UNIVERSAL
LIBRARY

OU_160245

UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No. 541.378 S46M Accession No. 28221

Author Selwood, P.W.

Title Magnetochemistry

This book should be returned on or before the date last marked below.

MAGNETOCHEMISTRY

MAGNETOCHEMISTRY

by PIERCE W. SELWOOD

Associate Professor of Chemistry

Northwestern University, Evanston, Illinois

INTERSCIENCE PUBLISHERS, INC., NEW YORK

1943

Copyright, 1943, by
INTERSCIENCE PUBLISHERS, INC.
215 Fourth Avenue, New York, N. Y.

Printed in the United States of America
by the Lancaster Press, Lancaster, Pa.

PREFACE

People who write books in wartime should have compelling reasons for doing so. This book was started before the full impact of the war effort reached the shores of Lake Michigan. It was finished in the hope that it might contribute, however infinitesimally, to the labors of that army of scientists who seek through nature's secrets to parry the blows of an ingenious and pitiless enemy.

Magnetochemistry began with Michael Faraday more than one hundred years ago. It enjoyed a vigorous growth under the guidance of Pierre Curie and A. Pascal at the end of the 19th and beginning of the 20th centuries, but it did not reach its prime until Gilbert N. Lewis pointed out the relationship between atomic magnetic moment and chemical valence. The past few years have seen magnetic susceptibility take its place along with dielectric constant, electron diffraction, x-ray diffraction, and molecular and atomic spectra, as one of the most powerful tools at the disposal of the chemist.

In order to keep the book within reasonable bounds, it has been necessary to define magnetochemistry rather severely. The following definition has been adopted: *Magnetochemistry is the application of magnetic susceptibilities and of closely related quantities to the solution of chemical problems.* No more than mention will be found of several important branches of magnetism, particularly of magnetoöptical phenomena, of the gyromagnetic effect, and of adiabatic demagnetization. The field of atomic magnetism has been slighted, so far as the theoretical side is concerned, and little has been said of technologically important magnetic properties of the ferrous alloys. But these are topics which have received more than adequate treatment elsewhere.

On the other hand, I have tried to omit no major branch of magnetochemistry, so defined. It is especially hoped that no important application of magnetism to structural chemistry has been overlooked.

The literature up to about 1934 has been covered in the excellent works of Van Vleck, Stoner, Klemm, and others. I have, therefore, omitted extensive reference to original publications before that date. But from 1934 to the end of 1942 over one thousand papers on magnetochemistry have appeared. A few very recent papers may have been overlooked because of the difficulty in obtaining some periodicals during the war, but in

some miraculous fashion the editor of Chemical Abstracts continues to receive abstracts of journals published in occupied and enemy countries.

Reference has only occasionally been made to papers reporting magnetic susceptibility measurements for their own sake, and no effort has been made to include tables of susceptibilities. Such data will be found in the International Critical Tables and in the forthcoming Annual Tables of Physical Constants and Numerical Data to be published under the auspices of the National Research Council.

I gratefully acknowledge the granting of permission by the American Chemical Society, the American Physical Society, the American Institute of Physics, the American Society for Metals, the American Institute of Mining and Metallurgical Engineers, the Williams and Wilkins Company, and the Editors of the Journal of Physical Chemistry and the Journal of Chemical Education for permission to reproduce diagrams from their respective publications. I am also indebted to the Fisher Scientific Company, and to Mr. S. E. Q. Ashley and the General Electric Company for information and diagrams. To Professor J. H. Van Vleck I am grateful for permission to reproduce diagrams from his works. It is a special pleasure to acknowledge the indispensable aid received from my wife, Alice Taylor Selwood, who, though marvelling that anyone could write such a dull book, has nevertheless twice read every word of it.

EVANSTON, ILLINOIS
October 1943

PIERCE W. SELWOOD

CONTENTS

CHAPTER		PAGE
Preface		v
I.	**Measurement of Magnetic Susceptibility**	1
	1. Explanation and Definition of Terