ethane type to triaryl methane and similar radicals have been made in solution. Ziegler and Ewald[583], for example, measured the heat of dissociation of hexaphenyl ethane from the temperature dependence of the equilibrium constant. The equilibrium constant was measured using the extinction coefficient. They obtained a value of 10–12 kcal, depending slightly on the solvent used. Other results for this compound are quoted by Szwarc[497], but they lie within these limits. The values for the dissociation in the vapour phase cannot be obtained, and the corrections required may

not wholly cancel. For example, Sidgwick[446] mentions that the heat of hydrogenation of hexaphenyl ethane to triphenyl methane is 40·5 kcal in the solid and 34·8 kcal in benzene solution, and suggests that this indicates the kind of discrepancies to be expected. Other equilibrium constant measurements have been made by Preckel and Selwood[397].

In these dissociation reactions the activation energy for recombination differs appreciably from zero, being 6–10 kcal for hexaphenyl ethane. Zeigler, Orth, and Weber[584] measured the rate of decomposition of hexaphenyl ethane in a variety of solvents and found 18–20 kcal for the activation energy, depending on the solvent. Thus measurements of rates can only give an upper limit to the energy. The frequency factor for such reactions is normal. For example, the decomposition of *sym* tetra-(2 : 6-dimethylphenyl) ethane, studied by Coops *et al.*[90] has an activation energy of 22·5, 22·9, 23·0, and 23·4 kcal in *o*-dichlorobenzene, *o*, *m*, and *p*-xylene respectively, and a frequency factor of 10^{12}.

9.6.6 (7). $D(\mathrm{NC-CN})$

The dissociation energy of cyanogen C_2N_2 has been the subject of much controversy, discussed by Gaydon[166] and by Long[313]. Long quotes values of 127, 77, 46, and 125–130 kcal, derived from direct measurement, and concludes that indirect estimation by way of determining the heat of formation of the CN radical by some other method is more likely to give reliable results. The long wavelength limits of the second regions of continuous absorption in methyl cyanide and iodine cyanide are 1,600 Å and 2,100 Å respectively. These regions are considered to correspond to photodissociation in which, as shown by fluorescence, the radicals are produced in the excited $B\,^2\Sigma$ state. Subtracting the excitation energy of the radical, 73·6 kcal, from these limiting energies Long obtains $D(\mathrm{CH_3-CN})$ and $D(\mathrm{I-CN})$ as 105·0 and 62·5 kcal. These are of course upper limits. They may be used with other thermochemical information to provide values of $\Delta H_f(\mathrm{CN})_{0°\,\mathrm{K}} = 92{\cdot}5$ and 91·8 kcal. Long further mentions that extrapolation of the vibrational levels in the absorption spectrum of HCN leads to 117 kcal for $D(\mathrm{H-CN})$, whence $\Delta H_f^\circ(\mathrm{CN}) = 95{\cdot}5$ kcal, in reasonable agreement with the previous value. Taking 92·5 kcal as the heat of formation of CN, Long concludes that $D(\mathrm{NC-CN}) = 113{\cdot}6$ kcal at 0° K.

The heat of formation of CN has also been determined directly by Brewer, Templeton, and Jenkins[56], who find $94{\cdot}3 \pm 0{\cdot}6$ kcal at 0° K, in good agreement with Long's value. Further, McDowell

and Warren[333] have deduced $D(CH_3 - CN)$ to be 104·2 kcal at 25° C, or about 103·3 kcal at 0° K. From this and thermochemical data they deduce $D(C_2N_2) = 112$ kcal, derived from $\Delta H_f^\circ(CN)_{25^\circ C} = 92{\cdot}7$ kcal, and from $\Delta H_f^\circ(C_2N_2) = 73{\cdot}84 \pm 0.43$, obtained by Knowlton and Prosen[274].

Thus $D(C_2N_2)$ can be taken as fairly well established as about 112 kcal. It would be nice to know why none of the direct measurements gave the right answer.

9.6.6 (7). $D(CH_3 - CN)$

The value determined by McDowell and Warren[333], ~103 kcal, fits well with photodissociation evidence and other evidence relating to $\Delta H_f(CN)$ (*see* above).

9.6.6 (8). $D(CH_2 - CO)$

The splitting of the CC bond is undoubtedly the primary step in the photolysis of ketene. The results suggest an energy requirement of approximately 80 kcal[467].

9.6.6 (8). $D(CH_3 - CO)$

The decomposition of the acetyl radical to methyl and carbon monoxide is a step usually assumed in the discussion of the photolysis of acetaldehyde, acetone, and diacetyl. Steacie[467] discusses the evidence and concludes that the activation energy for this process is probably about 18 kcal. Szwarc[497] quotes a set of values from various photolysis experiments, ranging from 9 to 18 kcal, all as upper limits. This appears to be based on a misinterpretation of the evidence. For example, Gorin[186], in an investigation of the photolysis of acetone in the presence of iodine, found that very little CO was formed at low temperatures. This was considered to be due to the preferential reaction of the acetyl radicals with the iodine. At higher temperatures CO is produced, but some acetyl iodide is still found even at 130° C. This suggests that acetyl is rather stable, and Gorin estimated a minimum of 17 kcal, instead of a maximum, as given by Szwarc. Other evidence, quoted by Steacie, leads to about the same value which appears to be fairly well established. The lower values apparently rest on a less detailed study of the photolysis.

9.6.6 (8). $D(CH_3 - CHO)$

Grahame and Rollefson[191] have measured the activation energy of the high temperature photolysis of acetaldehyde which is almost

entirely a radical reaction. This they combine with the value of the activation energy of the thermal decomposition to obtain E for

$$CH_3CHO \rightarrow CH_3 + CHO$$

to be $74{\cdot}8 \pm 1{\cdot}6$ kcal. This result is independent of all assumptions except that the radical mechanism of the photolysis is the same as that of the thermal decomposition, except, of course, that in the former the initial split is brought about photochemically and in the latter thermally. Steacie[467] has discussed this result and considers that the error limits are far too narrow and should be at least ± 5 kcal.

9.6.6 (9). $D(F_2C=CF_2)$

Atkinson[15] has investigated the mercury photosensitized reactions of tetrafluoroethylene, which differ considerably from the corresponding reactions of ethylene. The primary step is almost certainly dissociation of the carbon-carbon bond to form the radical CF_2, probably in the triplet state. We may deduce $D(F_2C=CF_2)<112$ kcal.

9.6.6 (9). $D(CH_3-CF_3)$ *and* $D(CF_3-CF_3)$

Dibeler, Reese, and Mohler[111] measured the appearance potentials of CH_3^+ and CF_3^+ in $CF_3 \cdot CH_3$ and C_2F_6, with the results given in *Table 9.6.6 (9). 1* from which they deduced $D(CH_3-CF_3)=117$ kcal, and $D(CF_3 \cdot CF_3)=124$ kcal. These results are upper limits and the values certainly seem rather high.

Table 9.6.6 (9). 1

Compound	*Ion*	*A*
$CH_3 \cdot CF_3$	CH_3^+	15·2 V
	CF_3^+	14·0 V
$CF_3 \cdot CF_3$	CF_3^+	14·3 V

9.6.7. $D(CN)$

The spectroscopic evidence on $D(CN)$ is not at all conclusive. $D(CN)$ is related to other dissociation energies as follows:

$$D(CN)=L_C+\tfrac{1}{2}D(N_2)-\Delta H_f(CN)$$

If we take $L_C=138$ kcal, $D(N_2)=7{\cdot}38$ eV (170 kcal) and $\Delta H_f(CN)=94$ kcal, of which quantities only the last may be taken as well established, we obtain $D(CN)=129$ kcal (5·6 eV). This does not agree with any of the values suggested from spectroscopic evidence.

Gaydon[166], who favours high values of L_C and $D(N_2)$, is naturally led to favour a much higher value for $D(CN)$, 7·5 or 8·2 eV. Long[313] gives 118 kcal or 5·11 eV as a possible spectroscopic value of $D(CN)$, which fits better with $D(CO) = 9{\cdot}14$ eV and $L_C = 125$ kcal.

9.6.7 (1). $D(CH_3 - NH_2)$

Electron impact measurements of the appearance potentials of various ions in the mass spectrum of methylamine and other amines by Collin[82] lead to upper limits to $D(CN)$ in these compounds which appear to be very much larger than the most probable values. These probable values are not directly determined, but can be obtained from the heats of formation of the amines and the radicals concerned. Collin, for example, gives ~140 kcal as an upper limit to $D(CH_3 - NH_2)$, whereas the most probable value is about 80 kcal.

9.6.7 (1). $D(CH_3 . N : N - CH_3)$

A recent kinetic study of the thermal decomposition of azomethane gives $D(CH_3 . N = N - CH_3) = 46$ kcal[377a].

9.6.7 (1). $D(C_6H_5 . CH_2 - NH_2)$

Szwarc has established the value of 59 ± 4 kcal for $D(CN)$ in benzylamine using his pyrolysis method[496]. The resulting value for $\Delta H_f(NH_2)$ agrees with that obtained by the pyrolysis of hydrazine.

9.6.7 (8). $D(CH_3 - NO_2)$

Cottrell, Graham, and Reid[94] studied the pyrolysis of nitromethane in a static system, and concluded from analyses of products that the most probable initial step was the fission of the CN bond. If this is correct $D(CH_3 - NO_2) = 53{\cdot}6$ kcal. This is in reasonably good agreement with the value obtained thermochemically from the heats of formation of CH_3, NO_2, and CH_3NO_2, provided $\Delta H_f(CH_3NO_2)$ given by Holcomb and Dorsey[227] is used. If, however, older data for the heat of formation of nitromethane[38] are used the thermochemical value of $D(CH_3 - NO_2)$ becomes 57 kcal, rather greater than the experimental activation energy. The older data for nitromethane are due to three different investigators, and are reasonably concordant, so there may be some doubt about the new value. All the other new values given by Holcomb and Dorsey for nitroparaffins are in agreement with the older ones where comparison is possible. This suggests that the interpretation of the kinetic evidence may be incorrect. The reaction has

been reinvestigated by Hillenbrand and Kilpatrick[221] at higher temperatures using a flow technique. They found that more formaldehyde was formed in the early stages of the reaction than could be accounted for by the mechanism suggested by Cottrell, and concluded that at least part of the reaction was taking place by an intramolecular rearrangement. Thus a value of 52–57 kcal for $D(CH_3-NO_2)$ is as close as can be given in the light of the present evidence.

Cottrell, Graham, and Reid[95] have shown that the pyrolyses of nitroethane and nitropropane probably do not proceed by a bond breaking mechanism.

9.6.8. D(CO)

D(CO) is perhaps the most controversial dissociation energy of all. It has been discussed in connection with L_C in Section 8.2.26, where reasons are given for the belief that the most likely values are 9·61 or 9·85 eV, although values of 9·14 and 11·11 eV have been much discussed. The value corresponding to the value taken here for L_C is $9{\cdot}7_3 \pm 0{\cdot}1_2$ eV, or ~224 kcal.

9.6.8. D(O – CO)

D(CO) in carbon dioxide may be derived from the heats of formation of carbon dioxide, carbon monoxide, and oxygen atoms to be 127 kcal.

9.6.8 (1). D(HCO – OH)

D(C – O), or an upper limit to it, in formic acid has been determined by the examination of its photodissociation in the Schumann ultra-violet. Normally the interpretation of photodissociation processes in polyatomic molecules is doubtful, because the identification of the primary step may depend on the assumed overall mechanism of the process. However, direct observation of the photodissociation process is possible when the absorbed quantum of energy is large enough to dissociate a molecule into excited radicals, which can then be detected by their emission. Terenin and Neujmin[513] observed that in the Schumann ultra-violet polyatomic molecules containing the OH and CN grouping showed bands belonging to excited OH and CN diatomic molecules. By subtracting the excitation energy (E) from the energy required for the process, an upper limit to the dissociation energy was obtained. Their results for several molecules are given in *Table 9.6.8 (1). 1.* An assessment of how close these D values are likely to be to the true ones can be obtained from their concordance with other

directly determined values where such exist. The values already adopted for $D(H-OH)$ and $D(CH_3CN)$, 116 and 103 kcal, are in very good agreement with those given here, although it should be noted that Terenin's results were among the evidence used by Long to fix $\Delta H_f(CN)$. The value for (NH_2-H) given by Terenin appears to be about 15 kcal too high, an error which is of course of the correct sign.

Table 9.6.8 (1). 1

Substance	*Process*	$D+E$ (kcal)	Å
H_2O	$H+OH^*$	115+92	1,400
CH_3OH	CH_3+OH^*	90+92	1,560
C_2H_5OH	$C_2H_5+OH^*$	90+92	1,560
HCOOH	$HCO+OH^*$	90+92	1,560
CH_3COOH	CH_3CO+OH^*	90+92	1,560
CH_3CN	CH_3+CN^*	105+73	1,600
NH_3	$H+NH_2^*$	117+55	1,650
I_2	$I+I^*$	35+159	1,460

The value of $D(C-O)$ in formic acid (90 kcal) is unlikely to be very far from the truth.

9.6.8 (1). $D(CH_3-OH)$

$D(CH_3OH)=90$ kcal, as deduced by Terenin[513], is in good agreement with the value of 91 kcal deduced from the known heats of formation of the methyl and hydroxyl radicals.

9.6.8 (1). $D(C_2H_5OH)$, $D(CH_3CO-OH)$

90 kcal, *see* above.

9.6.9. $D(C-F)$

Gaydon[166] gives $D(CF)$ in the diatomic molecule as $4{\cdot}6\pm0{\cdot}3$ eV, but this is not very certain. There is no direct evidence on $D(C-F)$ in polyatomic molecules.

9.6.15. $D(CP)$

Gaydon[166] gives 6 ± 1 eV for $D(CP)$ in the diatomic molecule, Herzberg[217] a doubtful 6·9 eV.

9.6.16. $D(CS)$

Gaydon[166] gives $7{\cdot}2\pm1{\cdot}0$ eV for $D(CS)$ in the diatomic molecule, Herzberg[217] gives a doubtful 7·8. In the gas phase CS shows the stability of a normal molecule[131].

9.6.16 (1). $D(R-SH)$

Franklin and Lumpkin[161] have determined some C – S, H – S, amd S – S bond dissociation energies by the electron impact method. They determined the heat of formation of the SH radical by measuring the appearance potentials of ethyl, *n*-propyl, and *t*-butyl ions obtained by electron bombardment of the mercaptans. This value of $\Delta H_f(SH)$ was then combined with the heats of formation of alkyl radicals and the heats of formation of the mercaptans to give $D(R-SH)$. The heats of formation of ethyl and *n*-propyl mercaptan were old values quoted by Barrow and Pitzer[16], and that of *t*-butyl mercaptan was determined by Franklin and Lumpkin themselves. They obtain $D(R-SH) = 74{\cdot}2$, $73{\cdot}4$, $72{\cdot}1$, $70{\cdot}6$, and $69{\cdot}4$ for R = Me, Et, *n*-Pr, *iso*-Pr, and *tert*-Bu respectively, using the heats of formation of the radicals given by Roberts and Skinner[421]. The accuracy suggested by the figures after the decimal point is illusory, and it is suggested in Section 8.2.2.16 that the electron impact results may perhaps be better interpreted by putting $\Delta H_f(SH) = 34$ kcal, or $4{\cdot}4$ kcal less than the value adopted by Franklin and Lumpkin. This would reduce the values of $D(R-SH)$ to 70, 69, 68, 66, and 65 kcal, probably ± 5 kcal, for R = Me, Et, *n*-Pr, *iso*-Pr, and *tert*-Bu respectively.

9.6.16 (1). $D(R-SR)$

Franklin and Lumpkin[161] also measured the heats of formation of the radicals CH_3S and C_2H_5S by the electron impact method. The most obvious method of doing this was to measure the appearance potentials of CH_3^+ from thioethers. This was tried, but the results were erratic. Therefore the appearance potentials of CH_3S^+ and $C_2H_5S^+$ from thioethers were measured, and combined with the appearance potentials of these ions from disulphides to give the heats of formation of the radicals. The heats of formation of the disulphides were required for the thermochemical calculation and were measured. The resulting heats of formation, ΔH_f, were $33{\cdot}0$ and $25{\cdot}0$ kcal for CH_3S and C_2H_5S respectively. These heats can then be combined with known values for the heats of formation of alkyl radicals to obtain $D(C-S)$ in thioethers. Franklin and Lumpkin give $D(Me-SMe) = 73{\cdot}2$, $D(Et-SMe) = 71{\cdot}8$, $D(Me-SEt) = 70{\cdot}6$, and $D(Et-SEt) = 69{\cdot}3$ kcal, and further values can of course be deduced.

9.6.17. $D(CH_3-Cl)$

A very doubtful direct value for $D(CH_3-Cl)$ has been obtained by Doty[117] using the hot wire method. It is 74 kcal, which is to be compared with the thermochemically derived value of 80 kcal.

9.6.34. D(CSe)

Gaydon[166] gives a value of 5 ± 1 eV for D(CSe) in the diatomic molecule, Herzberg[217] gives a doubtful 6·8 eV.

9.6.35. $D(CBr_3 - Br)$

D(C – Br) in carbon tetrabromide can be deduced from the results of an investigation of the bromine photosensitized oxidation of carbon tetrabromide[276]. The suggested mechanism, which is of the standard type, involves the step.

$$Br + CBr_4 \rightarrow CBr_3 + Br_2$$

Steacie[467] comments that if the mechanism is correct in principle, this reaction must have an activation energy not greater than 5 kcal. This implies that D(C – Br) in carbon tetrabromide must be less than 50 kcal, which Steacie considers to be a surprisingly low result. It is, however, in line with other recent evidence on D(C – Br) in other halogen substituted methanes.

9.6.35. $D(CH_3 - Br)$

The value of D(C – Br) in methyl bromide has been determined by the pyrolysis method by Szwarc to be 67 kcal. The strength of the C – Br bond is such that it is particularly suited to pyrolyses using the toluene carrier gas technique, and Szwarc and his collaborators have exploited this property very thoroughly*. It is convenient to list here the forty-odd values of D(C – Br) in various compounds obtained in this way. Ladacki and Szwarc[285] give the following values for the activation energy, frequency factor and rate constant of the pyrolysis. The constancy of the frequency factor over a

Table 9.6.35 (1). 1

R – Br	E kcal	ν(sec.$^{-1}$)	$k_{900°K}$ (sec^{-1})
$CH_2 : CH \cdot CH_2$-Br	47·5	$0{\cdot}5 \times 10^{13}$	16·0
CCl_3-Br	49	2	30·0
$C_6H_5 \cdot CH_2$-Br	50·5	1	6·0
C_6H_5CO-Br	57·0	5	0·60
9-*anthracyl*-Br	65·6	1·5	0·002
CH_3-Br	~67·0	~2	0·001
9-*phenanthryl*-Br	67·7	1	0·0004
β-naphthyl-Br	70·0	1·5	0·0002
α-naphthyl-Br	70·9	3·5	0·00028
phenyl Br	70·9	2	0·00016

* Pyrolysis of alkyl bromides can also take place by direct unimolecular decomposition, and this reaction has been studied by Maccoll *et al.*[192].

range of over 20 kcal in E and 10^5 in rate constant is confirmation of Szwarc's views on the mechanism of the reaction (Section 4.2). A further set of activation energies has been given by Szwarc and Williams[506] (*Table 9.6.35 (1). 2*). Values for some substituted

Table 9.6.35 (1). 2

Compound	D(C – Br)	*Compound*	D(C – Br)
bromobenzene	70·9 kcal	*p-phenyl bromobenzene*	70·7 kcal
p-fluorobromobenzene	70·4	*m*-C_6H_5 *bromobenzene*	70·1
p-Cl-*bromobenzene*	70·3	*o*-C_6H_5 *bromobenzene*	68·2
m-Cl-*bromobenzene*	69·9	*p*-CN *bromobenzene*	70·6
o-Cl-*bromobenzene*	69·7	*m*-CN *bromobenzene*	70·1
p-Br-*bromobenzene*	70·6	*o*-CN *bromobenzene*	70·3
o-Br-*bromobenzene*	69·1	*p*-OH *bromobenzene*	67·0
p-CH_3-*bromobenzene*	70·7	*o*-OH *bromobenzene*	67·1
m-CH_3-*bromobenzene*	70·7	3-Br-*pyridine*	75·9
o-CH_3-*bromobenzene*	70·1	2-Br-*pyridine*	71·5
		2-Br-*thiophene*	68·5

benzyl bromides have been given by Szwarc, Leigh, and Sehon[502]. The substituents and the difference D(kcal) between the bond dissociation energy in benzyl bromide and in the substituted compound are:

o-Cl, 0·9; *m*-Cl, 0·1; *p*-Cl, 0·4
m-Br, 0·3; *p*-Br, 0·3
o-Me, 2·0; *m*-Me 0·0; *p*-Me, 1·4
m-NO_2 2·1; *p*-NO_2 1·1
m-CN 1·4; p-CN 0·7

These values will not be listed separately in the following. Values of D(C – Br) obtained by other methods follow in the usual order. (*See also* 9.6.35 (9).)

9.6.35 (9). $D(CF_3 - Br)$

Pyrolysis gives 65 kcal[497].

9.6.35 (1). $D(C_2H_2 - Br)$

Szwarc[497] has given D(HCCH – Br) = 8 ± 4 kcal, from the work of Müller and Schumacher[360] on the photobromination of acetylene. Steacie has suggested 11 kcal on the basis of the same evidence.

9.6.35 (1). $D(CH_2 : CH . CH_2 - Br)$

The pyrolysis of allyl bromide has been studied by Maccoll[329]. He found an activation energy of 45·5 kcal which he identified with

D(C – Br). This is in good agreement with that found by Szwarc. He also found that the first order rate began to fall off at pressures below 300 mm, which seems rather a high pressure for this to happen.

9.6.35 (17). $D(CCl_3 - Br)$

The thermal exchange reaction between bromine and trichlorobromomethane has been studied by Miller and Willard [348] and by Sullivan and Davidson [484], using essentially the same methods. The former obtain 29·8 kcal for the activation energy of the overall reaction in the gas phase, the latter 33·1 kcal. The former result depends on kinetic measurements over the range 423–493° K, whereas the latter depends on measurements over the much smaller range 419–456° K. The actual rate constants in the two investigations are the same at about 440° K. A value of about 31 kcal for the activation energy seems indicated. This leads to 8 kcal for the activation energy of the reaction

$$CCl_3Br + Br \rightarrow CCl_3 + Br_2$$

and to an upper limit of 54 kcal to D(C – Br). The kinetics of the forward and the reverse reactions in the vapour phase thermal bromination of chloroform have been measured by Sullivan and Davidson [485], who conclude that $D(CH_3 - Br) - D(CCl_3 - Br) \sim$ 11–18, whence $D(CCl_3 - Br)$ 49–56 kcal. The pyrolysis result of 48 ± 1 kcal [504] is in agreement with this. This fairly reliable estimate of $D(CCl_3 - Br)$ gives support to the earlier mentioned value of ~50 kcal for $D(CBr_3 - Br)$.

9.6.35 (17). D(CHCl . CHCl – Br) and D(CHClBrCHCl – Br)

Values of 11 ± 3 and 51 ± 4 for D(CHCl . CHClBr) and D(CHClBr . CHCl – Br) have been deduced by Szwarc [497] from the kinetic results on the photobromation of dichlorethylene studied by Müller and Schumacher [361]. Steacie [467] remarks that the reaction is too complicated for the mechanism to have been reliably established, and that too much reliance should not be placed on the results.

9.6.53 (1). $D(CH_3 - I)$

Butler and Polanyi [64] have measured the rate of pyrolysis of methyl iodide at one temperature and calculated the activation energy from the first order rate constant using the relation $\log k(\text{sec}^{-1}) = 13 - (E/4{\cdot}57\ T)$, that is, they assumed that the frequency factor is 10^{13} sec^{-1}. They obtained $E = 54$ kcal, and they consider this to be

$D(CH_3 - I)$. The technique was applied to several other iodides, some of the results being given in the paper by Butler and Polanyi already mentioned, and the others reported by Butler, Mandel, and Polanyi[63]. The method has been criticized in general by Szwarc[497] and discussed in Section 4.2. The example of methyl iodide has recently been examined in more detail by Horrex and Lapage[231]. They found that using the same techniques and conditions as those used by Butler and Polanyi, a value of about 60 kcal was obtained for E. They further found that the rate was very sensitive to the precise conditions used, and that the mechanism was certainly not a simple first order decomposition. These findings suggest that the initial derivation of 54 kcal for $D(CH_3 - I)$ is fortuitously close to the correct value.

That $D(CH_3 - I)$ is somewhere near 54 kcal can be shown thermochemically. This has been confirmed by an electron impact value of $52{\cdot}6 \pm 2{\cdot}3$ kcal[330].

9.6.53 (1). $D(C_2H_5 - I)$

Butler and Polanyi[64] obtained 52 kcal for $D(C_2H_5 - I)$ using their pyrolysis technique. Szwarc[497] gives 51 kcal from his own work on the same reaction.

9.6.53 (1). $D(CH_2 : CH \,.\, CH_2 - I)$

Szwarc[497] gives $D(C - I)$ in allyl iodide as 35–37 kcal, from the pyrolysis. This is only slightly less than the value obtained by Butler and Polanyi[64].

9.6.53 (1). $D(C_6H_5 - I)$

Szwarc[497] gives $D(C - I)$ in phenyl iodide as >57 kcal from his own pyrolysis measurements. This is slightly greater than the Butler-Polanyi result.

9.6.53 (1). $D(C_6H_5 \,.\, CH_2 - I)$

Szwarc[497] gives $D(C - I)$ in benzyl iodide as $\sim$39 kcal from his own pyrolysis work. This is less than the Butler-Polanyi figure.

9.6.53. $D(R - I)$

The other values of $D(C - I)$ in organic compounds are unsupported results by the Butler-Polanyi technique[64], and probably not reliable. They are as follows:

$D(CHCl_2 - I) = 42?$ $\qquad$ $D(CHBr_2 - I) = 41?$

$D(CHI_2 - I) = 37?$ $\qquad$ $D(CH_2Cl \,.\, CH_2 - I) = 46?$

$D(CH_2=CH-I)=55?$ $D(n\text{-}C_3H_7-I)=50?$

$D(iso\text{-}C_3H_7-I)=46?$ $D(n\text{-}C_4H_9-I)=49?$

$D(tert\text{-}C_4H_9-I)=45?$ $D(cyclo\text{-}C_6H_{11}-I)=49?$

$D(C_6H_5 . CH_2 . CH_2I)=50?$ kcal.

9.6.80 $D(C-Hg)$

The thermal decomposition of mercury dimethyl and mercury diethyl has been studied by Gowenlock, Polanyi, and Warhurst[189]. They used the flow method with low pressure of substrate and short contact times, and found that although the velocity constant was slightly pressure dependent, the activation energy apparently was not. They found $E=52{\cdot}1$ kcal for $HgMe_2$ and $E=41{\cdot}5$ kcal for $HgEt_2$. An earlier value of 42 kcal for $HgMe_2$[324] is low because of an effective shortening of the reaction zone at high temperatures in the reactors described, owing to a 'humped temperature profile'[323]. The authors consider that the rate-determining process is the fission of the Hg – C bond. They combine their results with thermochemical data to obtain the following values of the Hg – C bond dissociation energy:

R	$D(RHg-R)=D_1$	$D(Hg-R)=D_2$
Me	$51{\cdot}4\pm2$	6 kcal
Et	$41{\cdot}0\pm2$	6 kcal

The theromochemical data on D_1+D_2, from which D_2 is deduced, are as follows: $HgMe_2$, $(D_1+D_2)=57{\cdot}3\pm4$; $HgEt_2$, $(D_1+D_2)=45{\cdot}1\pm6$[357] and the more recent and more precise results of $57{\cdot}1\pm2$ and $48{\cdot}5$ respectively[67]. These values of $D(Hg-R)$ resemble that of Hg – H in being remarkably low. A theoretical interpretation is offered by Gowenlock, Polanyi, and Warhurst[190].

9.7.7. $D(NN)$

$D(N_2)$ is controversial and has been discussed in Section 8.2.2.7. The value is either 7·38 eV, or 9·76 eV, and reasons are given in Section 8.2.2.7 for preferring the former.

9.7.7 (1). $D(H_2N-NH_2)$

Pyrolysis of hydrazine leads to $D(H_2N-NH_2)=60\pm4$ kcal[495]. This gives a heat of formation of the NH_2 radical close to that obtained by the pyrolysis of benzylamine.

9.7.7 (8). $D(O_2N-NO)$

$D(N-N)$ in N_2O_3 may be derived as 10 kcal from an equilibrium study[534].

9.7.7 (8). $D(O_2N-NO_2)$

Equilibrium studies give $D(O_2N-NO_2)=12{\cdot}9$ kcal[172].

9.7.8. $D(NO)$

The spectroscopic evidence on $D(NO)$ is not conclusive. A value of 5·3 or 6·5 eV is obtained thermochemically depending on whether the lower or higher value of $D(N_2)$ is preferred. The lower value appears to the present author to be preferable. Electron impact studies on $D(NO)$ lead unequivocally to 5·3 eV (*see* Section 8.2.2.7) and this is possibly the strongest evidence for the low value of $D(NO)$.

9.7.8. $D(O-NO)$

The heats of formation of NO_2, NO and $D(O_2)$ lead to $D(O-NO)=72$ kcal.

9.7.8 (16). $D(RO-NO)$

The thermal decomposition of a series of alkyl nitrites has been studied by Steacie and co-workers[467]. The primary step is almost certainly

$$RONO \rightarrow RO+NO,$$

and the NO formed inhibits chain reactions. The activation energy is therefore likely to be equal to $D(RO-NO)$. Steacie gives the following values

Substance	*E*
Me nitrite	36·4 kcal
Et ,,	37·7
n-Pr ,,	37·7
iso-Pr ,,	37·0
n-Bu ,,	37·0

From these results, and thermochemistry, Charnley, Skinner, and Smith[74] deduce $\Delta H_f(CH_3O)=-1{\cdot}9$ kcal mole^{-1} and $\Delta H_f(C_2H_5O)=-8{\cdot}7$ kcal. Both values are in fair agreement with results deduced from the pyrolysis of nitrates, and the latter is in good accord with the value (−8·1 kcal) deduced by Rebbert and Laidler[410] from the pyrolysis of diethyl peroxide.

9.7.8 (1, 6). $D(RO-NO_2)$

The first step in the pyrolysis of the alkyl nitrates has been supposed to be O – N bond fission to give NO_2 and an alkoxy radical. The activation energy is 39·5 kcal for methyl nitrate[10], and 39·91 or 34·6 kcal[390] for ethyl nitrate. If the latter value for ethyl nitrate is taken, and assumed to be $D(EtO-NO_2)$ a value for the heat of formation of the ethoxy radical in good agreement with that given by Rebbert and Laidler[410] is obtained, so apparently we may put $D(MeO-NO_2)=40$ kcal, and $D(EtO-NO_2)=34$ kcal. In the opinion of the present author, however, the mechanism of the reaction is not sufficiently well established to allow this to be done. The discrepancy between the result of Adams and Bawn[1] and that of Phillips[390] is large and may well be because of the different pressure ranges in which these authors worked. A further examination of the effect of pressure on rate constant is necessary before it can be taken as established that the reaction is of the first order.

9.7.14. $D(SiN)$

$4{\cdot}5 \pm 0{\cdot}4$ eV[166, 217].

9.7.15. $D(PN)$

$D(P{\equiv}N)$ in the diatomic molecule is $6{\cdot}0 \pm 0{\cdot}8$ eV[166, 217].

9.7.16. $D(NS)$

Gaydon[166] gives $5{\cdot}0 \pm 0{\cdot}1$ eV, Herzberg[217] 5·9 eV.

9.7.17 (8). $D(Cl-NO)$

Szwarc[497] gives $D(Cl-NO)$ as 37 kcal from the equilibrium study of the reaction $2NO + Cl_2 \rightleftharpoons 2NOCl$[30].

9.7.33. $D(AsN)$

Gaydon[166] gives 5 ± 1 eV, Herzberg[217] 6·5.

9.7.35. $D(NBr)$

Gaydon[166] gives $2{\cdot}5 \pm 0{\cdot}5$, Herzberg[217] 3·0 eV.

9.7.35 (8). $D(Br-NO)$

Szwarc[497] gives $D(Br-NO)$ as 28 kcal from the equilibrium $2NO + Br_2 \rightleftharpoons 2NOBr$[42].

9.7.51. $D(SbN)$

Gaydon[166] gives $3{\cdot}1 \pm 0{\cdot}5$ eV, Herzberg[217] 4·8 from a linear Birge-Sponer extrapolation.

9.8.8. $D(O_2)$

$D(O_2) = 5{\cdot}08$ eV (Section 8.2.2.8).

9.8.8 (1). $D(HO - OH)$

A value of 48 kcal for $D(HO - OH)$ may be obtained thermochemically knowing $D(OH)$.

9.8.8 (1, 6). $D(C_2H_5O - OC_2H_5)$

The kinetics of the thermal decomposition of diethyl peroxide have been studied by Harris and Egerton [203] using a static system, and by Rebbert and Laidler [410] using a flow system. They obtain 31·5 kcal and 31·7 kcal respectively for the activation energy of the reaction. This may be set equal to $D(EtO - OEt)$. Using the value for the heat of formation of diethyl peroxide obtained by combustion by Rebbert and Laidler, it yields a value of $-8{\cdot}1$ kcal for $\Delta H_f(C_2H_5O)$, which is in agreement with that found by other methods. The value these authors obtain for $\Delta H_f((C_2H_5O)_2; g)$ is $-47{\cdot}8$ kcal mole^{-1} ($\Delta H_R(1) = -662{\cdot}2$ kcal). This presumably supersedes the earlier value due to Stathis and Egerton [466].

9.8.8 (1, 6). $D(C_3H_7O - OC_3H_7)$

Pyrolysis of di-*n*-propyl peroxide leads to $D(O - O) \sim 35$ kcal [202].

9.8.8 (1, 6). $D((CH_3)_3 . CO - OC(CH_3)_3)$

The pyrolysis of di-*tert*-butyl peroxide has been studied by several workers (Section 4.2). The value of 37 kcal for $D(O - O)$ is probably correct [324]. The error found in Lossing and Tickner's activation energies is probably not present at the temperature used in this investigation [323].

9.8.8 (1, 6). $D(CH_3COO - OCOCH_3)$

Szwarc [497] gives 30 kcal from the pyrolysis of diacetyl peroxide by Walker and Wild [545].

9.8.12. $D(MgO)$

The spectroscopic evidence on $D(MgO)$ and other metallic oxides gives a very different result from the thermochemical. Gaydon [166] has suggested that the ground state may not be correctly identified, and prefers a thermochemical value of $4{\cdot}5 \pm 0{\cdot}7$ eV. Drummond and Barrow [122], in a recent publication, give a thermochemical value of 5·2 eV, but Brewer [50a] considers this too high.

9.8.13. D(AlO)

The pressure of AlO over Al_2O_3 has been measured by Brewer and Searcy [55] by the effusion method. From this they deduce D(AlO) thermochemically to be 138 kcal, which is accepted by Gaydon [166]. The spectroscopic evidence suggests $D(AlO) < 3{\cdot}75$ eV (86·6 kcal) [217], but this must be considered unreliable.

9.8.14. D(SiO)

A thermochemical value of 165 kcal for D(SiO) is given by Brewer and Mastick [53]. Herzberg [217] and Gaydon [166] concur.

9.8.15. D(PO)

In the diatomic molecule, $D(PO) = 6{\cdot}3 \pm 0{\cdot}5$ eV [166, 217].

9.8.15 (9). $D(F_3P{=}O)$

A value of 129·8 kcal for $D(P{=}O)$ in POF_3 has been derived by Charnley and Skinner [73] on the basis of a direct measurement of the heat of oxidation of PF_3 by Ebel and Bretscher [132].

9.8.15 (17 *and* 35). $D(Cl_3P{=}O)$ *and* $D(Br_3P{=}O)$

The heats of hydrolysis of liquid PCl_3, PBr_3, $POCl_3$, and crystalline $POBr_3$ have been measured by Charnley and Skinner [73] and used to derive the heats of formation of these compounds as $\Delta H^\circ_{f\,25^\circ C} = -79{\cdot}4$, $-46{\cdot}5$, $-143{\cdot}8$, and $-110{\cdot}1$ kcal mole^{-1}. Another recent determination of $\Delta H_f(PCl_3; 1)$ and $\Delta H_f(POCl_3; 1)$ by the same method gave $-79{\cdot}6$ and $-144{\cdot}4$ kcal [363], in good agreement with Skinner's results. These values therefore supersede older values in the literature. They lead to $D(O-PCl_3)$ and $D(O-PBr_3) = 121{\cdot}8$ and 119·3 kcal respectively. The accuracy of these values depends also on the accuracy of the subsidiary thermal data used. They are probably good to ± 2 kcal.

9·8.16. D(SO)

Spectroscopic evidence on D(SO) in the diatomic molecule leads to 4·00 or 5·18 eV. Herzberg [217] favours the lower, Gaydon [166] the higher. The result depends on the assumed products of a predissociation.

9.8.17. D(ClO)

D(ClO) in the diatomic molecule depends upon the spectroscopic observation of bands almost to a convergence limit of 4·70 eV. Depending on the assumed products, $D(ClO) = 63{\cdot}5$ or 60·9 kcal [220, 395]. Gaydon [166] prefers the higher.

9.8.17. $D(OCl-O)$

The average bond energy in ClO_2 is about 60 kcal[183, 395], whence, with $D(ClO)$ we have $D(OCl-O)=57$ kcal. It is doubtful if the heat of formation of ClO and other quantities are sufficiently accurately known for there to be a significant difference between $D(O-ClO)$ and $D(ClO)$.

9.8.17 (1). $D(HO-Cl)$

$D(HO-Cl)$ has been deduced to be 60 kcal by thermochemical calculations, knowing $\Delta H_f(OH)$ *etc.*[169].

9.8.20. $D(CaO)$

The spectroscopic evidence on $D(CaO)$ and $D(SrO)$ is in violent disagreement with two types of thermochemical evidence, though that for $D(BaO)$ is in fair agreement. Gaydon has concluded that the ground state may have been wrongly identified. The spectroscopic results on $D(CaO)$ and $D(SrO)$ are therefore to be neglected and the thermochemical values preferred. Huldt and Lagerqvist[236] measured the concentration of metallic atoms from the emission intensity in an acetylene–air flame into which a known quantity of metallic salts had been sprayed. The concentration of free metal was in defect of the total amount of metal present. From this defect, assuming that the remainder was present as diatomic oxide, it is possible to obtain the equilibrium constant and hence the dissociation energy of the oxide. A derivation of these dissociation energies by third law methods using the known vapour pressures has been made by Drummond and Barrow[119], who obtain results in good agreement with Huldt and Lagerqvist. They obtain $D(CaO)$, $D(SrO)$, and $D(BaO)=115{\cdot}7\pm4{\cdot}0$, $110{\cdot}4\pm3{\cdot}5$, and $128{\cdot}7\pm3{\cdot}5$ kcal respectively. Gaydon[166] gives $4{\cdot}7\pm0{\cdot}5$, $4{\cdot}6\pm0{\cdot}5$, and $5{\cdot}4\pm0{\cdot}5$ eV respectively (108, 106, and 124 kcal). The values are slightly lower, but the order is the same.

9.8.21. $D(ScO)$

Gaydon[166] gives 6 ± 1 eV, Herzberg gives 7 eV. The value is doubtful.

9.8.22. $D(TiO)$

Gaydon[166] gives $6{\cdot}5\pm1$ eV. Brewer and Mastick[53] give an upper limit of 184 kcal (8 eV) from a study of the thermochemistry in the literature. The heat of formation of TiO has recently been determined by combustion calorimetry by Humphrey[237] as $-123{\cdot}9$. Brewer[50a] has now given $D(TiO)$ as 160 ± 2 kcal.

9.8.23. D(VO)

Gaydon[166] gives $5{\cdot}5 \pm 1$ eV, Herzberg[217] 6·4 eV.

9.8.24. D(CrO)

Gaydon[166] gives $4{\cdot}2 \pm 0{\cdot}5$ eV, Herzberg[217] 3·8 eV. Brewer[50a], has suggested 5·4 eV from a reconsideration of thermochemistry.

9.8.25. D(MnO)

Gaydon[166] gives $4{\cdot}0 \pm 0{\cdot}4$ eV, Herzberg[217] 4·4 eV, and Brewer and Mastick[53] give an upper limit of $4{\cdot}6_5$ eV (107 kcal) from thermochemical evidence.

9.8.26. D(FeO)

Gaydon[166] gives 4 eV, Herzberg[217] 4·8 eV, and Brewer and Mastick[53] an upper limit of $4{\cdot}2_5$ eV (98 kcal) from thermochemical evidence.

9.8.28. D(NiO)

Brewer and Mastick[53] give a thermochemical value of $\leqslant$99 kcal. There appears to be no relevant spectroscopic evidence.

9.8.28. D(CuO)

Brewer and Mastick[53] give 113 kcal. The spectroscopic evidence is not reliable[166].

9.8.30. D(ZnO)

Brewer and Mastick[53] give $D(\mathrm{ZnO}) \leqslant 92$ kcal.

9.8.31. D(GaO)

Gaydon[166] gives $D(\mathrm{GaO}) = 2{\cdot}5 \pm 0{\cdot}5$ eV, Herzberg[217] 2·9, doubtful.

9.8.32. D(GeO)

Gaydon[166] gives $6{\cdot}5 \pm 1{\cdot}5$ eV, Herzberg[217] 6·9, doubtful.

9.8.33. D(AsO)

In the diatomic molecule $D(\mathrm{AsO}) = 4{\cdot}9 \pm 0{\cdot}1$ eV[166, 217].

9.8.34. D(SeO)

Spectroscopic results on D(SeO) are very doubtful. Gaydon[166] gives $3{\cdot}5 \pm 1$ eV, Herzberg[217] 5·4.

9.8.35. D(BrO)

Herzberg[217] gives a spectroscopic value of 2·2 eV, Gaydon[166] 1·8 ± 0·5. The spectroscopic evidence is uncertain, and Gaydon's upper limit, which agrees with Herzberg's value from a Birge-Sponer extrapolation, is more in accord with D(ClO), but even then seems rather low. (*See* D(O – BrO) and D(HO – Br).)

9.8.35. D(O – BrO)

The heat of formation of solid BrO_2 is given as 12·5 ± 0·7 kcal by Pflugmacher, Schwarz, and Rabben[389]. This therefore sets a lower limit to $\Delta H_f(BrO_2; g)$, and hence 133 kcal is an upper limit to the heat of atomization, which is unlikely to be more than about 10 kcal greater than the true value, if the experimentally determined heat of formation is correct. Thus the average bond dissociation energy in BrO_2 is over 60 kcal. If D(BrO) is 2·2 eV (50 kcal) then D(O – BrO) is over 70 kcal. This seems a little unlikely by comparison with ClO_2, where the first and second dissociation energies are nearly equal, and if anything in the reverse order.

9.8.35 (1). D(HO – Br)

D(HO – Br) has been calculated from thermochemical data to be 56 ± 3 kcal[169]. Again by analogy with D(HO – Cl) and D(O – Cl), this suggests that the spectroscopic value for D(O – Br) may be a little low.

9.8.38. D(SrO)

~110 kcal (*see* Section 9.8.20).

9.8.39. D(YO)

Very doubtful. Gaydon[166] gives 7 ± 2 eV, Herzberg[217] 9 eV.

9.8.40. D(ZrO)

Gaydon[166] gives 6·5 ± 1·5 eV, Herzberg[217] 7·8 eV, doubtful.

9.8.41. D(NbO), *i.e.* (CbO)

4 ± 1 eV[166].

9.8.47. D(AgO)

Gaydon[166] gives 1·4 ± 0·4 eV, Herzberg[217] 1·8 eV, doubtful.

9.8.48. D(CdO)

Brewer and Mastick[53] give 88 kcal (3·8 eV) as a thermochemically derived upper limit.

9.8.49. D(InO)

Herzberg[217] gives 1·3 eV, doubtful, Gaydon[166] 1·1 ±0·2 eV.

9.8.50. D(SnO)

Herzberg[217] gives 5·6 eV, doubtful. Taking spectroscopic and thermal evidence into account, Gaydon[166] gives 5·5 ±0·2 eV. Brewer and Mastick[53] give 5·7 eV (132 kcal). This has been questioned by Drummond and Barrow[120], but recently confirmed by Brewer and Porter[54].

9.8.51. D(SbO)

Gaydon[166] gives 3·2 ±0·4 eV, Herzberg[217] 3·8 eV, doubtful.

9.8.52. D(TeO)

Herzberg[217] gives 2·73 or 3·45 eV, depending on assumed products at convergence limit. Gaydon[166] prefers the lower value.

9.8.53. D(IO)

Gaydon[166] gives 1·9 ±0·2 eV, and the spectroscopic evidence for this seems fairly well established.

9.8.53 (1). D(HO – I)

Thermochemically, $D(\mathrm{HO-I}) = 56 \pm 3$ kcal (2·4 eV) may be derived[169]. This is larger than the spectroscopic value of D(OI), whereas the corresponding chlorine compounds give nearly the same value.

9.8.56. D(BaO)

~129 kcal (*see* Section 9.2.20).

9.8.57. D(LaO)

Gaydon[166] gives 7 ±2 eV, Herzberg[217] 9 eV, doubtful.

9.8.58. D(CeO)

Gaydon[166] gives 6·5 ±2 eV, Herzberg[217] 7·7 eV, doubtful.

9.8.64. D(GdO)

Gaydon[166] gives 6 ±2? eV, Herzberg[217] 5·9.

9.8.71. D(LuO)

Gaydon[166] gives 4·3 ±1·5 eV, Herzberg[217] 5·3, doubtful.

9.8.73. D(TaO)

5 ±2 eV[166].

9.8.82. D(PbO)

Gaydon[166] gives $4{\cdot}1 \pm 0{\cdot}3$ eV, Herzberg[217] 4·3, doubtful, and Brewer and Mastick[53] 4·3 eV (98 kcal).

9.8.83. D(BiO)

Gaydon[166] gives 4 ± 1 eV, doubtful, Herzberg[217] 2·9 eV, doubtful.

9.9.9. $D(F_2)$

36 kcal (1·6) eV (*see* Section 8.2.2.9).

9.9.11. D(NaF)

Gaydon[166] states that thermochemistry leads to D(NaF) $= 3{\cdot}85 \pm 0{\cdot}1 + \frac{1}{2}D(F_2)$ and concludes $4{\cdot}6_5 \pm 0{\cdot}25$ eV. In view of the improved knowledge of $D(F_2)$ recently obtained, this error limit is perhaps too large. Herzberg[217] gives an upper limit of 5·3 eV, but this is derived taking into account the possibility that the old high value of $D(F_2)$ might be correct. This is certainly not so; Herzberg's upper limit could therefore be reduced to Gaydon's.

9.9.12. D(MgF)

Gaydon[166] gives $3{\cdot}2 \pm 0{\cdot}7$ eV, Herzberg[217] 4·2 eV, doubtful.

9.9.13. D(AlF)

The evidence on this molecule is very confusing. Extrapolation of the vibrational levels of the ground state gives 1·8 eV[166]. A revised analysis by Rowlinson and Barrow has been used by Welti and Barrow[561] to give 4·4 eV from the extrapolation of ground state vibrational levels. By analogy with GaF and InF, this would be expected to be about two-thirds of the true value. Another spectroscopic value obtained by extrapolation of vibrational levels of an upper state gives 7·2 eV. However, reliable thermochemical data lead to $6{\cdot}3_5$ eV, so there is probably a potential maximum in the upper state[432].

9.9.14. D(SiF)

Gaydon[166] gives $3{\cdot}8 \pm 0{\cdot}4$ eV, Herzberg[217] 4·8 eV, doubtful.

9.9.17. D(ClF)

D(Cl – F) = 2·62 or 2·56 eV, depending on assumptions about the excited states of products[166, 217]. The higher value is preferred (*see* Section 8.2.2.9).

9.9.19. D(KF)

Barrow and Caunt[17] have made a careful study of the spectroscopic and thermodynamic evidence on the dissociation energies of some alkali metal halides. They state that 122·6 kcal is a spectroscopic upper limit to $D(K-F)$, and 118·9 kcal is the best thermochemical value based on $D(F_2) = 37{\cdot}4$ kcal. These refer to 25° C, and should be reduced by about 0·7 kcal to refer to 0° K. Gaydon[166] gives $5{\cdot}0 \pm 0{\cdot}25$ eV, from thermochemical evidence (115 kcal), but the error limits are perhaps too great; 118 kcal seems the most likely value.

9.9.20. D(CaF)

< 3.15 eV[166, 217].

9.9.25. D(MnF)

$3{\cdot}5 \pm 1$ eV[166] or 3·9 eV, doubtful[217].

9.9.29. D(CuF)

3·1 eV[166], or 3·0 eV, doubtful[217].

9.9.31. D(GaF)

Gaydon[166] gives $6{\cdot}1_5$ eV, from the work of Welti and Barrow[561]. These authors studied the spectra of gallium and indium fluoride and found $D = 6{\cdot}1_5$ and $5{\cdot}4_1$ eV respectively. There is, however, a possibility that there may be a potential maximum in the curves for the upper states of these molecules, and these dissociation energies may therefore be upper limits.

9.9.32. D(GeF)

Gaydon[166] gives 4 ± 1 eV, Herzberg[217] 4·9, doubtful.

9.9.35. D(FBr)

D(FBr) is 2·19 or 2·60 eV, depending on assumption about excited products[217]. Gaydon[166] gives 2·16 eV.

9.9.37. D(RbF)

Barrow and Caunt[17] give a spectroscopic upper limit of 125 kcal, and a thermochemical value of 118·8 kcal, corrected to 0° K (*see* Section 9.9.19).

9.9.38. D(SrF)

Gaydon[166] gives $2{\cdot}7 \pm 1$ eV, Herzberg[217] 3·5 eV, doubtful.

9.9.41. D(InF)

See Section 9.9.31.

9.9.50. D(SnF)

Gaydon gives $3{\cdot}3 \pm 0{\cdot}5$ eV, Herzberg 3·9 eV, doubtful.

9.9.51. D(SbF)

Gaydon [166] gives 4 ± 1 eV, Herzberg [217] 4·2 eV, doubtful.

9.9.53. D(IF)

D(IF) = 1·98 eV, but this depends on the correct identification of products, which is not certain [166].

9.9.55. D(CsF)

Barrow and Caunt [17] give a spectroscopic upper limit of 129·2 kcal, and a thermochemical value of 121·3, corrected by 0° K (*see* Section 9.9.19).

9.9.56. D(BaF)

Gaydon [166] gives 3 ± 1 eV, Herzberg [217] 3·8 eV, doubtful.

9.9.80. D(HgF)

Gaydon [166] gives $1{\cdot}4 \pm 0{\cdot}5$ eV (32 kcal) Herzberg 1·8 [217], doubtful. This is very high for a single bond to mercury.

9.9.80. D(F – HgF)

The average bond energy in HgF_2 is 66 kcal derived from thermochemistry [317], whence the first dissociation energy is about 100 kcal.

9.9.81. D(TlF)

Gaydon [166] gives $4{\cdot}75 \pm 0{\cdot}2$ eV, Herzberg [217] <4·72 eV.

9.9.82. D(PbF)

$3{\cdot}2 \pm 0{\cdot}4$ eV [166, 217].

9.9.83. D(BiF)

$3{\cdot}2 \pm 0{\cdot}4$ eV [166, 217].

9.11.11. $D(Na_2)$

$0{\cdot}75 \pm 0{\cdot}03$ eV [166, 217].

9.11.17. D(NaCl)

Gaydon [166] gives $4{\cdot}24 \pm 0{\cdot}05$ eV. This depends on well established thermochemical data, and Gaydon's estimate of the accuracy cannot be far out. Herzberg [217] gives 3·58 eV, and this result is stated to be from thermochemical data. It is presumably in error.

9.11.19. D(NaK)

$0{\cdot}62 \pm 0{\cdot}003$ eV [166, 217].

9.11.35. D(NaBr)

Gaydon [166] gives $3{\cdot}80 \pm 0{\cdot}1$ eV, from thermochemistry.

9.11.37. D(NaRb)

$0{\cdot}57 \pm 0{\cdot}04$ eV [166].

9.11.53. D(NaI)

Gaydon [166] gives $3{\cdot}07 \pm 0{\cdot}1$ eV, from thermochemistry.

9.12.16. D(MgS)

Herzberg [217] gives 2·9 eV, but Gaydon points out that this may be very much in error [166] (*see* Section 9.8.12).

9.12.17. D(MgCl)

Gaydon [166] gives $2{\cdot}7 \pm 0{\cdot}7$ eV, Herzberg [217] 3·2 eV, doubtful.

9.12.17. D(Cl – MgCl)

Skinner [453] gives $D(\mathrm{Cl - MgCl}) = 136 \pm 20$ kcal, from thermochemistry and D(MgCl).

9.12.35. D(MgBr)

Gaydon [160] gives $2{\cdot}5 \pm 1$ eV, Herzberg [217] $\leqslant 3{\cdot}3_5$ eV.

9.13.17. D(AlCl)

Gaydon [166] gives $5{\cdot}1 \pm 0{\cdot}2$ eV, based on thermochemistry. Extrapolation of ground state vibrational levels of AlCl is not likely to give a reliable value of D(AlCl). Compare AlF, Section 9.9.13. Herzberg gives 3·1 eV, doubtful, from spectrum [217].

9.13.35. D(AlBr)

Gaydon [166] gives $4{\cdot}3 \pm 0{\cdot}2$ eV, from thermochemistry. The spectral value of 2·4 eV [217] is probably much too low (*see* Sections 9.13.17 and 9.9.13).

9.13.53. D(AlI)

Gaydon[166] gives $3{\cdot}9_2 \pm 0{\cdot}1$ eV. There is a thermochemical value of $3{\cdot}7 \pm 0{\cdot}7$ eV, and a dissociation limit at $3{\cdot}9_2$ eV, which was previously taken to be to excited products. Herzberg[217] gives 2·9 eV, doubtful.

9.14.14 (1). $D(H_3Si - SiH_3)$

Emeleus, Maddock, and Reid[145] have suggested that the energy of the Si – Si bond is probably given approximately by the activation energy for the pyrolysis of disilane (51·3 kcal)[146]. Radicals are certainly present in the pyrolysis of disilane, but there is no evidence that the activation energy is equal to the Si – Si dissociation energy. The reaction has been studied again by Stokland[482], who obtained an activation energy of 48·9 kcal. The mechanism has not been completely elucidated. The activation energy is almost the same as that found for the thermal decomposition of monosilane (51·7 kcal)[226].

9.14.16, 17, 34, 35, 52. D(SiS *etc.*).

We have the following suggested values,

Molecule	*Gaydon*[166]	*Herzberg*[217]
SiS	$6{\cdot}4 \pm 0{\cdot}4$ eV	6·6 doubtful
SiCl	$3{\cdot}3 \pm 0{\cdot}5$	4·0 ,,
SiSe	$5{\cdot}8 \pm 0{\cdot}3$	5·8 ,,
SiBr	$3{\cdot}0 \pm 0{\cdot}5$	3·7 ,,
SiTe	$5{\cdot}3 \pm 0{\cdot}4$	5·5 ,,

9.15.15. $D(P_2)$

5·03 eV, well established[166, 217].

9.16.16. $D(S_2)$

Probably 4·4 eV, but lower values have been suggested (*see* Section 8.2.2.16).

9.16.16 (1). D(HS – SH)

Franklin and Lumpkin[161] deduce $D(HS - SH) = 80{\cdot}4$ kcal using thermochemical data which may not be reliable and their value for the heat of formation of SH, determined by the electron impact method. We have given reasons for believing that their value for ΔH_f(SH) is about 4 kcal too large, which reduces their estimate of D(HS – SH) to 72 kcal. It is still noticeably larger than D(HO – OH).

9.16.16 (1, 6). D(RS – SR)

Franklin and Lumpkin[161] have measured the heat of formation of the RS radical by the electron impact method, and the heats of formation of some disulphides by combustion. They deduce the following values for D(MeS – SMe), D(MeS – SEt), and D(EtS – SEt) $73{\cdot}_2$, $71{\cdot}_5$, and $70{\cdot}_0$ kcal respectively.

9.16.20. D(CaS)

Gaydon[166] gives $5{\cdot}0 \pm 0{\cdot}5$ eV, Herzberg[217] $\leqslant 5{\cdot}2$ eV.

9.16.30. D(ZnS)

Gaydon[166] gives $4{\cdot}2 \pm 0{\cdot}3$ eV, Herzberg[217] $< 4{\cdot}4$ eV.

9.16.32. D(GeS)

Herzberg[217] gives 5·6 eV, doubtful. Gaydon originally gave $5{\cdot}0 \pm 0{\cdot}5$ eV because a linear Birge-Sponer extrapolation for the ground state, which might be expected to give a slightly high value, led to 5·6 eV. An examination of excited states shows a convergence limit at 5·79 eV, but the products are not certain[121]. Gaydon[166] now gives $5{\cdot}6_6 \pm 0{\cdot}1_3$ eV.

9.16.38. D(SrS)

Gaydon[166] gives $2{\cdot}3 \pm 0{\cdot}2$ eV, doubtful. The long wavelength limit of continuous absorption gives D(SrS) $< 2{\cdot}75$ eV[217].

9.16.48. D(CdS)

Gaydon[166] gives $3{\cdot}9 \pm 0{\cdot}2$ eV, Herzberg[217] $\leqslant 3{\cdot}9$ eV.

9.16.50. D(SnS)

The spectroscopic evidence on SnS is controversial. Gaydon[166] gives $3{\cdot}0_1$ eV, based on a predissociation, but there is a possibility that a much higher value is correct. Vago and Barrow[531], from a convergence limit of an upper state, give 5·40 eV. A further analysis of the spectrum by Barrow, Drummond, and Rowlinson[18] gives $\sim$4·8 eV, and this result is supported by thermochemical evidence if the higher value for $D(S_2)$ is correct. There is an uncertainty of about 0·3 eV in the heat of vaporization of tin, however.

9.16.56. D(BaS)

Gaydon[166] gives $2{\cdot}3 \pm 0{\cdot}4$ eV, Herzberg[217] 2·3 eV, doubtful.

9.16.80. D(HgS)

D(HgS) = 2·8 eV [166], ⩽2·8 eV [217].

9.16.82. D(PbS)

3·25 ± 0·3 eV [166], 4·7 doubtful [217]. The interpretation of the spectrum is uncertain.

9.17.17. $D(Cl_2)$

2·475 eV (*see* Section 8.2.2.17).

9.17.19. D(KCl)

The most recent estimate is that by Barrow and Caunt [17], who give D(KCl)⩽107·4 kcal (spectroscopic) = 101·3 (thermochemical). These values have been reduced to 0° K. Barrow and Caunt actually give values for 25° C. This result is in good accord with other estimates. Gaydon [166], for example, gives 4·40 eV (102 kcal).

9.17.20. D(CaCl)

⩽2·76 eV [166, 217].

9.17.20. D(Cl – CaCl)

Skinner [453] gives 176 ? kcal, from thermochemistry and an estimate of D(CaCl). This is obtained assuming that D(CaCl) is in fact equal to the upper limit given above.

9.17.22. D(TiCl)

Gaydon [166] gives 1·1 ± 0·5 eV, Herzberg [217] 1·0 eV, doubtful.

9.17.24. D(CrCl)

Gaydon [166] gives 0·3 eV, doubtful.

9.17.25. D(MnCl)

Gaydon [166] gives 3 ± 1 eV, Herzberg [217] 3·3 eV, doubtful.

9.17.26. D(FeCl)

Gaydon [166] gives 3 ± 2 eV, this is based on a short and poor vibrational extrapolation for the ground state, and is very doubtful.

9.17.28. D(NiCl)

Gaydon [166] gives 5 ± 2 eV, Herzberg [217] 7·3 eV, doubtful.

9.17.29. D(CuCl)

Gaydon [166] gives 3·8 ± 0·25 eV, thermochemical.

9.17.30. D(ZnCl)

Gaydon[166] gives $2{\cdot}1 \pm 0{\cdot}2$ eV, Herzberg[217] 3·0 eV. Both these values are doubtful.

9.17.30. D(Cl – ZnCl)

Skinner[453] gives D(Cl – ZnCl) = 96 kcal, but this is very doubtful. It depends on thermochemistry and D(ZnCl).

9.17.31. D(GaCl)

Gaydon[166] gives $4{\cdot}99 \pm 0{\cdot}02$ eV from predissociation and short extrapolation of vibrational levels of excited state. Herzberg[217] gives 3·7 eV, doubtful, from poor extrapolation of ground state vibrational levels.

9.17.32. D(GeCl)

Gaydon[166] gives $3{\cdot}5 \pm 0{\cdot}2$ eV, Herzberg[217] 4·0 eV, both values doubtful.

9.17.35. D(ClBr)

2·26 eV thermochemically derived[166, 217].

9.17.37. D(RbCl)

The most recent examination gives D(RbCl) $\leqslant$ 108·6 kcal (spectroscopic) = 102·1 kcal (thermochemical)[17].

9.17.38. D(SrCl)

Gaydon[166] gives $2{\cdot}5 \pm 1$ eV, Herzberg[217] 3·0 eV, both doubtful.

9.17.47. D(AgCl)

Gaydon[166] gives a revised thermochemical result of $3{\cdot}3 \pm 0{\cdot}2$ eV, Herzberg[217] gives 3·1 eV. The lower value is more likely to be correct, particularly in view of more recent evidence on the heat of atomization of silver (*see* Section 8.2.2.47).

9.17.48. D(CdCl)

Gaydon[166] gives $2{\cdot}0 \pm 0{\cdot}5$ eV, Herzberg[217] 2·8 eV, both doubtful.

9.17.48. D(Cl – CdCl)

Skinner[453] gives 84 kcal for D(Cl – CdCl), but this is very doubtful. It depends on thermochemistry and D(CdCl).

9.17.49. D(InCl)

Gaydon[166] gives $4{\cdot}5 \pm 0{\cdot}1$ eV, Herzberg[217] $\leqslant 4{\cdot}54$ eV.

9.17.49. D(Cl – InCl)

D(Cl – InCl) is quoted as 46 kcal by Wehrli and Milazzo [558] from Wenk [562].

9.17.50. D(SnCl)

Gaydon [166] gives 3·2 ± 0·2 eV, Herzberg [217] 3·6 eV, both doubtful.

9.17.51. D(SbCl)

Gaydon [166] gives 3·7 ± 0·5 eV, Herzberg [217] 4·6 eV, both doubtful.

9.17.53. D(ICl)

D(ICl) = 2·152 eV, from a convergence limit [166, 217].

9.17.55. D(CsCl)

Barrow and Caunt [17] give D(CsCl) ⩽ 110·2 kcal (spectroscopic), 101·0 (thermochemical). This is in accord with other estimates.

9.17.56. D(BaCl)

Gaydon [166] gives 2·2 ± 0·5 eV, Herzberg [217] 2·7eV, both doubtful.

9.17.70. D(YbCl)

Gaydon [166] gives 1 ± 0·5 eV, Herzberg [217] 1·2 eV, both doubtful.

9.17.79. D(AuCl)

Gaydon [166] gives 2·8 ± 0·5 eV, Herzberg [217] 3·5 eV, doubtful.

9.17.80. D(HgCl)

1·0 ± 0·1 eV [166, 217].

9.17.80. D(Cl – HgCl)

D(Cl – HgCl) has been determined photochemically and also from D(HgCl) and thermochemical data: the results are in good accord and give 80·5 ± 1·5 kcal as the most probable value [569].

9.17.80 (35 *and* 53). D(Cl – HgBr) *and* D(Cl – HgI)

Wehrli and Milazzo [558] give D(Cl – HgBr) and D(Cl – HgI) as 77·2 and 74·5 kcal respectively.

9.17.81. D(TlCl)

3·78 ± 0·1 eV, thermochemically derived [166, 217].

9.17.82. D(PbCl)

Gaydon[166] gives $3{\cdot}1 \pm 0{\cdot}3$ eV, Herzberg[217] $3{\cdot}1_2$ eV. The original authors have changed their estimates in different papers.

9.17.83. D(BiCl)

Gaydon[166] gives $2{\cdot}9 \pm 0{\cdot}2$ eV, Herzberg[217] 3·0 eV, doubtful.

9.19.19. $D(K_2)$

Herzberg[217] gives 0·514 eV, Gaydon[166] gives $0{\cdot}51 \pm 0{\cdot}05$ eV, putting in these error limits because of the possibility of a potential maximum.

9.19.35. D(KBr)

Barrow and Caunt[17] give $D(KBr) \leqslant 94{\cdot}4$ (spectroscopic), 91·4 kcal (thermochemical).

9.19.53. D(KI)

Barrow and Caunt[17] give $\leqslant 79{\cdot}9$ (spectroscopic), 76·5 kcal (thermochemical).

9.20.35. D(CaBr)

Herzberg[217] gives a doubtful 2·9 eV, but Gaydon[166] considers the data inadequate to give any value at all.

9.20.53. D(CaI)

Gaydon[166] gives $2{\cdot}5 \pm 1$ eV, Herzberg[217] 2·8 eV, doubtful.

9.25.35. D(MnBr)

Gaydon[166] gives $2{\cdot}5 \pm 1$ eV, Herzberg[217] 2·9 eV, doubtful.

9.25.53. D(MnI)

Gaydon[166] gives $1{\cdot}2 \pm 1$ eV.

9.29.35. D(CuBr)

Gaydon[166] gives $3{\cdot}4 \pm 0{\cdot}25$ eV, in agreement with the latest thermochemical result[52]. Herzberg[217] gives 2·5 eV, doubtful, based on earlier thermochemical evidence on AgBr together with an interpolation method.

9.29.53. D(CuI)

Gaydon[166] gives $2{\cdot}0 \pm 0{\cdot}2$ eV, but this is doubtful. A thermochemical result is $\leqslant 3{\cdot}27$ eV[52]. An old thermochemical estimate was 2·1 eV. Herzberg[217] gives 3·0 eV, doubtful, based on linear Birge-Sponer extrapolation.

9.30.30. $D(Zn_2)$

Herzberg[217] gives 0·25 eV, doubtful. Gaydon[166] mentions this value but considers the interpretation of the spectral data uncertain.

9.30.34. $D(ZnTe)$

Gaydon[166] gives $2{\cdot}1 \pm 0{\cdot}3$ eV, Herzberg[217] $<2{\cdot}2$ eV.

9.30.53. $D(ZnI)$

Gaydon[166] gives $1{\cdot}4 \pm 0{\cdot}3$ eV, Herzberg[217] 2·0 eV, doubtful.

9.30.53. $D(I - ZnI)$

Skinner[453] gives $D(I - ZnI) = 53 \pm 15$ kcal, derived from $D(ZnI) = 41 \pm 15$ kcal (1·8 eV).

9.31.35. $D(GaBr)$

Gaydon[166] gives $3{\cdot}5 \pm 0{\cdot}8$ eV, doubtful, and Herzberg[217] gives 2·7 eV, doubtful.

9.31.53. $D(GaI)$

Gaydon[166] gives $2{\cdot}9 \pm 0{\cdot}2$ eV, Herzberg[217] $\leqslant 2{\cdot}88$ eV.

9.32.32. $D(Ge - Ge)$

The activation energy of the pyrolysis of digermane[144] has been interpreted to be the Ge – Ge bond dissociation energy[452]. This makes $D(H_3Ge - GeH_3) = 34$ kcal. The reaction is 1st order over the middle period, has an induction period, and is retarded towards the end. It is almost certainly a chain process, and there appears to be little justification for this interpretation of the activation energy.

9.32.34. $D(GeSe)$

Gaydon[166] gives $4{\cdot}9_8 \pm 0{\cdot}25$ eV, Herzberg[217] 4·1 eV, doubtful. Gaydon's figure is based on excited state dissociation.

9.32.35. $D(GeBr)$

Gaydon[166] gives $2{\cdot}6 \pm 0{\cdot}3$ eV, Herzberg[217] 3·0 eV, doubtful.

9.32.52. $D(GeTe)$

Gaydon[166] gives $4{\cdot}1 \pm 0{\cdot}4$ eV, Herzberg[217] 3·2 eV, doubtful.

9.33.33. $D(As_2)$

Gaydon[166] gives 3·94 eV, Herzberg[217] $\leqslant 3{\cdot}96$ eV.

9.34.34. $D(Se_2)$

Gaydon [166] gives $2{\cdot}8 \pm 0{\cdot}1$ eV, Herzberg [217] $\leqslant 3{\cdot}55$ eV. (*See* Section 8.2.2.34.)

9.34.48. D(CdSe)

$\leqslant 3{\cdot}2$ eV [166, 217].

9.34.50. D(SnSe)

Gaydon [166] gives 3 ± 1 eV, doubtful, Herzberg [217] 4·6 eV, doubtful. An upper state dissociates at 4·54 eV, and it has been claimed that this is to normal products [531], though Gaydon rejects this interpretation.

9·34.80. D(HgSe)

Herzberg [217] gives $\leqslant 2{\cdot}7$ eV, and states that Gaydon's [166] estimate of $\leqslant 2{\cdot}0$ eV is 'erroneous'. This is, however, based on a reinterpretation of the published data.

9.34.82. D(PbSe)

Gaydon [166] gives 3 ± 1 eV, Herzberg [217] 4·7 eV, doubtful. (*See* Section 9.34.50.)

9.35.35. $D(Br_2)$

$\doteqdot 1{\cdot}971$ eV well established [166, 217].

9.35.37. D(RbBr)

Barrow and Caunt [17] give $\leqslant 94{\cdot}7$ (spectroscopic) and 90·2 (thermochemical). This is in good agreement with other estimates.

9.35.38. D(SrBr)

Herzberg [217] gives 2·8 eV, doubtful. Gaydon [166] considers the data inadequate.

9.35.47. D(AgBr)

Gaydon [166] gives $3{\cdot}0 \pm 0{\cdot}3$ eV, a revised thermochemical value. Herzberg gives 2·6 eV (thermochemical) [217].

9.35.48. D(CdBr)

Gaydon [166] gives $1{\cdot}6 \pm 1$ eV, doubtful, Herzberg [217] 3·3 eV, doubtful.

9.35.48. D(Br – CdBr)

Skinner[453] gives D(Br – CdBr) = 76 ± 10 kcal, based on D(CdBr) = 35 ± 10 kcal (1·5 eV).

9.35.49. D(InBr)

Gaydon[166] gives 3·4 ± 0·2 eV, and refers to a thermochemical value of 3·95 ± 0·5 eV; Herzberg[217] gives <3·3 eV.

9.35.49. D(Br – InBr)

Wehrli and Milazzo[558] give D(Br – InBr) = 42 kcal, taking D(InBr) = 85 kcal (3·7 eV).

9.35.55. D(SnBr)

Gaydon[166] gives 2·0 ± 1 eV, Herzberg[217] 3·0 eV, doubtful.

9.35.53. D(IBr)

1·817 eV, well established[166, 217].

9.35.50. D(CsBr)

Barrow and Caunt[17] give ⩽97·2 kcal (spectroscopic) and 90·8 kcal (thermochemical). This agrees with other estimates.

9.35.56. D(BaBr)

Herzberg[217] gives 2·8 eV, doubtful. Gaydon[166] considers the data inadequate.

9.35.80. D(HgBr)

Herzberg[217] gives 0·7 eV, Gaydon[166] 0·7 ± 0·4 eV.

9.35.80. D(Br – HgBr)

From the heats of formation and vaporization of solid $HgBr_2$, the latter depending on vapour pressure data described by Kelley[259] as being in exceptionally good agreement, we may deduce D(Br – HgBr) = 72 kcal, taking D(HgBr) = 17 kcal (0·7 eV)[529].

9·35.80 (17 *and* 53). D(Br – HgCl) *and* D(Br – HgI)

Wehrli and Milazzo[558] give D(Br – HgCl) = 70 kcal, and D(Br – HgI) = 68 kcal.

9.35.81. D(TlBr)

Gaydon[166] gives 3·2 ± 0·1 eV, Herzberg[217] ⩽3·19 eV. There is good thermochemical as well as spectroscopic evidence.

9.35.82. D(PbBr)

Gaydon[166] gives $2{\cdot}5 \pm 0{\cdot}4$ eV, Herzberg[217] $2{\cdot}9_7$ eV. The predissociation data are difficult to interpret.

9.35.83. D(BiBr)

$2{\cdot}74 \pm 0{\cdot}01$ eV[166, 217].

9.37.37. $D(Rb_2)$

$0{\cdot}47 \pm 0{\cdot}05$ eV[166, 217].

9.37.53. D(RbI)

Barrow and Caunt[17] give $\leqslant 81{\cdot}9$ (spectroscopic) and 77·0 kcal (thermochemical). This is in good agreement with other estimates.

9.38.53. D(SrI)

Gaydon[166] gives 2 ± 1 eV, Herzberg[217] 2·2 eV, doubtful.

9.47.53. D(AgI)

Gaydon[166] gives $2{\cdot}6 \pm 0{\cdot}25$ eV, thermochemical, Herzberg[217] $2{\cdot}98_3$ eV, spectroscopic, from convergence limit in B state.

9.48.48. $D(Cd_2)$

Gaydon[166] gives 0·09 eV, Herzberg[217] 0·087 eV.

9.48.53. D(CdI)

Gaydon[166] gives $1{\cdot}4 \pm 0{\cdot}2$ eV, Herzberg[217] 1·6 eV, doubtful.

9.48.53. D(I – CdI)

Skinner[453] gives D(I – CdI) $= 57 \pm 10$ kcal, taking D(CdI) $= 25 \pm 10$ kcal (1·1 eV).

9.49.53. D(InI)

Gaydon[166] gives $2{\cdot}8 \pm 0{\cdot}2$ eV, Herzberg[217] $\leqslant 2{\cdot}7$ eV.

9.49.53. D(I – InI)

Wehrli and Milazzo[558] give D(I – InI) = 42 kcal, taking D(In – I) = 69 kcal (3 eV).

9.50.52. D(SnTe)

Gaydon[166] gives 3 ± 1 eV, doubtful, Herzberg[217] 4·2 eV, doubtful.

9.51.51. $D(Sb_2)$

Gaydon[166] gives $3{\cdot}0 \pm 0{\cdot}5$ eV, Herzberg[217] 3·7 eV, doubtful (*see* Section 8.2.2.51).

9.51.83. $D(SbBi)$

Gaydon[166] gives 3 ± 2 eV, Herzberg[217] 3·0 eV, doubtful.

9.52.52. $D(Te_2)$

Gaydon[166] gives $2{\cdot}3 \pm 0{\cdot}2$ eV, doubtful, Herzberg[217] $\leqslant 3.18$ eV (*see* Section 8.2.2.52).

9.52.82. $D(PbTe)$

Gaydon[166] gives $3{\cdot}5 \pm 1$ eV, Herzberg[217] 3·5 eV, doubtful.

9.53.53. $D(I_2)$

1·542 eV, well established[166, 217].

9.53.55. $D(CsI)$

Barrow and Caunt[17] give $\leqslant 81{\cdot}3$ (spectroscopic) and 74·7 kcal (thermochemical).

9.53.80. $D(HgI)$

Gaydon gives $0{\cdot}32 \pm 0{\cdot}05$ eV, Herzberg 0·36 eV.

9.53.80. $D(I - HgI)$

Combination of $D(HgI)$ with well established thermochemical data leads to $D(I - HgI) = 60$ kcal.

9.53.80 (17 *and* 35). $D(I - HgCl)$ *and* $D(I - HgBr)$

Wehrli and Milazzo[558] give $D(I - HgCl)$ and $D(I - HgBr) = 62{\cdot}5$ and 63·5 kcal respectively.

9.53.81. $D(TlI)$

Gaydon[166] gives $2{\cdot}6 \pm 0{\cdot}1$ eV, Herzberg[217] $\lesssim 2{\cdot}64$ eV.

9.53.82. $D(PbI)$

Gaydon[166] gives $2{\cdot}0 \pm 0{\cdot}4$ eV, Herzberg[217] $2{\cdot}8_4$ eV. $2{\cdot}8_4$ is founded on a predissociation which is obviously difficult to interpret[166, 217].

9.53.83. $D(BiI)$

Gaydon[166] gives $2{\cdot}5 \pm 1$ eV, Herzberg[217] 2·7, doubtful.

9.55.55. $D(Cs_2)$

0·45 eV [166, 217].

9.80.80. $D(Hg_2)$

$D_0^\circ(Hg_2)$ is given by Winans and Heitz [574] as 0·14 eV. This is a correction of an earlier value of 0·12 eV [573] obtained by the same authors. The concentration of Hg_2 molecules at various conditions of temperature and pressure was determined spectroscopically, and the dissociation energy deduced as 0·071 eV. This value refers to the dissociation energy of the rotating molecule, which is less than the true dissociation energy, by the kinetic energy of rotation at the temperature concerned. The value of 0·14 eV is obtained when a correction for this is applied. Gaydon and Herzberg both give lower values.

9.80.81. $D(HgTl)$

Herzberg [217] gives 0·031 eV, doubtful. Gaydon [166] considers the data inadequate.

9.82.82. $D(Pb_2)$

Gaydon [166] gives $0·6 \pm 0·2$ eV, Herzberg [217] 0·7 eV, doubtful.

9.83.83. $D(Bi_2)$

$1·70 \pm 0·01$ eV [166, 217].

10

NUMERICAL VALUES OF THERMOCHEMICAL BOND ENERGY TERMS IN POLYATOMIC MOLECULES

NUMERICAL values of thermochemical bond energy terms, derived from heats of atomization of molecules, are given in this chapter. An attempt is made to assess the reliability of the experimental information on which they are based. Only molecules for which an unambiguous valence bond structure can be written are discussed so that the question of 'empirical resonance energies' is not treated.

The definition of bond energy term is that given in Chapter 6. For this reason the bond energy terms for diatomic molecules differ slightly from the dissociation energies given in Chapter 9. The latter refer to 0° K, whereas the present values refer to 25° C. This small correction is applied in the final table of bond properties, *Table 11.5.1*, and only those values for diatomic molecules about which further discussion is required are given here. The arrangement is the same as in Chapter 9.

10.1.6. E(C – H)

Bond energies to carbon cannot be given absolutely because of lack of reliable knowledge of L_C. Reasons have been given in Section 8.2.2.6 for believing that it is about 138 kcal, and this value is adopted here.

The CH bond is primary in two compounds, methane and the diatomic molecule CH. E(CH) in CH_4 can readily be obtained from the heat of formation of methane to be $(56{\cdot}6 + \frac{1}{4}L_C)$ kcal, or 91·1 kcal. E(CH) in the diatomic molecule is 81 kcal. CH is also of course primary in the methyl and methylene radicals, but it is only possible to give a reliable value for E(CH) in the former. If $D(CH_3 - H)$ is 101 kcal at 0° K, and 102 kcal at 25° C, we may deduce $\Delta H_f(CH_3, g)_{25°C} = 32$ kcal, and E(CH) in CH_3 $= (41{\cdot}4 + \frac{1}{3}L_C)$ kcal or 87·4 kcal. Any of the suggested values for L_C imply that E(CH) in CH_4, CH_3, and CH decreases in that order.

This has been correlated with the increase in r_0 from 1·09 4 Åin CH_4 to 1·131 Å in CH.

These changes in E(CH) correspond to gross changes in valence and are not relevant to the discussion of the constancy of bond energy terms as normally understood. The concept is generally only applied to compounds in which the elements exhibit their normal valence. It is not possible to say on thermochemical evidence, without the use of auxiliary assumptions, whether the more subtle changes of valence state involved in changes of hybridization involve a change in bond energy terms.

Although it is convenient in developing the theory of bond energy terms in a logical way to derive E(CH) as primary, there is some disadvantage in practice in doing so. This appears if we use bond energy terms to predict the heats of formation of carbon compounds. In the *n*-paraffins, for example, if we derive E(CH) from methane, we can deduce E(CC) in ethane directly from its heat of formation. We can deduce E(CC) in propane, butane *etc.* in a similar way. It is found that if we do this, there is a drift in the value of E(CC) as we go down the series. Expressed simply in terms of heats of formation, without the introduction of the concept of bond energies, the increment per CH_2 group to the heat of formation (ΔH_f) of the *n*-paraffins is in general $-4{\cdot}9_3$ kcal, whereas the increment in going from methane to ethane is only $-2{\cdot}3_5$ kcal. This could be interpreted as implying that primary CH bonds are stronger than secondary CH bonds, and it certainly shows that the assumption of constancy in its simplest form breaks down. The simplest treatment is to neglect the breakdown in the constancy assumption, and to choose the bond energy terms so as to introduce the least error in heats of formation predicted using them. If we take E(CH) derived from methane as primary, and use it to estimate heats of formation of compounds containing a large number of CH bonds, we shall introduce a large error, because of the large number of bonds in the compound. On the other hand, if we deduce E(CH) from the increment for the *n*-paraffins, little error will be introduced for compounds containing large numbers of CH bonds, and even for methane the absolute error will not be large, although of course the error per bond will be the same.

Thus it is more convenient to take E(CH) for general purposes of organic chemistry as about 0·6 kcal less than the value for E(CH) in methane.

This question is discussed more fully in Section 10.6.6, where the C – C bond is considered.

10.1.7. E(NH)

As with carbon, we are faced with the difficulty that the heat of atomization of nitrogen is uncertain (Section 2.2.7). Taking the lower value, E(NH) in NH_3 is 84·3 kcal (*see* Section 8.1). A slightly lower value given by Pauling[382] is due to a slightly lower value taken for $D(N_2)$ and $D(H_2)$. E(NH) in the diatomic molecule is not well established. In ammonia, as with methane, the dissociation energy of the first bond to hydrogen is greater than the bond energy term for the molecule, with the consequence that the bond energy term in the radical is less than in the molecule.

Glockler[175] gives values for E(NH) in a variety of compounds. As with all Glockler's results, these refer to 0° K, and he has used $D(N_2) = 272{\cdot}1$ kcal or 11·8 eV. There is no direct evidence in support of this very high value for $D(N_2)$, and it has been adopted to fit various empirical relationships. Even with this value E(NH) in ammonia is still slightly less than $D(NH_2 - H)$.

10.1.8. E(OH)

E(OH) in H_2O is well established as 110·6 kcal (*see* Section 8.1), again less than the first dissociation energy.

10.1.9. E(HF)

The value is 135 kcal, from the diatomic molecule. Long[317] gives 148·5 kcal, but this value depends on the old erroneous, high value for $D(F_2)$ (Section 8.2.2.9). Almost all tables of bond energies give this high value, which has now been superseded. Pitzer[391], in his table of bond energies at 0° K, gives an intermediate value which is also incorrect.

10.1.14. E(SiH)

There is some doubt about the value of $\Delta H_f(SiH_4; g)$. Von Wartenberg[554] studied the equilibrium between solid silicon, hydrogen, and silane and deduced $\Delta H_f(SiH_4; g) = -8{\cdot}7$ kcal. The earlier calorimetric value for the heat of combustion of SiH_4, 324·3 kcal, obtained by Ogier and quoted by von Wartenberg, is stated by the latter to lead to $\Delta H_f = -8 \pm 4$ kcal. This, however, is based on an unsatisfactory estimate of $\Delta H_f(SiO_2)$, 195 kcal (± 2 per cent), obtained by von Wartenberg himself. This value is almost certainly too low, probably because of impurity in the silicon. A recent determination of the heat of combustion of silicon in a bomb calorimeter has been made by Humphrey and King[238], who found $\Delta H_f(SiO_2;$ cristobalite$) = -209{\cdot}33 \pm 0{\cdot}25$ kcal. Thompson[521] deduced ΔH_f for amorphous silica to be

−208·14 kcal from the results of Humphrey and King. Combining this figure with Ogier's value for the heat of combustion we obtain $\Delta H_f(SiH_4) = -21$ kcal. The N.B.S.[529] take −14·8 kcal. In view of the difficulties involved in the combustion of silicon compounds, perhaps von Wartenberg's equilibrium value should be preferred. In addition there is a slight uncertainty in the heat of atomization of silicon. Thus E(SiH)∼76 kcal, with an uncertainty of about ±2 kcal.

A rather higher value (80 kcal) has been given by Emeléus, Maddock, and Reid[145] and also by Skinner[452]. This is based on an overestimate of the heat of atomization of silicon.

10.1.15. E(PH)

There is considerable uncertainty about the heat of formation of phosphine, PH_3. The equilibrium measurements of Ipatiew and Frost[242] give $\Delta H_f(PH_3; g) = -2·36$ kcal, but, as has been pointed out by Stevenson and Yost[479], the ΔH values are not very consistent. There is a spread of 11 kcal in the calorimetric results. On the basis of the evidence the N.B.S.[529] give $\Delta H_f(PH_3) = 2·21$ kcal, but it is not certain that this is more reliable than Bichowsky and Rossini's[38] direct choice of −2·3. Hence E(PH) = 77 kcal, probably ±2 kcal. The much lower value given by Pauling[382] is due to the use of a lower and incorrect value for the heat of atomization of phosphorus.

10.1.16. E(S − H)

Here $\Delta H_f(H_2S; g)$ is well established as −4·8 kcal[582], but the heat of atomization of sulphur is in doubt. Using the value preferred in Section 8.2.2.16 for this quantity, we deduce E(SH) = 87·7 kcal. Lower values are due to the use of a lower value for the heat of atomization of sulphur.

10.1.33. E(As − H)

There is only one early determination of $\Delta H_f(AsH_3; g)$ available[373]. The accuracy of this is not known, but it may well not be very reliable. Nor is the value of the heat of atomization of arsenic certain. We obtain E(As − H) = 58·6 kcal, with an unknown, but probably large, uncertainty. The much lower value given by Pauling is due to the use of a much lower estimate of the heat of atomization.

10.1.34. E(Se − H)

In the face of a doubtful value of the heat of atomization of selenium (Section 8.2.2.34), and an uncertainty of about 2 kcal in

$\Delta H_f(H_2Se; g)$ (*see* Bichowsky and Rossini[38] for references), we obtain $E(Se - H) = 66$ kcal.

10.1.52. $E(Te - H)$

A value of 57 kcal for $E(Te - H)$ in H_2Te is based on old thermal data[38] and an uncertain heat of atomization (Section 8.2.2.52).

10.4.17. $E(Be - Cl)$

The heat of the reaction $Be(s) + Cl_2(g) \rightarrow BeCl_2(s)$ has been measured directly by Mielenz and von Wartenberg[346]. They obtained $\Delta H_f(BeCl_2, s) = -112{\cdot}6$ kcal. This is the value quoted by Bichowsky and Rossini[38]. On the other hand, the N.B.S.[529] give $-122{\cdot}3$ kcal, referring to the same paper. There is some not very satisfactory evidence that Mielenz and von Wartenberg's result may be low. An earlier and less reliable estimate gave -155 kcal[394]. Mielenz and von Wartenberg also gave $\Delta H_f(BeO; s)$ as $-135{\cdot}9 \pm 1{\cdot}1$ kcal. More recently, however, Cosgrove and Snyder[91] have remeasured the heat of formation of BeO to be $-143{\cdot}1$ kcal, approximately 5 per cent greater than the previous value. If this discrepancy were due to impurity, an upward revision of the value for $BeCl_2$ might be indicated, but it would be very uncertain. Combination of the original result with a heat of sublimation of 29 kcal[155] and with the most recent value of the heat of atomization of beryllium gives $E(Be - Cl) = 109$ kcal. A slightly lower estimate[453] is due to a slightly lower value for the heat of atomization of beryllium.

10.4.35. $E(Be - Br)$

$E(Be - Br)$ in $BeBr_2$ may be deduced to be 89 kcal. The heat of formation of $BeBr_2$ depends on that of $BeCl_2$[38].

10.4.53. $E(Be - I)$

$E(Be - I)$ in BeI_2 is 69 kcal. The heat of formation of BeI_2 depends on that of $BeCl_2$[38].

10.5.6. $E(B - C)$

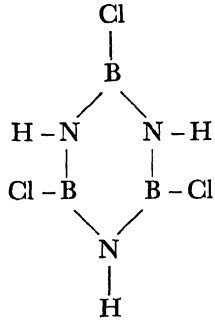
The heat of combustion of boron trimethyl has been determined by Long and Norrish[319], who obtained $\Delta H = -705{\cdot}4$ kcal for combustion of $BMe_3(l)$ to B_2O_3 (amorphous). If we take the value of Prosen *et al.*[405] for $\Delta H_f(B_2O_3)$, we obtain $\Delta H_f(BMe_3; g) = -32$ kcal. Long and Norrish used a larger value for $-\Delta H_f(B_2O_3)$ and hence obtained the slightly higher value for $-\Delta H_f$, 47·6 kcal.

Using E(CH) given in Section 10.1.6, we deduce E(C – B) = 66 kcal.

We have used the N.B.S.[529] value for the heat of atomization of boron. It should be remembered that this is not certainly established.

10.5.7. E(B – N)

E(B – N) has been estimated from the heat of formation of B-trichloroborazole (formula below) by Van Artsdalen and Dworkin[12]. This compound contains 6 B – N bonds, three B – Cl



bonds, and 3 N – H bonds. The last two bond energies were taken as 92·9 and 84·3 kcal respectively, and E(B – N) deduced to be 82·5 kcal. It should be pointed out that the value for E(B – Cl) is lower than that given in Section 10.5.17.

The experimentally measured heat quantity was the heat of hydrolysis of B-trichloroborazole to dilute aqueous ammonium chloride and boric acid, $\Delta H = -113{\cdot}8 \pm 0{\cdot}7$. This was combined with other data to give $\Delta H_f(B_3N_3H_3Cl_3; s) = -252{\cdot}2$ kcal*, and with the value of 17·1 kcal for the heat of sublimation to give the heat in the gas phase. The N.B.S.[529] values for subsidiary quantities were used.

A value of E(B – N) = 80 kcal, in good agreement with the above, has recently been derived from trisdimethylaminoborine, $B(NMe_2)_3$, by Skinner and Smith[455a].

10.5.8. E(B – O)

An estimate of E(B – O) can be obtained from the heats of formation of the alkyl borates, recently determined by Skinner *et al.*[74]. The values of E(B – O) deduced depend on E(C – O), E(C – C), and E(C – H), and are 110, 113, 114, and 115 kcal from methyl, ethyl,

* Use of Prosen's value for $\Delta H_f(B_2O_3)$ alters this to –258·5 kcal[455a].

n-propyl, and *n*-butyl borates respectively. The N.B.S.[529] value of 97·2 kcal for the heat of atomization of boron has been used.

Skinner *et al.* deduced the average value of $D(B-O)$ in these compounds to be 110 ± 5 kcal, in reasonably good agreement with the above bond energy term.

10.5.9. $E(B-F)$

$E(B-F)$ is obtained as 139 kcal from the heat of formation of BF_3, assuming the N.B.S.[529] value for the heat of atomization of boron. The heat of formation of BF_3 used is also that given by the N.B.S.[529]. It depends on the heat of formation of H_3BO_3, and on an old measurement of the heat of reaction of H_3BO_3 with HF (*see* Bichowsky and Rossini[38] for references) and is therefore somewhat uncertain.

10.5.17. $E(B-Cl)$

The most recent and apparently the most reliable data on the heat of formation of BCl_3 are due to Skinner and Smith[455]. They obtain $\Delta H_f(BCl_3;\ liq) = -103{\cdot}0 \pm 1$ kcal, whence $\Delta H_f(BCl_3;\ g) = -97{\cdot}5$ kcal and $E(B-Cl) = 94$ kcal.

10.5.35. $E(B-Br)$

$E(B-Br) = 74{\cdot}0$ kcal, in BBr_3, from the N.B.S.[529] values, but this is uncertain.

10.6.6. $E(C-C)$

The uncertainty in the heat of atomization of carbon introduces uncertainty in the absolute values of its bond energy terms. The following discussion will, however, be concerned largely with differences, where this difficulty does not arise.

If the assumption of constancy held exactly, it would be possible to deduce $E(CH)$ from methane and $E(C-C)$ from ethane, and to use these values to give the heats of formation of all paraffins. This is not in fact possible. The increment per CH_2 group to the heat of formation is not constant for the lower *n*-paraffins, but becomes so only at *n*-pentane[406]. Moreover, if the assumption of constancy held exactly, all isomeric paraffins should have the same heat of formation. This is not so. For example, the heats of formation ($-\Delta H_f$) at 298·16° K of *n*-butane and *iso*-butane are $29{\cdot}8_1$ kcal and $31{\cdot}4_5$ kcal respectively, and those of *n*-pentane and *neo*-pentane are $35{\cdot}0_0$ and $39{\cdot}6_7$ kcal. This effect persists at 0° K[92, 428]. If the CC and CH bonds are further classified, it is, however, possible to set up an additive scheme for the heats of formation of the hydro-

carbons. C – C bonds may be classified as n_{11}, n_{12}, n_{13}, n_{22}, n_{23} *etc.*, the subscripts 1, 2, 3, 4 meaning that the left or right carbon atom is primary, secondary, tertiary, or quaternary. Similarly a CH bond may be n_1, n_2, n_3. Such a scheme has been given by Tatevskii [509, 510]. The differences per bond are not, however, very large. Even the difference between the heats of formation of *n*-pentane and *neo*-pentane is only 0·3 kcal per bond.

The importance of these small effects depends on the purpose for which bond energy terms are being used. If we are interested in the differences in energy terms for bonds between different pairs of atoms, for example, say, in why C – C should be weaker than C – O, these small differences do not matter. Also, if we are simply interested in prediction of the heats of formation of organic compounds, we might ignore these differences for some purposes or we might take account of them in some fairly rough and ready way. On the other hand, the cause of differences in energy between isomers is a topic for research in its own right. The seriousness of our attempts to take account of small differences in bond energy terms will depend on how appropriate we consider this method of approach to be. It is the opinion of the present author that consideration of the molecule as a whole is more relevant to these small differences, but the prevalence in the literature of explanations in terms of bond energies shows that there are many who disagree with him. In this connection, reference must be made to the work of Glockler [178], who has been assiduous in the attempt to give a detailed and accurate account of the heats of formation of hydrocarbons in terms of bond energies, given by him as functions of bond length.

For our present purposes we follow the approach of Coates and Sutton [80]. We have converted their values to those based on our estimates of the heats of atomization of carbon and hydrogen. They deduce E(C – C) and E(C – H) from the constant CH_2 increment for the *n*-paraffins above *n*-pentane [406]. Using their method we obtain E(C – C) = 66·2 kcal, and E(C – H) = 90·5 kcal. The value for E(C – H) is 0·6 kcal less than that deduced directly from methane, but it is considered that these values will be of wider applicability than those derived for methane and ethane. Similarly, E(C=C) is deduced by combination of these values with the values of the heats of formation of the 1-olefines [407]. We obtain E(C=C) = 112·9 kcal. If E(C – C) and E(C – H) are taken as constant, and the whole of the variation in energy thrown on to E(C=C), we find for various olefines the following values of E(C=C): ethylene, 110·0 kcal; propene, 112·8 kcal; 1-butene, 112·5 kcal; *cis*-3-hexene, 114·6 kcal; *trans*-3-hexene, 115·6 kcal.

The differences are not very large, but it is essential to remember and allow for this 'substitution' effect when small differences are being considered. It is particularly important when attempting to predict the bond energy sum for aromatic structures. For instance, the appropriate value for $E(C=C)$ in the Kekulé structure of benzene would seem to be that derived from *cis*-3-hexene, rather than that derived from the 1-olefines [98], although this is essentially a matter of definition. Glockler [179], for example, has defined the Kekulé structure of benzene to be that made up of C – H bonds as in methane, C – C bonds as in ethane, and C=C bonds as in ethylene, and gets quite a different value for the 'resonance energy'.

Similarly, Coates and Sutton derive $E(C=C)$ from 1-ynes. Then $E(C\equiv C)$ is 150·3 kcal. The value in 2-ynes is 3·6 kcal higher. In acetylene, $E(C\equiv C)$ is 145 kcal, assuming the same value of $E(C-H)$ as before.

$E(C-C)$ may also be taken as half the heat of atomization of diamond [382] or about 69 kcal. This is in quite good agreement with the values for the paraffins (*see* $E(Si-Si)$ and $E(Ge-Ge)$).

10.6.7. $E(C-N)$

The derivation of $E(C-N)$ has been discussed by Coates and Sutton [80]. They used a slightly different value of the heat of atomization of nitrogen from that adopted here. We have corrected to our value. $E(C-N)$ is obtained from the aliphatic amines as follows: methylamine 50·8 kcal, ethylamine 51·1, *n*-propylamine 51·4, *n*-butylamine 57·8, *iso*-amylamine 58·5, *n*-hexylamine 58·9, *n*-heptylamine 59·5, dimethylamine 48·4, diethylamine 54·0, di*iso*butylamine 56·4, di*iso*amylamine 57·8, triethylamine 56·1, tri*iso*butylamine 58·1, tri*iso*amylamine 53·4 kcal. These results are taken directly from Coates and Sutton's paper, with the addition of $\frac{1}{4}\Delta L_C + \frac{1}{3}\Delta Q_a N$, where ΔL_C is the difference between the values of the heat of atomization of carbon, and $\Delta Q_a N$, the difference between the values of the heat of atomization of nitrogen. These individual values are not to be relied upon to better than ±3 kcal, because the heats of formation of the amines are not very well known; particular values used by Coates and Sutton were from Kharasch's compilation [262]. The mean is 55·5 kcal. Pauling [382] used a slightly lower value.

$E(C=N)$ has been obtained from the heat of formation of *n*-butyl *iso*butylidine amine, which was determined by Coates and Sutton [80]. Their value, corrected, is 112 kcal.

$E(C\equiv N)$ may be deduced from the heat of formation of acetonitrile to be 160·4 kcal. *n*-Butyronitrile gives 162·7 kcal, *iso*valeroni-

trile 160·9 kcal. These heats of combustion are from Kharasch; the heat of vaporization of *iso*valeronitrile was assumed to be equal to that of *n*-valeronitrile. Coates and Sutton[80] adopt an average value of 160·6 kcal. The constancy of these values is evidence for the practical utility of the constancy assumption. HCN shows the same effect as acetylene, in that $E(C{\equiv}N)$ is 6 kcal less than the general $E(C{\equiv}N)$ value.

Glockler[175] gives a comprehensive list of CN bond energies in various molecules, which differ from those given above. Converting to our heats of atomization his value for $E(C-N)$, from methylamine, is 57·2 kcal, and for $E(C{=}N)$ from $CH_3 . N{=}C{=}O$ is 91·7 kcal. Syrkin and Dyatkina[491] give $E(C-N)$ in amines 56·5, $E(C{\equiv}N)$ nitrile, 159 kcal, and $E(C{=}N)$ presumably from $CH_3 . N{=}C{=}O$ 90 kcal, after conversion to our heats of atomization.

10.6.8. E(CO)

Coates and Sutton[80] give a value of $E(C-O)$ which, after conversion to our heats of atomization, is 77·1 kcal. This was derived to give the best fit to the values for the heats of formation of the alcohols[427], using the previously adopted values of $E(C-C)$, $E(C-H)$, and $E(O-H)$ from water. With these values there appears to be a slight upward drift in the apparent value of $E(C-O)$ with chain length. The figure adopted fits *n*-pentanol, but results in an overestimate of the heat of atomization of methanol by 5·3 kcal, and that of ethanol by 1·7 kcal. The agreement for the other *n*-alcohols is better. This value for E(CO) fits the heats of formation of the acetals quite well; for example methylal gives $E(CO) = 77{\cdot}7$ kcal. (Heats of combustion, all early work, from Kharasch[262].)

$E(C{=}O)$ appears to be variable. It comes to 149 kcal, in formaldehyde, 159 kcal in acetaldehyde, and 162 kcal in ketones. The heats of formation are mainly due to early work. $E(C{=}O)$ in carbon dioxide is a good deal higher, 175 kcal. This is in accord with the fact that the CO distance is less than in carbonyl compounds and has been attributed to resonance[382]. The interpretation in terms of resonance has, however, been severely criticized[62, 316, 320].

10.6.9. $E(C-F)$

$E(C-F)$ may be derived as a primary bond energy term from the heat of formation of carbon tetrafluoride. Unfortunately this quantity is not certainly known. The heat of formation $(-\Delta H_f)$

from the elements was measured directly by von Wartenberg and Schütte[556] to be 162 kcal. The reaction did not proceed satisfactorily with carbon in the form of graphite, so they used wood charcoal, and corrected for the heat of conversion of charcoal to graphite, determined by combustion. This is not entirely satisfactory, but the result was accepted for some time. More recently von Wartenberg and Riteris[555] have measured the heat of the reaction $4K + CF_4 \rightarrow C$ graphite $+ 4$ KF. This gives $\Delta H_f(CF_4; g) = -231$ kcal. If the earlier value is correct, we deduce $E(C-F) = 94$ kcal, if the latter, $E(C-F) = 111$ kcal. Long[317] takes the high value, but uses the old high value for $D(F_2)$.

It is unfortunate that there are no other simple organic compounds of fluorine for which ΔH_f is known. Some indication may, however, be obtained from β-fluoroethanol $CH_2F \cdot CH_2OH$, the heat of formation of which has been determined by combustion. From this we deduce $E(C-F) = 95$ kcal, in agreement with the value obtained from the lower heat of atomization of carbon tetrafluoride. This is not completely certain, however, since the heat of formation of this compound may not be reliably known. Nevertheless, under the circumstances we must prefer $E(C-F) = 94$ kcal.

10.6.13. E(C – Al)

The heat of formation of aluminium trimethyl has been obtained by combustion by Long and Norrish[319]. Using our bond energy term $E(C-H)$ and the heat of atomization given in Section 8.2.2.13, we obtain $E(C-Al) = 53$ kcal. Long and Norrish give the much higher figure, 94 kcal. This is based on the view that the relevant value of $L_C = 190$ kcal, and that the proper reference state for aluminium is the excited $^4P_{\frac{1}{2}}$ state. They also adopt a value for the heat of atomization of aluminium to the ground state which is 9 kcal greater than that used here.

10.6.14. E(C – Si)

$E(C-Si)$ has been deduced from the heat of formation of carborundum[382], and also from those of some organo-silicon compounds[521].

There is considerable uncertainty about the heat of formation of carborundum, silicon carbide. A value of $\Delta H_f = -28$ kcal, based chiefly on the results of von Wartenberg and Schütte[556], has been frequently used, but other evidence[38] leads to values differing from this by over 20 kcal. Under these circumstances, the resulting $E(C-Si) = 64$ kcal is not to be taken very seriously.

Thompson[521] has measured the heats of combustion and deduced the heats of formation of some linear polymethylsiloxanes: the difficulties of this work have already been emphasized (Ch. 7). Values of $E(\mathrm{Si-C})$ and $E(\mathrm{Si-O})$ of 56 and 117 kcal, after conversion to our values of heats of atomization, are obtained. These values do not fit the compounds from which they were derived particularly well, nor do they fit other combustion results on organosilicon compounds obtained by Tanaka *et al.*[508]. Pauling's bond energy terms fare no better. It is not clear whether these discrepancies are due to the breakdown of the constancy assumption in organo-silicon compounds or to the difficulty in obtaining reliable heats of formation of these compounds.

10.6.16. $E(\mathrm{CS})$

$E(\mathrm{C-S})$ can be obtained from thioethers and mercaptans, the heats of formation of some of which have recently been collected by Barrow and Pitzer[16]; these are chiefly old values, probably not accurate to better than ± 3 kcal. Combining these results with $E(\mathrm{C-H})$, $E(\mathrm{C-C})$, and $E(\mathrm{S-H})$ we obtain $E(\mathrm{C-S}) = 59$ kcal. This fits the results fairly well. Pauling's[382] value, converted to our heats of atomization, is 58 kcal.

$E(\mathrm{C{=}S})$ may be obtained from the heat of formation of CS_2 or from COS. $\Delta H_f(\mathrm{COS};\ g) = -32{\cdot}9$ kcal, was derived by Terres and Wesemann[514] from their measurement of the equilibrium $H_2S + CO_2 \rightleftharpoons H_2O + COS$. This is in fairly good agreement with other estimates[38], and taking $E(\mathrm{C{=}O})$ from CO_2, we obtain $E(\mathrm{C{=}S}) = 121$ kcal. $\Delta H_f(CS_2)$ is less well established. The measurements of Terres and Wesemann[514] on the equilibrium $H_2S + COS \rightleftharpoons H_2O + CS_2$ lead to $\Delta H_f(CS_2;\ g) = 33{\cdot}9$ kcal. Thomsen's combustion data yield 28·6 kcal[38], and various other values have been suggested from 17 kcal upwards[38]. If 28·6 kcal is taken, we obtain $E(\mathrm{C{=}S}) = 121$ kcal, in agreement with the value from COS.

10.6.17. $E(\mathrm{C-Cl})$

The generally accepted[38, 529] value of the heat of formation of carbon tetrachloride is due to Bodenstein *et al.*[44], who measured the heat of the reaction $CCl_4 + 2H_2 \rightarrow C + 4HCl$. They obtained $\Delta H_f(CCl_4;\ g) = -25{\cdot}5$ kcal, but in view of the slight uncertainty about the heat of formation of the form of carbon produced, the figure after the decimal point is probably not justified. From this $E(\mathrm{C-Cl}) = 70{\cdot}0$ kcal. The heat of formation of methyl chloride is due to a combustion by Thomsen[523], and is -20 kcal. From

this figure, using the $E(C-H)$ value adopted here, we obtain $E(C-Cl)=71{\cdot}8$. Using $E(C-H)$ directly from methane, we obtain 70·0 kcal. The heat of formation of ethyl chloride is well established[290]; using it we obtain $E(C-Cl)=73{\cdot}5$ kcal. A value of $E(C-Cl)=73$ kcal is probably satisfactory except for the chloromethanes, where a slightly smaller value is indicated.

10.6.30. $E(C-Zn)$

The heats of formation of zinc dimethyl and zinc diethyl have been measured both by combustion[319] and by other thermochemical methods[68], the results agreeing to within $\pm 0{\cdot}1$ kcal of the mean. Using our other bond energy terms, we deduce $E(Zn-C)$ to be 32 kcal in $ZnMe_2$ and 27 kcal in $ZnEt_2$. The average values of $D(Zn-C)$ in these compounds are 41 and 34 kcal respectively, and it is expected that D_1 will be very much greater than D_2. This follows the usual pattern of $D(CH_3-X)$, which is in general larger than $E(CH_3-X)$. It is also generally found in these metallic alkyls that $E(C-M)$ deduced from the methyl compound is about 4 kcal greater than $E(C-M)$ deduced from the ethyl compounds. Combustion data only are available for zinc di-*n*-propyl and zinc di-*n*-butyl. From these we deduce $E(C-Zn)=29$ and 31 kcal respectively, in agreement with the other results. Long and Norrish referred their results to $L_C=190$ kcal and to an excited state of Zn.

10.6.34. $E(CSe)$

A rough estimate of $E(C-Se)$ may be obtained from the heat of combustion of diethyl selenide, measured by Merten and Schlüter[345] to be $749{\cdot}7 \pm 0{\cdot}7$ kcal, the selenium-containing product being selenium dioxide. Estimating the heat of vaporization, we obtain $E(C-Se) \sim 50$ kcal.

The heat of combustion of CSe_2 was measured by the same authors, whence, estimating the heat of vaporization, $E(C{=}Se)=96$ kcal. There is some doubt about the heat of atomization of selenium.

10.6.35. $E(C-Br)$

It should be noted that the heats of formation of CBr_4, CH_2Br_2, and $CHBr_3$ given by the N.B.S. are 'calculated'. Methyl bromide has been burned by Thomsen[523], but in view of the difficulties attending the combustion of halogen-containing compounds we prefer to deduce $E(C-Br)$ from ethyl bromide, the heat of formation of which has been obtained by equilibrium methods[290] in

agreement with combustion results. We obtain $E(C-Br) = 60$ kcal, and by analogy with the chloro-compounds expect a value 2–3 kcal less to apply to bromomethanes. This is borne out by such experimental evidence as is available.

10.6.48. $E(C-Cd)$

The heats of formation of cadmium dimethyl and diethyl have been determined by Skinner *et al.*[68] and lead to $E(C-Cd) = 24$ and 19 kcal respectively. The corresponding $\bar{D}(C-Cd)$ values are 33 and 27 kcal (*see* Section 10.6.30). A value for CdMe in agreement with this has been obtained by Long and Norrish[319] from their heat of combustion of that compound. They, however, refer the bond energy to excited Cd.

10.6.50. $E(C-Sn)$

The heat of formation of tin tetraethyl is quoted by Long and Norrish[319], and they obtain $E(C-Sn) = 81$ kcal. This is based on $L_C = 190$ kcal, a value of 50·9 kcal for the heat of atomization of tin, and an excitation energy of 113·2 kcal to the appropriate excited state. Reduced to ground state atoms, and taking our values of heats of atomization $E(C-Sn)$ becomes 45 kcal. The same result is obtained using the bond energy term values given here.

10.6.53. $E(C-I)$

The heats of formation of both methyl and ethyl iodide are fairly well known, and have been discussed in Chapter 7. We deduce $E(C-I) = 43$ and 44 kcal respectively for these two compounds.

10.6.80. $E(C-Hg)$

The heats of formation of various mercury alkyls are given by Skinner *et al.*[357]. We deduce $E(Hg-C) = 19$, 15, and 15 kcal from $HgMe_2$, $HgEt_2$, and Hg-*n*-Pr_2 respectively. The low values of the bond energy terms in mercury alkyls were used by Sidgwick and Springall[448] as an argument in favour of the high value of L_C, but they neglect the effect of valence state and the difference between D and E.

Long and Norrish[319] give values of $E(Hg-C)$ based on older values of the heats of formation of these compounds, which are not believed to be accurate[357].

10.7.7. $E(NN)$

$E(N-N)$ may be estimated from the heat of formation of hydrazine[235] to be 20·8 kcal. $E(N{=}N)$ has been estimated by

Coates and Sutton[80] from the heat of formation of azo*iso*propane to be 63·7 kcal. $E(N{\equiv}N)$ is the dissociation energy of nitrogen at 25° C, for which we take 171·1 kcal (*see* Section 8.2.2.7).

10.7.8. $E(NO)$

$E(N-O)$ may be deduced from the heat of formation of hydroxylamine, NH_2OH. This is not very reliably established[38] and the heat of vaporization must be estimated, so the resulting value of $E(N-O)$, 39 kcal, may not be very accurate. It is also possible to estimate $E(N-O)$ by noting that the heat of atomization of a nitric ester is greater than that of the corresponding nitrocompound by $E(C-O)+E(O-N)-E(C-N)$. Using the figures for ethyl nitrate[523] and nitroethane[227], and putting $E(C-O)=77{\cdot}1$ kcal, $E(C-N)=52$ kcal, we deduce $E(N-O)=44$ kcal, in quite good agreement with the value from hydroxylamine. $E(N{=}O)$ may be obtained from alkyl nitrites. Using Thomsen's figures for ethyl nitrite, we obtain $E(N-O)+E(N{=}O)=170$ kcal, whence $E(N{=}O)=126$ kcal. Syrkin and Dyatkina[491], using a similar method involving nitrites and nitrates, agree that $E(N-O)+E(N{=}O)=169$ kcal, but put $E(N-O)=61$ kcal and $E(N{=}O)$ 108 kcal. This does not fit so well with hydroxylamine.

10.7.9. $E(N-F)$

Ruff and Wallauer[438] measured the heat of the reaction $NF_3+\frac{3}{2}H_2 \rightarrow \frac{1}{2}N_2+3HF$ and deduced $-\Delta H_f(NF_3;\,g)=26$ kcal, whence $E(N-F)=56$ kcal.

10.7.17. $E(N-Cl)$

The heat of formation of nitrogen trichloride in carbon tetrachloride solution is known[38]. Rice[415] has estimated the heat of vaporization to be 6 kcal, whence $E(N-Cl)=37$ kcal.

10.8.8. $E(O-O)$

$E(O-O)$ in hydrogen peroxide may be deduced to be 35 kcal[80, 382]. It has been suggested that it is unsatisfactory to put $E(OH)$ in H_2O_2 equal to $E(OH)$ in water, and various estimates of the 'correct' value to be taken for $E(OH)$ have resulted in $E(OO)=52$ kcal[452] and 64 kcal[550], but these suggestions are rather speculative. $E(O-O)$ in diethyl peroxide may be deduced to be 47 kcal, if the heat of formation of this substance obtained by Rebbert and Laidler[410] is correct. It should be noted that heats of combustion of organic peroxides are difficult to obtain reliably.

10.8.9. $E(O-F)$

The heat of formation of F_2O seems to be well established[38], and from it we obtain $E(O-F) = 45{\cdot}3$ kcal.

10.8.14. $E(SiO)$

$E(Si-O)$ is deduced from the heats of formation of some linear polydimethyl siloxanes to be 117 kcal by Thompson[521]. He also obtains 104 kcal for $E(Si-O)$ in amorphous silica (*see* Section 10.6.14). The reliability of bond energy terms in the prediction of heats of formation of organo-silicon compounds is doubtful; the situation has been discussed by Thompson[521].

10.8.15. $E(PO)$

$E(P-O)$ has been given by Charnley and Skinner as 99 kcal[73], based on a rather roundabout measurement of the heat of formation of liquid P_4O_6[277]. Dainton[105] has given values of 80 kcal for $E(P-O)$ in P_4O_6 and bridge $(P-O)$ in P_4O_{10}, and 156 kcal for $E(P-O)$ apical, in P_4O_{10}. These are not very well established. $E(P{=}O)$ in $POCl_3$ and $POBr_3$ is deduced to be 122 and 119 kcal respectively[73].

10.8.16. $E(SO)$

The heats of formation of SO_2 and SO_3 are well established, and lead to $E(S{=}O) = 128$ kcal and 113 kcal respectively[38].

10.8.17. $E(O-Cl)$

$E(O-Cl)$ in Cl_2O may be deduced as 45 kcal[317], but the heat of formation of this compound is in some doubt[38]. Pauling[382] gives 49 kcal. This is in better agreement with the value of 52 kcal in HOCl, which we obtain from Gelles' estimate of $D(O-Cl)$ in this compound[169].

10.8.33. $E(As-O)$

Dainton[105] has given a discussion of As – O bond energies. He points out that the heat of formation of $As_4O_6(g)$ is fairly well established, and that $E(As-O)$ is 72 kcal. This is $E(AsO)$ in the 'bridge' form. The heat of formation of $As_4O_{10}(g)$ is not very well established, but taking the available data Dainton deduces $E(As-O)$, 'apical', to be 93 kcal.

10.8.35. $E(O-Br)$

$E(O-Br)$ in HOBr is 48 kcal, obtained from $D(O-Br)$ in this compound[169].

10.8.51. E(Sb – O)

It is possible to estimate E(Sb – O) in Sb_4O_6(g) and Sb_4O_{10}(g), though the thermochemical data are not complete. Details are given by Dainton[105], who gives 71 kcal for E(Sb – O) 'bridge' and 95 kcal for E(Sb – O) 'apical'. These estimates are not very reliable.

10.8.53. E(O – I)

E(O – I) in HOI is 48 kcal[169].

10.8.76. E(Os=O)

Long[317] gives E(Os=O) = 123 kcal from OsO_4.

10.9.14. E(Si – F)

The heat of formation of SiF_4 is fairly well known[38, 556]. We deduce E(Si – F) = 131 kcal.

10.9.16. E(S – F)

The heat of formation of sulphur hexafluoride has been determined directly by Yost and Claussen[579]. Hence E(S – F) = 73 kcal. Long's figure[317] differs because he takes different values for the heats of atomization of sulphur and fluorine.

10.9.33. E(As – F)

The heat of formation of liquid arsenic trifluoride was determined indirectly by Yost and Sherborne[580], who measured ΔH for the reactions

$$2AsF_3(l) + 6NaOH(1N) \rightarrow 6NaF(\text{in } 1N\,NaOH) + As_2O_3 (\text{in } 1N\,NaOH) + 3H_2O(l) \quad \ldots\ (1)$$

$$6NaF(s) + As_2O_3(s) \rightarrow 6NaF(\text{in } 1N\,NaOH) + As_2O_3 (\text{in } 1N\,NaOH) \quad \ldots\ (2)$$

They found $\Delta H_1 = -64{\cdot}5$ kcal and $\Delta H_2 = -10{\cdot}7$ kcal, whence, knowing the heats of formation of NaOH(1N), H_2O(l), As_2O_3(s), and NaF(s), we obtain $\Delta H_f(AsF_3;\ l) = -226{\cdot}8$ kcal. Yost and Sherborne apparently added ΔH_2 to ΔH_1, instead of subtracting it, and, using I.C.T. heats of formation, obtained $-198{\cdot}3$ kcal, but the correct result is given by the N.B.S.[529]. The heat of vaporization was determined to be 8·5 kcal[439], whence $\Delta H_f(AsF_3;\ g) = -218$ kcal, and E(As – F) = 111 kcal. The heat of atomization of arsenic is uncertain.

10.9.34. E(Se – F)

E(Se – F) from selenium hexafluoride[579] is 68 kcal. The heat of atomization of selenium is uncertain.

10.9.52. E(Te – F)

E(Te – F) from tellurium hexafluoride[579] is 80 kcal. The heat of atomization of tellurium is not certain.

10.9.53. E(I – F)

In the diatomic molecule E(I – F) = 46 kcal (*see* Section 9.9.53). Long[317] gives 63 kcal (corrected to our value for the heat of atomization of fluorine) from IF_5[577].

10.9.75. E(Re – F)

Rhenium hexafluoride has been described by Ruff and Kwansik[437]. The N.B.S.[529] give the heat of formation, referring to this work. The paper referred to does not, however, mention the heat of formation of ReF_6. Long[317] uses the N.B.S. value, together with their value of the heat of atomization of rhenium, to give E(Re – F) = 96 kcal, corrected to our value of the heat of atomization of fluorine. The reliability of this value is unknown to the present author.

10.9.77. E(Ir – F)

Ruff and Fischer[436] made three very rough direct determinations of the heat of formation of iridium hexafluoride, giving values of $\Delta H_f(IrF_6; l)$ of –100, –140, and –150 kcal. They adopted an approximate mean value of 130 kcal, from which E(Ir – F) = 67 kcal, according to Long[317], corrected to our value of the heat of atomization of fluorine. The value for the heat of atomization of iridium is itself doubtful, so that this estimate of E(Ir – F) is wildly approximate.

10.9.80. E(Hg – F)

Long[317] gives E(Hg – F) from HgF_2 as 66 kcal, corrected to our value for the heat of atomization of fluorine. The heat of formation of HgF_2 he uses is due to Brewer *et al.*

10.9.92. E(U – F)

Referring to Brewer *et al.* (unpublished data) the N.B.S.[529] give the heat of formation of uranium hexafluoride, from which Long[317] derives E(U – F) = 124 kcal, after correction.

10.14.14. E(Si – Si)

Skinner[452] has estimated E(Si – Si) from the activation energy for the thermal decomposition of disilane, but this is probably not valid. Pauling[382] takes E(Si – Si) equal to half the heat of atomization of the element, whence E(Si – Si) = 45 kcal.

10.14.16. E(Si – S)

Pauling[382] has given a value for E(Si – S) of 62 kcal, corrected to our values of heats of atomization. This is obtained from the heat of formation of solid SiS_2, dividing by the number of bonds (four) per stoichiometric molecule. The heat of formation of SiS_2 used by Pauling is not very well established, however, since it is referred to colloidal aqueous SiO_2[38]. A recent investigation also suggests that the starting material may not have been pure. Using purified material and hydrolysis to aqueous Na_2SiO_3 and Na_2S, a value of $\Delta H_f(SiS_2; s) = -60$ kcal was obtained[163a]. This leads to E(Si – S) = 70 kcal, but it is affected by an unknown uncertainty in the value for the heat of formation of Na_2SiO_3.

10.14.17. E(Si – Cl)

E(Si – Cl) = 87 kcal may be derived from the heat of formation of $SiCl_4$. This quantity appears to be moderately well established[38], but again the result is directly related to the heat of formation of colloidal aqueous SiO_2, which may not be completely satisfactorily defined.

10.14.35. E(Si – Br)

E(Si – Br) in $SiBr_4$ is 70 kcal. The heat of formation of this substance depends upon the measurement of its heat of reaction with water and the heat of formation of the SiO_2 formed[38].

10.14.53. E(Si – I)

From SiI_4, E(Si – I) = 52 kcal (*see* Section 10.14.35).

10.15.15. E(P – P)

E(P – P) may be derived from the heat of formation of gaseous P_4, which contains 6 P – P bonds. The thermochemistry of the various forms of phosphorus has been critically reviewed by Stevenson and Yost[479]; their considerations yield $\Delta H_f(P_4; g) = 13{\cdot}1$ kcal. From this we obtain E(P – P) = 48 kcal, as pointed out by Dainton[105]. The $\widehat{PPP}$ angle in P_4 is only 60°, and considerations of steric strain arise. Pauling and Simonetta[386] have calculated

that the strain energy is 22·8 kcal, and that the value of E(PP) for the 'normal single bond' is 51·3 kcal. Earlier, Moffitt[351] had calculated a slightly greater value for the strain energy, leading to 54·5 kcal for the unstrained bond. Pitzer[391] has estimated 53 kcal for unstrained P – P from the heat of vaporization of red phosphorus.

E(P≡P) is equal to the dissociation energy of P_2, 117 kcal (Section 9.15.15).

10.15.17. E(P – Cl)

E(P – Cl) in PCl_3 is given by Charnley and Skinner[73] as 78 kcal.

10.15.35. E(P – Br)

E(P – Br) in PBr_3 = 63 kcal[73].

10.15.53. E(P – I)

Skinner[452] gives E(P – I) in PI_3 = 44 kcal, after correction to the heat of atomization of phosphorus. The heat of formation of PI_3(s) is based on old data[38] and the heat of vaporization is an estimate by Rice[415] so that the reliability of this value is doubtful.

10.16.16. E(SS)

The heat of formation of H_2S_2 does not appear to have been directly determined. We obtain ~67 kcal from the available information[161, 529]. The heat of combustion and formation of dimethyl and diethyldisulphide have been determined by Franklin and Lumpkin[161]. From dimethyldisulphide we obtain E(S – S) = 67 kcal, from diethyldisulphide we obtain 70 kcal. Pauling[382] has deduced E(S – S) to be 64 kcal from the heat of formation of S_8. This is an interesting contrast to the corresponding bonds to oxygen; we have that E(C – O) > E(O – O), whereas E(C – S) < E(S – S). E(S=S) is the dissociation energy of S_2, which is probably 102 kcal (Section 9.16.16).

10.16.17. E(S – Cl)

The heat of formation of S_2Cl_2 seems to be fairly well established[38]. Following Pauling[382], we assume the structure to be Cl – S – S – Cl, whence E(S – Cl) = 65 kcal. Pauling takes a slightly lower value for E(S – S), whence a slightly higher value for E(S – Cl).

10.16.35. E(S – Br)

Pauling[382] obtained E(S – Br) in the same way as E(S – Cl), but the heat of formation of S_2Br_2 is not so reliably established[38]. E(S – Br) = 56 kcal is therefore open to some doubt.

10.17.22. $E(\mathrm{Ti-Cl})$

The heat of formation of $TiCl_4(g)$ depends upon the heat of vaporization of the liquid, the heat of solution of the liquid in water, and the heat of reaction of aqueous $TiCl_4$ with NaOH, and thus finally on the heat of formation of the hydrated precipitate of TiO_2 formed [38]. This last quantity was estimated by Bichowsky and Rossini [38]. The heat of formation of TiO_2 has recently been redetermined by direct combustion to be $-\Delta H_f(TiO_2;\ s) = 225{\cdot}5 \pm 0{\cdot}2$ kcal by Humphrey [237], a value 7 kcal higher than that adopted by Bichowsky and Rossini on the basis of some not very concordant earlier determinations. Thus the datum from which Bichowsky and Rossini estimated the heat of formation of the hydrated precipitate of TiO_2 has changed, and the value of $-\Delta H_f(TiCl_4;\ g)$ therefore should be increased by about 7 kcal to approximately 179 kcal. From this $E(\mathrm{Ti-Cl}) = 102$ kcal. Long [317] gives 100 kcal. There is obviously some uncertainty about the exact value of this quantity.

10.17.32. $E(\mathrm{Ge-Cl})$

The heat of formation of $GeCl_4(g)$ depends on the heat of vaporization, the heat of reaction of the liquid with water, and the heat of formation of GeO_2 [38]. ΔH for vaporization is given by Kelley [259] as 8·1 kcal, the heat of reaction to give solid GeO_2 and aqueous hydrochloric acid was measured by Roth and Schwartz [431]. Bichowsky and Rossini [38] combined this with an 'estimate' of the heat of formation of GeO_2 which differs by 100 kcal from the value given by Becker and Roth [27]. Subsequent work [253] has confirmed Becker and Roth's result, so that $-\Delta H_f(GeCl_4;\ g) = 120$ kcal, whence $E(\mathrm{Ge-Cl}) = 81$ kcal. Long [317] gives a slightly lower value because he adopts a slightly lower value for the heat of atomization of germanium.

10.17.33. $E(\mathrm{As-Cl})$

$E(\mathrm{As-Cl})$ may be derived as 70 kcal from the heat of formation of $AsCl_3$. Thomsen [523] obtained $-\Delta H_f(AsCl_3;\ l) = 71{\cdot}5$ kcal, both by direct measurement and by measuring the heat of reaction with water. Kelley [259] gives 8·7 kcal for the heat of vaporization, whence $-\Delta H_f(AsCl_3;\ g) = 62{\cdot}8$ kcal. The N.B.S. [529] take Thomsen's result to apply to the gas, and using this Long [317] has given $E(\mathrm{As-Cl}) = 73$ kcal. In the German edition of Thomsen's book [523], the state of the $AsCl_3$ is not clearly given: it is, however, in the English translation [524].

10.17.34. E(Se – Cl)

E(Se – Cl) may be devised as 58 kcal from the heat of formation of $SeCl_2$, which depends on the dissociation of $SeCl_4$ [38].

10.17.49. E(In – Cl)

E(In – Cl) in $InCl_2$ = 75 kcal (*see* Section 9.17.49).

10.17.50. E(Sn – Cl)

The heat of formation of $SnCl_4$ is well established [38]. We derive E(Sn – Cl) = 76 kcal.

10.17.51. E(Sb – Cl)

E(Sb – Cl) is derived as 74 kcal from $\Delta H_f(SbCl_3)$ [38, 523].

10.17.80. E(Hg – Cl)

E(Hg – Cl) = 54 kcal from $\Delta H_f(HgCl_2)$ [38, 259, 529].

10.17.83. E(Bi – Cl)

E(Bi – Cl) is given from $BiCl_3$ [523] by Long [317] as 67 kcal. The heat of vaporization of bismuth is uncertain.

10.32.32. E(Ge – Ge)

Skinner [452] has given a value for E(Ge – Ge) based on the activation energy for the decomposition of digermane, but this is probably not valid. Pauling [382] puts E(Ge – Ge) equal to half the heat of atomization of the element. Hence E(Ge – Ge) = 45 kcal.

10.32.35. E(Ge – Br)

Evans and Richards [147] have measured the heats of formation of germanium tetrabromide and tetraiodide by measuring the heats of solution of these compounds, and that of germanium dioxide, in aqueous caustic soda. They deduced E(Ge – Br) and E(Ge – I) to be 63·5 and 48·1 kcal respectively, using the N.B.S. [529] value for the heat of atomization of germanium. After correction to the value for the heat of atomization of germanium adopted here, they become 66 and 51 kcal respectively.

10.32.53. E(Ge – I)

E(Ge – I) = 51 kcal (*see* Section 10.32.35 above).

10.33.33. E(As – As)

E(As – As) may be taken as one-sixth of the heat of atomization of As_4 [105, 382, 452]. Thus E(As – As) = 35 kcal, for a bond angle of 60°, using the values given in Section 8.2.2.33. E(As≡As) = 91 kcal from $D(As_2)$ (*see* Section 9.33.33).

10.33.35. E(As – Br)

E(As – Br) in $AsBr_3$ is 58 kcal, although the heat of formation of this compound is not particularly well established [38].

10.33.53. E(As – I)

From AsI_3 [38], E(As – I) = 43 kcal. The heats of formation of $AsBr_3$ and AsI_3 were determined by Berthelot by measurement of the heat of solution in aqueous caustic potash.

10.34.34. E(Se – Se)

Skinner [452] has deduced E(Se – Se) from Se_6(g) to be 41 kcal. On the other hand we may note that E(Se – Se) is equal to the difference between the heats of atomization of Se_2Cl_2 and $SeCl_2$, which is approximately 50 kcal, using our value of the heat of atomization of selenium. The heats of formation are perhaps not very certainly known [38] and we have had to estimate the heat of vaporization of Se_2Cl_2.

E(Se=Se) is $D(Se_2)$ or 65 kcal (*see* Section 9.34.34).

10.35.49. E(In – Br)

E(In – Br) in $InBr_2$ = 63 kcal (*see* Section 9.35.49).

10.35.80. E(Hg – Br)

E(HgBr) = 44 kcal from $HgBr_2$, and E(Hg – Br) = 40 kcal from E(Hg – Cl) and HgClBr (*see* Section 9.35.80).

10.49.53. E(In – I)

E(In – I) in InI_2 = 55 kcal (*see* Section 9.49.53).

10.51.51. E(Sb – Sb)

E(Sb – Sb) may be taken as one-sixth of the heat of atomization of Sb_4. The heat of formation of Sb_4, is, however, very doubtful. The information on the vapour density of antimony has been discussed in this connection by Dainton [105], who concludes that E(Sb – Sb) lies between 27 and 35 kcal, probably closer to the lower value.

E(Sb≡Sb) is 70 kcal, from $D(Sb_2)$ (*see* Section 9.51.51). Dainton [105] prefers 75 ± 10 kcal.

10.52.52. E(Te=Te)

E(Te=Te) = 54 kcal, from Te_2 (*see* Section 9.52.52).

10.53.80. E(Hg – I)

E(Hg – I) from HgI_2 [38] is 35 kcal.

11

OTHER MEASURES OF BOND STRENGTH

11.1. FORCE CONSTANTS

11.1.1. *Definition and Discussion*

IN Section 1.3 three measures of bond strength were suggested, the bond dissociation energy, the bond energy term, and the bond stretching force constant. We now examine the definition and status of the third of these quantities.

The force constant is the constant of proportionality between the force tending to restore the equilibrium configuration of a system and an infinitesimal displacement from that configuration. It has the dimensions of force per unit displacement. The bond stretching force constant is that governing the resistance of a molecule to deformation from the equilibrium configuration by stretching a chemical bond. Together with the atomic masses it determines the frequency of the stretching vibration. This definition assumes that the force is proportional to the displacement, and the potential energy to the square of the displacement; that is, the definition assumes that the system is a harmonic oscillator.

The application of this result to the determination of bond stretching force constants in molecules encounters two difficulties. First, real molecules are not exactly harmonic oscillators. Secondly, although the only mode of vibration possible in diatomic molecules is a bond stretching motion, the vibrations of polyatomic molecules are much more complicated, and cannot be expressed as consisting only of a combination of bond stretching motions. We discuss these two problems in turn in the next two sections.

The discussion will be on a fairly superficial level because although a large number of attempts have been made to correlate force constants with bond energies and dissociation energies, it may be argued that force constants are not concerned with facts of direct chemical interest. The force constant is a measure of the resistance of the bond to small perturbations, and the perturbations involved in chemical reactions are not small. It will only bear a definite relationship to the dissociation energy, for example, if the form of the curve of potential energy against interatomic distance is the same

for all bonds. This is only very approximately true. For example, Linnett[308] has calculated the dissociation energy of 45 states of diatomic molecules on the assumption that they all fit the same form of potential energy curve; the average deviation from the correct value was as large as 20 per cent. On the other hand, it does seem to be true that larger force constants tend to be associated with larger dissociation energies[23]; but the relationship is not exact. It is not the purpose of this book to examine these relationships in detail.

11.1.2. *The Effect of Anharmonicity*

In the following we shall first of all confine ourselves to a qualitative discussion of the effect of anharmonicity in diatomic molecules, where the situation is not complicated by the existence of several modes of vibration.

The vibrational motion in real molecules is quantized. The ground vibrational state has vibrational energy, the zero point energy, due to the uncertainty principle. This energy is sufficiently great for higher terms than the second in the power series for the potential energy to become important. The classical amplitude of vibration for a diatomic molecule in the ground vibrational state is of the order 10^{-9} cm, compared with an interatomic distance of the order 10^{-8} cm. The rapid steepening of the repulsive force with decreasing separation suggests that the nuclei will move together less readily, and move apart more readily, than would be expected for the simple harmonic oscillator. Thus we should expect r_0, the average internuclear distance in the vibrational ground state, to be greater than r_e, the equilibrium internuclear distance. This effect is found, typical values being the following for the molecule carbon monoxide $C^{12}O^{16}$: $r_e = 1{\cdot}1282$, $r_0 = 1{\cdot}1308 \times 10^{-8}$ cm. Similarly, we might expect the true force constant, k_e, referring to classical vibrations of infinitesimal amplitude, to be greater than the value k deduced from the fundamental vibration frequency, which corresponds to the energy of transition from the ground to the first excited vibrational level. For CO we have $k_e = 19{\cdot}02 \times 10^5$ dyne . cm^{-1}, $k = 18{\cdot}55 \times 10^5$ dyne . cm^{-1}. The method of obtaining these quantities is described in detail in Herzberg's book[217]; it essentially consists in the experimental determination of several vibrational levels and expressing the potential energy as a power series. In general, cubic terms are sufficient near the bottom of the potential energy curve.

The same situation exists in polyatomic molecules. The true force constant for classical vibrations of infinitesimal amplitude

is usually higher than the force constant obtained directly from the fundamental vibration frequency, the required correction to the latter being about 3 per cent for most bonds and about 8 per cent for bonds to hydrogen [310].

Since the correction for anharmonicity requires a knowledge of higher vibrational levels, and this knowledge is not normally completely available for polyatomic molecules, the published bond stretching force constants in polyatomic molecules are rarely corrected for anharmonicity. This does not matter very greatly if we are concerned with variation in the force constant for the same type of bond from molecule to molecule, because it is likely that the anharmonicity correction will not vary greatly.

In *Table 11.5.1*, values of force constants for diatomic molecules are given both as k_e and k, so that the magnitude and variation of the anharmonicity effect may be assessed by the reader.

11.1.3. *Bond Force Constants in Polyatomic Molecules*

Difficulty arises when we attempt to specify 'bond force constants' in polyatomic molecules. It was mentioned in Chapter 1 that molecular geometry of itself does not imply the existence of chemical bonds. Now force constants are the measure of the resistance of the molecule to infinitesimal displacements from the equilibrium configuration; that is, to infinitesimal alterations in molecular geometry. And just as molecular geometry does not require the structure of the molecule to be stated in terms of bonds, so the force constants which express its resistance to change do not need to be stated in terms of bonds. Indeed, it is often inconvenient to do so.

In order to discuss the general derivation of bond force constants it will be necessary to go into the treatment of molecular vibrations in a little detail. Full treatments are given by Wu [578] and Herzberg [216], and a review is given by Linnett [310]. Before we do so, however, we may mention one possible simplification which makes it possible to deduce bond stretching force constants for certain bonds fairly reliably without the complex apparatus of a complete vibrational treatment for the molecule. The stretching frequency of bonds to hydrogen such as CH, NH, and OH is so much higher than the other frequencies in many molecules that these bonds can often be treated separately. Thus the variation in the CH stretching force constant from molecule to molecule is fairly well known [309], and the same is true for some OH and NH bonds [416].

For the general treatment of the vibrations of a polyatomic molecule we choose a system of Cartesian displacement coordinates, q_i, with the origin for each nucleus at its equilibrium position.

There are $3n$ such coordinates where n is the number of atoms. To the harmonic oscillator approximation, we may write for the potential energy:

$$2V = \Sigma_{ij} a_{ij} q_i q_j$$

where the summation covers all combinations of the coordinates, including squared terms. Solution of the equations of motion with this potential leads to an expression for the vibration frequencies of the form:

$$\left.\begin{aligned} \lambda^{3n} + \alpha_1 \lambda^{(3n-1)} + \alpha_2 \lambda^{(3n-2)} + \ \ldots \ + \alpha_{n-1}\lambda + \alpha_n = 0 \\ \lambda = 4\pi^2 \nu^2 \end{aligned}\right\}$$

where the α are dependent on the atomic masses and the constants a_{ij} in the potential function. This equation has $3n$ solutions, some of which are zero and correspond to translational and rotational motion of the molecule as a whole. For linear molecules there are $3n-5$ non-zero solutions leading to vibration frequencies; for non-linear molecules there are $3n-6$. In practice, the known vibration frequencies, obtained spectroscopically, are used to obtain information about the force constants.

These a_{ij} in general are not directly related to bond properties. They simply measure the resistance to displacement of each atom in a general way, and the coordinates need not be aligned along bond directions at all. It will be possible of course to deduce from the geometry of the system and the a_{ij} what the resistance to displacement along a bond direction is. However, this treatment may be too general. If individual chemical bonds have properties largely independent of their molecular environment, then the only important forces acting in a molecule will be those along chemical bonds, given by bond stretching force constants, and those resisting the bending of bonds, governed by bond bending force constants. This leads to a very special force field, usually known as the simple valence force field (S.V.F.F.).

On this view we write for the potential

$$2V = \Sigma k_{AB} (\Delta r_{AB})^2 + \Sigma k_a (\Delta \theta_a)^2$$

Here Δr_{AB} is the change in the length of the bond AB. $\Delta\theta_a$ is the change in the bond angle θ_a. k_{AB} is a bond stretching force constant, k_a a bond bending force constant. These valence coordinates are geometrically related to the q_i already mentioned. It will be appreciated that the summations above involve a drastic reduction in the number of terms from those necessary in the complete harmonic oscillator expression.

This represents a considerable simplification, but one which can only be justified by the facts. Linnett[310] gives the example of the tetrahedral molecules methane and carbon tetrachloride. In these molecules, as in several others, there are more vibration frequencies than there are force constants in the S.V.F.F. expression. Thus if the S.V.F.F. is a good representation of the molecular force field, there must be a relation between the observed frequencies independently of the actual values of the force constants. In the molecule CX_4, the relationship is

$$\nu_3\nu_4/\nu_1\nu_2 = \left[\frac{2}{3}\left(1+\frac{4m_x}{m_c}\right)\right]^{\frac{1}{2}}$$

where $\nu_1 \ldots \nu_4$ are the four observed frequencies. For methane the L.H.S. is 0·89 and the R.H.S. 0·94, which is good agreement. For carbon tetrachloride, on the other hand, the L.H.S. is 2·44, whereas the R.H.S. is 2·92, the difference being about 20 per cent. Other tetrahalides are similar to carbon tetrachloride; the discrepancy with S.V.F.F. is most conveniently ascribed to fairly strong interactions between the non-bonded halogen atoms.

Two interesting points may be mentioned in connection with this example. The first is that as far as we can tell from the thermal data alone, it is as legitimate to carry $E(C-Cl)$ values deduced from CCl_4 to other molecules as it is to carry $E(C-H)$ values from CH_4. Thus the range in which the bond energy terms may be assumed constant is not the same as the range of applicability of S.V.F.F. The second point is that although S.V.F.F. is a fairly good approximation for methane, it is not sufficiently good for a detailed discussion of the molecular forces. Nor, it would appear, are valence coordinates necessarily the most convenient for such a discussion. Dennison, for example, uses quite different coordinates in his exact treatment of methane[108].

The essential difference between the S.V.F.F. and the complete harmonic oscillator treatment does not of course lie in the choice of valence coordinates; it lies in the fact that the former represents the potential energy as the sum of a set of squared terms only; that is, no interactions in the form of cross-products are allowed. It is possible to obtain a complete description of the force field to the harmonic oscillator approximation using valence coordinates if all the cross terms of the form $kr_{AB} \cdot r_{AC}$ *etc.* are inserted. (It should be noted here that although the q coordinates run from $q_1 \ldots q_{3n}$, there need only be $3n-6$ valence coordinates. This is because 6 of the solutions of the equations for the frequencies lead to zero values; they represent translation and rotation of the molecule. Thus 6 of

the q's are redundant coordinates, and may by a suitable transformation be eliminated from the vibrational problem.)

In the complete expression there are in general more force constants than there are vibration frequencies. Omission of interaction terms may give an inaccurate picture of the molecular force field, whereas inclusion of all possible interaction terms makes it generally impossible to obtain unique values of all or any of the force constants from vibrational frequencies. This difficulty may be overcome in special cases in two different ways: (*a*) in some molecules the symmetry is such that unambiguous determination of some of the force constants may be obtained from the vibration frequencies, (*b*) it is possible to extend the information available by determining the vibration frequencies of molecules containing isotopes of some or all of the atoms. To a very good approximation isotopic substitution alters the frequencies only by alteration of the masses; that is, by alteration of the kinetic energy, leaving the potential energy unchanged.

There are two general ways in which the difficulty may be met. One is to put in such interaction constants as chemical knowledge suggests may be important. The other is to put in all the force constants in the general potential function using valence coordinates. It is then possible to obtain ranges of permissible solutions from the known vibration frequencies. A particular 'best' set is then chosen on the basis of some parameter such as an accurately known bond length used in conjunction with an accepted relationship between force constants and bond length. The former procedure was the first to be adopted.

Linnett[310] gives a discussion of the use of valence force field with the addition of selected cross terms. One method of reducing the number of constants to be determined from the frequencies is to carry over from molecule to molecule certain force constants for squared terms and even for cross terms. Linnett mentions in this connection the work of Crawford and Brinkley[103], who studied acetylene, ethane, methylacetylene, dimethylacetylene, hydrogen cyanide, methyl cyanide and the methyl halides in this way, and were able, for all the molecules, to account for 84 frequencies with 31 constants. Linnett[307] treated some of these compounds using a different force field. He was able to account satisfactorily for 25 frequencies using 11 force constants. From our point of view the trouble with these results is that Linnett obtained a value for the C – C force constant in these acetylene derivatives which was different from that obtained by Crawford and Brinkley. For C – C in methyl cyanide for example, Linnett obtained

$5{\cdot}3 \times 10^5$ dyne . cm^{-1} whereas Crawford and Brinkley obtained $4{\cdot}94 \times 10^5$. In general the values obtained for bond stretching constants depend on the force field assumed. It is therefore doubtful whether force constants obtained in this way have any clearly defined significance.

The attempt to obtain allowed ranges of force constants, using the complete set of general constants, was suggested by Glockler and Tung[180]. They also suggested a method for obtaining a 'best' set. Neither Linnett[310] nor Simpson[449] considers the method reliable. The practice of obtaining ranges of solutions has become widely adopted[124, 517, 518, 519, 526, 527]. Thomas[519] has worked out a method of obtaining 'best' values of force constants using Gordy's relation[185] between bond order, length, and force constant, in conjunction with reference molecules whose force constants are known explicitly. It is claimed that use of this method leads to strictly comparable sets of force constants and many of the arbitrary features of earlier treatments are removed. Consistent trends in the signs and magnitudes of interaction constants are obtained.

Much work has been devoted to the understanding of these interaction constants on the basis of valence theory. However, since we are concerned with bond properties, while these studies are more related to the wider topic of molecular structure, one or two references only need be given here[100, 208, 311].

There is a considerable variation on the force constants quoted by different authors for the same bond, depending on the force field assumed. Linnett[310], for example, quotes for C – Cl in methyl chloride 3·44, 3·61, 4·42, 3·35, 3·64, and $3{\cdot}37 \times 10^5$ dyne . cm^{-1} stating that the last is probably the best. It is not immediately obvious which type of force field will give the value of the constant most suitable for comparison with other measures of bond strength. The force constant occurring in the general valence force function might appear at first sight to be the best, because it is part of the best representation of the actual molecular force field. But the potential function in which it appears includes cross terms, which represent potential energies not split up into contributions from independent bonds. In the S.V.F.F., the whole potential energy is written as a function of bond properties only, and this may be compared with the assumption behind the bond energy concept—that the energy is the sum of terms attributed to individual bonds.

11.1.4. *Assignment of Observed Frequencies*

In order to deduce the potential function governing vibration, it is necessary to be able to interpret the observed infra-red and Raman

spectrum of the compound concerned in terms of the fundamental frequencies of vibration of the molecule. No simple guide to this process can be given, and the reader is referred to Herzberg[216]. It should be mentioned that an error in the frequency assignment may cause an error in derived force constants.

11.2. IONIZATION POTENTIALS AND BOND ORDER

'Bond order' is usually understood to mean a quantity related to the multiplicity, in the chemist's sense, of a bond, and is usually theoretically derived. For this reason it does not fall within the scope of this book; a review is given by Cottrell and Sutton[99]. However, Walsh[547] has chosen to define bond order as the 'summed total electronic energy per bond'. On this view it should be a direct measure of bond strength.

The ionization potential of the electrons concerned in the bond is considered to be a measure of the bond order thus defined, in a manner which may be illustrated by the following example. Ethylene has two π electrons, the ionization potential for one of which is quoted by Walsh to be 10·45 eV, so that the 'mobile' bond order is proportional to 20·90 eV. Acetylene has four π electrons, each of ionization potential 11·35 eV, giving a mobile order proportional to 45·40 eV. Electrons in hydrocarbons have an ionization potential of 12·0 eV. The total bond order is obtained by adding this to the mobile bond order. The results are scaled to ethylene having a mobile bond order of 1, or total bond order 2. A smooth relation is found when bond length is plotted against bond order. A more or less smooth curve is obtained when order is plotted against a set of bond energies. One interesting result of this approach is that the bond order of *cyclo*hexane is rather less than the bond order in ethane, a conclusion which is also indicated by other evidence[92].

The concept has not, however, been further used, so for the detailed arguments the reader is referred to Walsh's paper.

11.3. POLARITY AND BOND STRENGTH

It has been suggested[548, 549] that *ceteris paribus*, for a given bond, the force constant and energy decrease and the length increases with increasing polarity. Walsh[548, 549] has given a detailed discussion of this principle with particular application to the carbonyl link. The reader is referred to the original papers.

11.4. BOND LENGTH AND BOND STRENGTH

It appears to be broadly true that for a bond between a given pair of atoms, the strength decreases as the length increases. For example $E(C{\equiv}C)$ is much greater than $E(C-C)$, and the triple bond is usually about 80 per cent of the length of the single. Cottrell and Sutton[99] give references to various discussions of this relationship; a recent detailed application to hydrocarbons is due to Glockler[178]. The treatment of correlations of this nature is outside the scope of this book, as is the discussion of methods of determining bond length.

11.5. BOND PROPERTIES

Although this book has been mainly concerned with bond strengths as measured by dissociation energies and bond energy terms, it was considered that its usefulness would be increased by the inclusion of a summary table giving all the known bond dissociation energies (D) and energy terms (E), together with values for the corresponding bond lengths and force constants.

It should be emphasized that whereas the compilation of D and E values is intended to be comprehensive, and (apart from the values for diatomic molecules already discussed by Gaydon[166] and Herzberg[217]) critical, this claim is not made for the values of r and k. Only for bonds for which D or E is known are included values of r and k. This has involved the exclusion of quite a large number of data on the dimensions of simple polyatomic molecules, but it has been necessary to keep the material within the bounds of the plan of the book. In any case, Allen and Sutton[4] give a compilation of those data on molecular dimensions obtained by electron diffraction. The values of D and E are those discussed in Chapters 9 and 10 respectively. Where the uncertainty of the value appears to be appreciably greater than that suggested by the number of significant figures given, the value is marked with a question mark. The point will be found to be discussed in Chapters 9 and 10, or in the references there cited.

Wherever possible, values of r_e the equilibrium internuclear distance, and r_o, the average internuclear distance in the ground state, are both given. For diatomic molecules, unless otherwise specified, they are taken from Herzberg[217]. For polyatomic molecules they are taken from various compilations and the more recently obtained values are taken directly from the literature. Where more than one apparently equally plausible value has been found, all are quoted. In other cases the present author has selected what appears

to be the best value, but the compilation is not critical, and the reader is advised to consult the references cited. The number of significant figures quoted is a rough guide to the expected accuracy of the values, an uncertainty of about 2 in the last figure quoted being usual. Values almost all refer to the gas phase, but one or two results, such as those for dibenzyl and dinitrogen tetroxide, are taken from x-ray work on the solid.

Values for k_e, the force constant for infinitesimal displacements from the equilibrium position, and for k, the force constant calculated from the observed frequencies without correction for anharmonicity, are both given. For diatomic molecules, they are calculated from the molecular data given by Herzberg [217], unless otherwise indicated. The number of figures given are those justified by the number of figures to which the frequencies and masses are known. For polyatomic molecules, some of the values are taken from the compilations of Wu [578] and Herzberg [216], and many from the original literature. In general, they are from molecules treated using some form of modified valence force field. Since the details of interaction constants used differ from author to author, the force constants given are not strictly comparable, and the reader who is interested in small differences is advised to consult the references cited. Where the values were obtained using the unmodified S.V.F.F. for molecules to which it might not be expected to apply, they are marked with an asterisk. Occasionally more than one value is quoted where there is no obvious reason to select one in particular.

Table 11.5.1. Bond Properties

Atomic numbers	*Bond*	D kcal	E kcal	r_e Å	r_0 Å	k_e dyne . cm^{-1} $\times 10^5$	k dyne . cm^{-1} 10^5
1–1	HH	103·24	104·18	0·7417	0·7509	5·733	5·135
1–3	LiH	~58		1·595	1·607	1·026	0·959
1–4	BeH	~53		1·343	1·353	2·263	2·109
1–5	BH	~70		1·233	1·243	3·03	2·80
1–6	CH (*diatomic*)	80	81	1·120	1·130	4·484	4·090
1–6	CH – H	~92					
1–6	CH_2 – H	~87					
1–6	CH_3 – H	101	91·1		1·094 216	5·394 201	5·04 158 4·97 309
1–6	C – H (*general*)		90·5		1·08		
1–6	HC≡C – H	<121		1·060 216 1·064 439a	1·060 216	6·24 578	6·05 309 5·92 158
1–6	H_2C=CH – H	<121?			1·071 164	5·28 578 6·126 104	5·08 309 5·05 158
1–6	H_3C . CH_2 – H	96			1·102 201	5·35 201	4·81 309 4·78 158
1–6	*n*-C_3H_7 – H	100					4·75 158
1–6	*iso*-C_3H_7 – H	94					4·56 158
1–6	*n*-C_4H_9 – H	101					4·75 158
1–6	*tert*-C_4H_9 – H	89					4·56 158
1–6	*neo*-C_5H_{11} – H	95					
1–6	C_6H_5 – H	102			1·08 257		5·10 309
1–6	$C_6H_5CH_2$ – H	77·5					
1–6	*o*-$CH_3.C_6H_4.CH_2$ – H	75					
1–6	*m*-$CH_3.C_6H_4.CH_2$ – H	77					
1–6	*p*-$CH_3.C_6H_4.CH_2$ – H	76					
1–6	$C_6H_5CHCH_3$ – H	75					
1–6	$C_6H_5C(CH_3)_2$ – H	74					

1–6	$CH_3.C_6H_4.CHCH_3-H$	74					
1–6 (7)	H – CN	114		1·066 118	1·059 216	6·292 118	5·7 578
1–6 (7)	α-$C_5H_4N.CH_2-H$	75					
1–6 (7)	β-$C_5H_4N.CH_2-H$	76					
1–6 (7)	γ-$C_5H_4N.CH_2-H$	77					
1–6 (8)	H – CO	<26?					
1–6 (8)	H – CHO	<78?					4·43 309 4·2 578
1–6 (9)	$F.C_6H_4CH_2-H$ (*o*, *m*, *and p*)	78					
1–6 (17)	CCl_3-H	90			1·073 171		4·96 309
1–6 (35)	CH_2Br-H	99					4·95 309
1–7	NH	~85		1·038	1·048	6·0	
1–7	NH_2-H	102	84·3		1·014 216	7·171 128	6·38 416
1–8	OH	103		0·971	0·980	7·791	7·117
1–8	HO – H	116	110·6	0·958 216	0·957 216	8·425 208	7·76 416 7·66 216
1–9	HF	134	135	0·917	0·926	9·655	8·833
1–11	NaH	47		1·887	1·901	0·781	0·730
1–12	MgH	46		1·731	1·743	1·275	1·171
1–13	AlH	67		1·646	1·658	1·620	1·509
1–14	Si – H in SiH_4		~76		1·456 213		2·77 213
1–15	P – H in PH_3		~77		1·418 450 1·419 322 1·424 369		3·2 213 3·24 216
1–16	SH	85		1·34 409	1·35	4·20 409	3·84 409
1–16	H – SH	90?	87 7		1·334 216		4·01 125 4·14* 216 4·03 213
1–17	HCl	102·2	103·1	1·275	1·284	5·157	4·806
1–19	KH	43		2·244	2·255	0·561	0·529
1–20	CaH	⩽39		2·002	2·013	0·977	0·919
1–25	MnH	⩽55?		1·731	1·743		1·295
1–28	NiH	~60		1·475	1·486		2·166

Table 11.5.1. Bond Properties—continued.

Atomic numbers	*Bond*	D kcal	E kcal	r_e Å	r_0 Å	k_e dyne . cm^{-1} $\times 10^5$	k dyne . cm^{-1} $\times 10^5$
1–29	CuH	~62		1·463	1·475	2·200	2·035
1–30	ZnH	19·6		1·595	1·610	1·511	1·311
1–33	As – H *in* AsH_3		~59		1·523 370	2 878 128	2·7 213
1–34	Se – H *in* H_2Se		66?				3·16 213 3·24* 216
1–35	HBr	86·5	87·4	1·414	1·423	4 116	3·840
1–37	RbH	39		2·367	2·381	0·515	0·484
1–38	SrH	38		2·145	2·158	0·854	0·806
1–47	AgH	58		1·617	1 626	1·817	1·686
1–48	CdH	15 6		1·762	1·779	1·204	1·053
1–49	InH	57		1·838	1·851	1·280	1·195
1–50	SnH	<74			1·785		
1–52	Te – H *in* H_2Te		57?				
1–53	HI	70·5	71·4	1·604	1·615	3·141	2·929
1–55	CsH	42		2·494	2·507	0·467	0·441
1–56	BaH	42		2·232	2·243	0·809	0·760
1–79	AuH	72		1·524	1·535	3·138	2·908
1–80	HgH	8·6		1·740	1·766	1·136	0·881
1–81	TlH	46		1·870	1·885	1·142	1·069
1–82	PbH	42?		1·839	1·852	1·445	1·337
1–83	BiH	58		1·809	1·822	1·705	1·581
3–3	LiLi	25		2·672	2·679	0 255	0·248
3–9	LiF	137					
3–17	LiCl	115					
3–35	LiBr	101					
3–53	LiI	81				0·78	0·77
4–8	BeO	124		1 331?	1·335?	7·510?	7·273?
4–8	$Be(OH)_2$	$\bar{D}$ = 109	119				
4–9	BeF	92?		1·361	1·365	5·767	5·602

4–17	BeCl	69?		1·7		3·025	2·952
4–17	ClBe – Cl	147?	109				
4–35	Be – Br *in* $BeBr_2$		89				
4–53	Be – I *in* BeI_2		69				
5–5	B_2	69?		1·589	1·594	3·583	3·457
5–6	B – C *in* BMe_3		66		1·564		
5–7	BN	92?		1·281		8·328	8·060
5–7	B – N *in* $B_3N_3H_3Cl_3$		82		1·41101		
5–8	BO	~185		1·205	1·208	13·65	13·32
5–8	$B-(OR)_3$	$\bar{D}$ = 110	113		1·384		
5–9	BF	195?		1·262	1·270	8·045	7·787
5–9	B – F *in* BF_3		139		1·2914		8·83★216 5·98210 6·86187
5–17	BCl	117?		1·715	1·719	3·473	3·389
5–17	B – Cl *in* BCl_3		94		1·744		4·63★216 3·10210
5–35	BBr	97		1·887	1·891	2·665	2·610
5–35	B – Br *in* BBr_3		74		1·874		2·39210 3·66★216
6–6	C – C *in* C_2	137?		1·312	1·315	9·52	9·25
6–6	C – C (*for general use*)		66·2		1·54		4·5216
6–6	C = C (*for general use*)		112·9		$1\cdot3_5$		9·6216
6–6	C≡C (*for general use*)		150·3		1·21		15·6216
6–6 (1)	HC≡CH	166?	145	1·203216 1·201439a	1·207216	17·2578	15·72216
6–6 (1)	$H_2C=CH_2$	125?	110·0		1·353164	10·896104	9·57216
6–6 (1)	H_3C-CH_3	83			1·543201	4·57201	4·50480
6–6 (1)	$CH_2:CH.CH_2-CH_3$	61·5					
6–6 (1)	$CH_3CH_2-CH_2CH_3$	~78			1·514		
6–6 (1)	$C_6H_5CH_2-CH_3$	63					
	D(CC) *in some other alkyl substituted benzenes is given in* Section 9.6.6 (1)						

Table 11.5.1. Bond Properties—continued.

Atomic numbers	*Bond*	*D* kcal	*E* kcal	r_e Å	r_0 Å	k_e dyne . cm^{-1} × 10^5	*k* dyne . cm^{-1} × 10^5
6–6 (1)	$PhCH_2 - CH_2Ph$	47			1·48[250]		
6–6 (7)	NC – CN	112			1·37[102]		6·75[125]; 5·22*[216]
6–6 (1, 7)	$CH_3 - CN$	103			1·460[261]		5·2[519]; 4·94[578]
6–6 (1, 8)	$CH_2=CO$	~80			1·30[21, 60a]		9·8[520]
6–6 (1, 8)	$CH_3 - CO$	~17					
6–6 (1, 8)	$CH_3 - CHO$	~75			1·50[4]		
6–6 (9)	$F_2C=CF_2$	<112?			1·313[258]		9·2[354]
6–6 (9)	$F_3C - CF_3$	124			1·52[20]		5·45[377]
6–6 (1, 9)	$H_3C - CF_3$	117			1·53[4]		
6–7	CN	129?		1·172	1·175	16·29	15·88
6–7	C – N (*general*)		55·5		1·47		
6–7	C=N (*general*)		~112				
6–7	C≡N (*general*)		160·6				17·7[216]
6–7 (1)	HC≡N	164	155	1·153[118]	1·157[216]	18 583[118]	17·7[103]
6–7 (1)	$CH_3 - NH_2$	80	50 8		1·47[4]		4·86[133]; 4·99[279]
6–7 (1)	$CH_3.N : N - CH_3$	46			1·47[4]		
6–7 (1)	$C_6H_5CH_2 - NH_2$	59					
6–7 (1, 8)	$CH_3 - NO_2$	54?			1·47[4]		4·74[572]
6–8	CO	224 ± 3?		1·128	1·131	19 02	18·55
6–8	O=CO	127	175	1·162	1·163	15 9[578]	15·5[216]
6–8	C – O (*general*)		77·1				
6–8	C=O (*aldehydes*)		159		1·22[4]		
6–8	C=O (*ketones*)		162		1·22[3]		
6–8 (1)	$H_2C=O$		149		1·21[4]		12·1[578]
6–8 (1)	HCO – OH	~90			1·41[4]		6·4[516]
6 8 (1)	$CH_3 - OH$	~90	71·8		1·434[244]		5·77[578]; 4·99[279]

6–8 (1)	CH_3CO-OH	~90			1·43 [4]		
6–8 (1)	C_2H_5-OH	~90	75·4		1·43 [4]		
6–9	CF	~106					
6–9	C – F *in* CF_4		94?		1·36 [4]		9·14* [216] 5·4 [578] 4·32 [209]
6–13	C – Al *in* $AlMe_3$		53				
6–14	C – Si *in carborundum*		64?				
6–14	C – Si *in silicones*		56?				
6–15	CP	138?		1·562	1·565	7·830	7·658
6–16	CS	166?		1·534	1·537	8·488	8·316
6–16	C – S (*general*)		59				
6–16	C = S *in* CS_2		121		1·554 [4]		7·5 [216]
6–16 (1)	CH_3-SH	70			1·82 [4]		
6–16 (1)	C_2H_5-SH	69	59		1·81 [4]		
6–16 (1)	n-C_3H_7-SH	68					
6–16 (1)	*tert*-C_4H_9-SH	65					
6–16 (1)	CH_3-SCH_3	73	59		1·82 [4]		3·05 [279]
6–16 (1)	$C_2H_5-SCH_3$	72					
6–16 (1)	$CH_3-SC_2H_5$	71					
6–16 (1)	$C_2H_5-SC_2H_5$	69	61		1·81 [4]		
6–16 (8)	OC = S		121		1·561 [4]		7·5 [216]
6–17	C – Cl *in* CCl_4		70		1·761 [4]		4·38* [216] 1·86 [211] 1·79 [209]
6–17	C – Cl (*general*)		73		1·76		3·6 [216]
6–17 (1)	CH_3-Cl	~80	70		1·781 [349]		3·64 [103] 3·35 [306]
6–30	C – Zn *in* ZnR_2		~30				
6–34	CSe	115?				6·585	6·464
6–34	C = Se *in* CSe_2		96?				
6–34 (1)	C – Se *in* Et_2Se		50?				
6–35	CBr_3-Br	<50			1·942 [4]		3·36* [216] 1·49 [211] 1·38 [209]

Table 11.5.1. Bond Properties—continued.

Atomic numbers	*Bond*	*D* kcal	*E* kcal	r_e Å	r_0 Å	k_e dyne . cm^{-1} × 10^5	k dyne . cm^{-1} × 10^5
6–35 (1)	C – Br *in* C_2H_5Br (*for general use*)		60				3·1[216]
6–35 (1)	CH_3 – Br	67			1·939[349]		2·84[106]
6–35 (1)	C_2H_2 – Br	11					
6–35 (1)	CH_2 : $CH.CH_2$ – Br	46					
6–35 (1)	C_6H_5 – Br *A list of values of D*(CBr) *in substituted bromobenzenes is given in* Section 9.6.35	71					
6–35 (1)	$C_6H_5.CH_2$ – Br *a list of values of D*(CBr) *in substituted benzyl bromides and other aromatic compounds is given in* Section 9.6.35	51					
6–35 (1, 8)	C_6H_5CO – Br	57					
6–35 (9)	CF_3 – Br	65			1·91[445]		3·035[334]
6–35 (17)	CCl_3 – Br	49					
6–35 (1, 17)	CHCl.CHCl – Br	11?					
6–35 (1, 17)	CHClBr.CHCl – Br	51?					
6–48 (1)	C – Cd *in* $CdMe_2$		24				
6–48 (1)	C – Cd *in* $CdEt_2$		19				
6–50 (1)	C – Sn *in* $SnEt_4$		45		2·18[4] (*from* $SnMe_4$)		
6–53 (1)	CH_3 – I	53	43		2·139[349]		2·247[152a] 2·32[306]
6–53 (1)	C_2H_5 – I	51	44		2·32[4]		
6–53 (1)	CH_2 : $CH.CH_2$ – I	36					
6–53 (1)	C_6H_5 – I	57					

6–53 (1)	$C_6H_5.CH_2-I$ *other values for* $D(CI)$ *are given in* Section 9.6.53	39					
6–80 (1)	CH_3Hg-CH_3	51	19		2·234		
6–80 (1)	$C_2H_5-HgC_2H_5$	41	15				
6–80 (1)	$n\text{-}C_3H_7-HgC_3H_7$		15				
7–7	$N\equiv N$ *in* N_2	170·2	171·1	1·094	1 097	22·96	22·40
7–7 (1)	H_2N-NH_2	60	21		1·474		3·592[79]
7–7 (1, 6)	$N=N$ *in* $C_6H_{14}N_2$		64				
7–7 (8)	O_2N-NO	10					
7–7 (8)	O_2N-NO_2	12·9			1·6459		{1·47[216] 1·56[123]
7–8	NO	122?		1·151	1 154	15·94	15·48
7–8	O–NO	72			1·2079		9·13*[216]
					1·284		
7–8 (1)	H_2N-OH		39?				
7–8 (1, 6)	N–O *in nitrates and nitrites*		44				
7–8 (1, 6)	$N=O$ *in nitrites*		126				
7–8 (1, 6)	CH_3O-NO $D(NO)$ *in other nitrites is given in* Section 9.7.8 (1, 6)	36					
7–8 (1, 6)	CH_3O-NO_2	40					
7–8 (1, 6)	$C_2H_5O-NO_2$	35?	44				
7–9	$N-F$ *in* NF_3		56		1 374		
7–14	SiN	~104		1·572	1·574	7·291	7·126
7–15	$P\equiv N$ *in* PN	~138		1·491	1·494	10·16	9·95
7–16	NS	115?				8·537	8·322
7–17	$N-Cl$ *in* NCl_3		37				
7–17 (8)	Cl–NO	37			1 954		
7–33	$As\equiv N$ *in* AsN	115?				7 926	7·767
7–35	NBr	58?				3·37	3·27
7–35 (8)	Br–NO	28			2·144		
7–51	$Sb\equiv N$ *in* SbN	72?				6·564	6·409
8–8	$O=O$ *in* O_2	117·2	118·3	1·207	1 211	11·765	11·409

Table 11.5.1. Bond Properties—continued.

Atomic numbers	*Bond*	D kcal	E kcal	r_e Å	r_0 Å	k_e dyne . cm^{-1} $\times 10^5$	k dyne . cm^{-1} $\times 10^5$
8–8 (1)	HO – OH	48	35		1·484		3·83[279]
8–8 (1, 6)	$C_2H_5O - OC_2H_5$	32	47				
8–8 (1, 6)	n-$C_3H_7O - OC_3H_7$	35					
8–8 (1, 6)	$Me_3CO - OCMe_3$	37					
8–8 (1, 6)	MeCOO – OCOMe	30					
8–9	O – F *in* F_2O		45·3		1·414		5·57*[216] 4·26[125]
8–12	MgO	120?		1·749	1·753	3·484	3·394
8–13	AlO	138?		1·618	1·621	5·660	5·496
8–14	SiO	165		1·510	1·513	9·247	9·068
8–14	Si – O *in silica*		104				
8–14 (1, 6)	Si – O *in silicones*		117?				
8–15	PO	145?		1·449	1·451	9·409	9·211
8–15	P – O(*bridge*) P_4O_6		80?		1·664		
	P_4O_{10}				1·624		
8–15	P – O(*apical*) *in* P_4O_{10}		156?		1·394		
8–15 (9)	$F_3P=O$	130			1·564		
8–15 (17)	$Cl_3P=O$	122	122		1·584		
8–15 (35)	$Br_3P=O$	119	119		1·41 ± 0·074		
8–16	SO	119?		1·493	1·496	7·929	7·758
8–16	S=O *in* SO_2		128		1·434	10·17[126]	9·97*[216]
8–16	S=O *in* SO_3		113		1·434		10·77*[216] 9·2[210]
8–17	ClO	63				4·0	
8–17	O – Cl *in* ClO_2	57	60		1·484[88]	7·4[127]	
8–17	O–Cl *in* OCl_2		49?		1·684		4·93*[216]
8–17 (1)	HO – Cl	60	52				
8–20	CaO	116?				2·84?	2·72?
8–21	ScO	138?				6·559	6·453
8–22	TiO	160		1·620	1·622	7·184	7·053

8–23	VO	127?		1·890	1·893	7·353	7·212
8–24	CrO	97?				5·821	5·652
8–25	MnO	92?				5·157	5·038
8–26	FeO	92?				5·67	5·54
8–28	NiO	<99					
8–29	CuO	113					
8–30	ZnO	<92					
8–31	GaO	58?				4·516	4·368
8–32	GeO	150?		1·651	1·653	7·525	7·395
8–33	AsO	113				7·266	7·107
8–33	As – O *in* A_4O_6 (*bridge*)		72		1·794		
8–33	As – O(*apical*) *in* As_4O_{10}		~93				
8–34	SeO	81?				6 44	6·31
8–35	BrO	50?				3·99	3·83
8–35	O – BrO	70?	>60				
8–35 (1)	HO – Br	56	48				
8–38	SrO	110		1·921	1·924	3·40?	3·32?
8–39	YO	160?				5·803	5·736
8–40	ZrO	150?		1·416?		7·02?	6·91?
8–41	NbO, (CbO)	92?					
8–47	AgO	32?				1·996	1·930
8–48	CdO	<88					
8–49	InO	25				4·088?	4 002?
8–50	SnO	132		1·838	1·843	5·615	5·514
8–51	SbO	74?				5·561	5·418
8–51	SbO (*bridge*)		71				
8–51	SbO (*apical*)		95				
8–52	TeO	63?				5·304	5·211
8–53	IO	44					
8–53 (1)	HO – I	56	48				
8–56	BaO	129		1·940	1·942	3·786	3·740
8–57	LaO	162?				5·565	5·504
8–58	CeO	150?				6·327?	6·240?
8–64	GdO	139?				6·047?	5·941?
8–71	LuO	100?				6·115?	5·997?

Table 11.5.1. Bond Properties—continued.

Atomic numbers	*Bond*	D kcal	E kcal	r_e Å	r_0 Å	k_e dyne . cm^{-1} × 10^5	k dyne . cm^{-1} × 10^5
8–75	TaO	115?					
8–76	Os = O *in* OsO_4		123		1·664		
8–82	PbO	94?		1·922	1 934	4·557	4·464
8–83	BiO	92?				4·314	4·187
9–9	F_2	36	37		1·435		4·45
9–11	NaF	107					
9–12	MgF	74?			1 75	3·216	3·147
9–13	AlF	147				4·356	4·185
9–14	SiF	88?			1 603	4·891	4·785
9–14	Si – F *in* SiF_4		131		1 544		7·16★[216]; 5·7[209]; 4·5–7·2[537]
9–16	S – F *in* SF_6		73		1·584		3·55[212]
9–17	FCl	60 5		1·628	1·631	4·56	4·34
9–19	KF	118			2 55	1·24[17]	
9–20	CaF	<73			2 02	2·614	2·566
9–25	MnF	81?				3·184	3·122
9–29	CuF	70		1·743	1·748	3·332	3·249
9–31	GaF	<142					
9–32	GeF	92?				3 92	3·86
9–33	As – F *in* AsF_3		111		1·712		3·92[216]
9–34	Se – F *in* SeF_6		68				4·3[212]
9–35	BrF	50·6		1·756	1·762	4·07	4·00
9–37	RbF	119				1·39[17]	
9–38	SrF	62?				2·300	2·260
9–41	InF	<125					
9–50	SnF	76?				3·278	3·217
9–51	SbF	92?				3·652	3·586
9–52	Te – F *in* TeF_6		80				
9–53	IF	46?				3 64[129]	

9–53	I – F *in* IF_5		63		2·57[4]		
9–55	CsF	121		2·34	2·35	1·45[17]	
9–56	BaF	69?				2·162	2·128
9–75	Re – F *in* ReF_6		?				
9–77	Ir – F *in* IrF_6		67?				
9–80	HgF	32?				2·462?	2·382?
9–80	F – HgF	100	66				
9–81	TlF	109				2·310	2·274
9–82	PbF	74				2·637	2·589
9–83	BiF	74				2·675	2·634
9–92	U – F *in* UF_6		124		1·78, 1·99, 2·17, 1·86, 2·16[4]		
11–11	Na_2	17·3		3·078	3·082	0·172	0·169
11–17	NaCl	98			2·51	1·19	1·17
11–19	NaK	14·3				0·130	0·128
11–35	NaBr	88			2·64	1·04	1·03
11–37	NaRb	13·1				0·121	0·119
11–53	NaI	71			2·90	0·94	0·93
12–16	MgS	?				2·247	2·197
12–17	MgCl	62?				1·815	1·783
12–17	Cl – MgCl	136?	99?				
12–35	MgBr	57?				1·514	1·492
13–17	AlCl	118		$2·13_8$	$2·14_2$	2·078	2·044
13–35	AlBr	99		2·295	2·296	1·692	1·669
13–53	AlI	90				1·310	1·293
14–14	Si – Si *in* silicon		45				
14–14	$H_3Si – SiH_3$	51[3]			2·32[4]		
14–16	SiS	148[3]		1·929	1·931	4·937	4·870
14–16	Si – S *in* SiS_2		70?				
14–17	SiCl	76?				2·624	2·581
14–17	Si – Cl *in* $SiCl_4$		87		2·02[4]		3·75★[216] 2·55[209] 2·58[211]
14–34	SiSe	134				4·093	4·043

Table 11.5.1. Bond Properties—continued.

Atomic numbers	*Bond*	*D* kcal	*E* kcal	r_e Å	r_0 Å	k_e dyne . cm^{-1} × 10^5	k dyne . cm^{-1} × 10^5
14–35	SiBr	69?				2·214	2·183
14–35	Si – Br *in* $SiBr_4$		70		2·15[4]		2·92*[216] 2·01[209] 2·03[211]
14–52	SiTe	122				3·130	3·096
14–53	Si – I *in* SiI_4		52		2·43[4]		
15–15	P≡P *in* P_2	116·0	116·7	1·894	1·896	5·556	5·477
15–15	P – P *in* P_4		48		2·21[4]		2·00[455b]
15–17	P – Cl *in* PCl_3		78		2·043[265]		2·12*[216]
15–35	P – Br *in* PBr_3		63		2·20[4]		1·63*[216]
15–53	P – I *in* PI_3		44		2·47[4]		
16–16	S_2	102		1·889	1·892	4·959	4·881
16–16	S – S *in* S_8		64		2·08[4]		
16–16 (1)	HS – SH	72?	67?		2·05[4]		
16–16 (1, 6)	MeS – SMe	73	67				
16–16 (1, 6)	MeS – SEt	72					
16–16 (1, 6)	EtS – SEt	70	70				
16–17	S – Cl *in* S_2Cl_2		65		1·99[4]		
16–20	CaS	~115					
16–30	ZnS	98					
16–32	GeS	131				4·359	4·304
16–35	S – Br *in* S_2Br_2		56?				
16–38	SrS	53?					
16–48	CdS	90					
16–50	SnS	110?		2·06		3·536	3·498
16–56	BaS	53					
16–80	HgS	65					
16–82	PbS	75?		2·395	2·399	2·992	2·959
17–17	Cl_2	57·07	57·87	1·988	2·002	3·286	3·194
17–19	KCl	101			2·79	1·02[17] 0·86[217]	0·85[217]

17–20	CaCl	<64		$1{\cdot}8_6$?		1·504	1·483
17–20	Cl – CaCl	176?					
17–22	TiCl	25?					
17–22	Ti – Cl *in* $TiCl_4$		102		2·20[4]		3·11*[216] 2·46[209]
17–24	CrCl	?					
17–25	MnCl	69?				1·865	1·838
17–26	FeCl	69?					
17–28	NiCl	115?				2·288?	2·265?
17–29	CuCl	88				2·301	2·267
17–30	ZnCl	48?				2·046	2·014
17–30	Cl – ZnCl	96?					
17–31	GaCl	115				1·821	1·799
17–32	GeCl	81?				2·323	2·292
17–32	Ge – Cl *in* $GeCl_4$		81		2·08[4]		3·27*[216] 2·40[209] 2·44[211]
17–33	As – Cl *in* $AsCl_3$		70		2·161[265]		2·03[216]
17–34	Se – Cl *in* $SeCl_2$		58				
17–35	BrCl	52·1					2·67
17–37	RbCl	102			2·89	1·08[17]	
17–38	SrCl	58?				1·345	1·329
17–47	AgCl	72				1·832	1·807
17–48	CdCl	46?				1·716	1·691
17–48	Cl – CdCl	84?			2·23[4]		
17–49	InCl	104		2·32	2·32	1·591	1·571
17–49	Cl – InCl	46	75				
17–50	SnCl	74?				1·977	1·954
17–50	Sn – Cl *in* $SnCl_4$		76		2·30[4]		2·80*[216] 2·30[211]
17–51	SbCl	85?				2·179	2·157
17–51	Sb – Cl *in* $SbCl_3$		74		2·37[4]		1·78[216]
17–53	ICl	49·63		2·321	2·324	2·383	2·347
17–55	CsCl	101			2·88[328] 3·06[4]	0·95[17]	0·94[17]
17–56	BaCl	51?				1·282	1·265

Table 11.5.1. Bond Properties—continued.

Atomic numbers	*Bond*	*D* kcal	*E* kcal	r_e Å	r_0 Å	k_e dyne . cm^{-1} × 10^5	k dyne . cm^{-1} × 10^5
17–70	YbCl	23?					
17–79	AuCl	65?				2·563	2·528
17–80	HgCl	23			2·23	1·502	1·469
17–80	Cl – HgCl	81	54		2·30 [4]		2·66 [311]
17–80 (35)	Cl – HgBr	77					2·79 [558] / 2·13 [125]
17–80 (53)	Cl – HgI	75					2·9 [558]
17–81	TlCl	87			2·55	1·453	1·429
17–82	PbCl	71				1·626	1·608
17–83	BiCl	67				1·674	1·653
17–83	Bi – Cl *in* $BiCl_3$		67		2·48 [4]		1·19 [216]
19–19	K_2	11 8		3 923	3·927	0·098	0·097
19–35	KBr	91			2·94	0·83 [17]	0·82 [17]
19–53	KI	77			3·23	0·70 [17] / 0·79 [217]	0·69 [17] / 0·78 [217]
20–35	CaBr	67?				1·27	1·26
20–53	CaI	58?				1·05	1·04
25–35	MnBr	58?				1·609	1·590
25–53	MnI	28?					
29–35	CuBr	78				2·035	2·012
29–53	CuI	?				1·738	1·719
30–30	Zn_2	6?					
30–34	ZnTe	49					
30–53	ZnI	41?				1·250?	1·233?
30–53	I – ZnI	53?			2·42 [4]		
31–35	GaBr	81?				1 516	1·498
31–53	GaI	67?				1·232	1·221
32–32	Ge – Ge *in germanium*		45				
32–32	$H_3Ge – GeH_3$	34?			2·41 [4]		
32–34	GeSe	115				3·743	3·699
32–35	GeBr	60?				1·971	1·917

32–35	Ge – Br *in* $GeBr_4$		66		2·324		1·95211 1·90209 2·58*216
32–52	GeTe	94?				2·902	2·867
32–53	Ge – I *in* GeI_4		51		2·484		
33–33	As≡As *in* As_2	91				4·069	4·026
33–33	As – As *in* As_4		35		2·444		
33–35	As – Br *in* $AsBr_3$		58		2·334		
33–53	As – I *in* AsI_3		43		2·5414		
34–34	Se=Se *in* Se_2	65		2·16	2·18	3 612?	3·574?
34–34	Se – Se *in* Se_6		41		2·324		
34–34 (17)	Se – Se *in* Se_2Cl_2		50?				
34–48	CdSe	<74					
34–50	SnSe	105				3 064	3·036
34–80	HgSe	?					
34–82	PbSe	109?				2·595	2·576
35–35	Br_2	45·46	46·08	2 284	2·286	2·458	2·425
35–37	RbBr	90			3·064	0 80117	0·7917
35–38	SrBr	65?				1 146	1·135
35–47	AgBr	69				1·678	1·659
35–48	CdBr	35?				1 455?	1·443?
35–48	Br – CdBr	76?			2·394		
35–49	InBr	85?			2·57	1 366	1·350
35–49	Br – InBr	42?	63				
35–50	SnBr	46?				1 726	1·709
35–53	IBr	41·90				2·064	2·040
35–55	CsBr	91			3·14	0·86117 1·10217	0·8517 1·06?217
35–56	BaBr	65?				1·108	1·099
35–80	HgBr	17?				1 180	1·155
35–80	Br – HgBr	72	44		2·434		2·37311 2·47558
35–80 (17)	Br – HgCl	70	40				1·90125
35–80 (53)	Br – HgI	68					1·78125
35–81	TlBr	74			2 684	1·260	1·250
35–82	PbBr	58?				1 449	1·435

Table 11.5.1. Bond Properties—continued.

Atomic numbers	*Bond*	D kcal	E kcal	r_e Å	r_0 Å	k_e dyne . cm^{-1} × 10^5	k dyne . cm^{-1} × 10^5
35–83	BiBr	63·2				1·479	1·465
37–37	Rb_2	10·8				0·082	0·076
37–53	RbI	77			3·26	0·66	
38–53	SrI	46?				0·923	0·914
47–53	AgI	60?				1·453	1·441
48–48	Cd_2	2·1					
48–53	CdI	32?				1·119	1·103
48–53	I – CdI	50?			2·58[4]		
49–53	InI	65?			2·86	1 114	1·104
49–53	I – InI	46?	55				
50–52	SnTe	97?				2·439	2·420
51–51	Sb≡Sb *in* Sb_2	69?				2·611	2·588
51–51	Sb – Sb *in* Sb_4		29?				
51–83	SbBi	69?				2·193	2·171
52–52	Te_2	53?			2·59[4]	2·37	2·35
52–82	PbTe	81?				2·086	2·081
53–53	I_2	35·55	36·06	2·666	2·668	1·721	1·701
53–55	CsI	75			3·41	{0·55[17] 0·77[217]}	{0·55[17] 0·75[217]}
53–80	HgI	7?				0·722	0·697
53–80	I – HgI	60	35		2·60[4]		1·82[311, 558]
53–80 (17)	I – HgCl	63					2·1[558]
53–80 (35)	I – HgBr	64					1·51[125]
53–81	TlI	60			2·87[4]		
53–82	PbI	46?				1·194	1·187
53–83	BiI	58?				1·249	1·240
55–55	Cs_2	10·4				0·069	0·068
80–80	Hg_2	3·2					
80–81	HgTl	0·7				0·043	0·038
82–82	Pb_2	14?				0·401	0·383
83–83	Bi_2	39·2				1·836	1·822

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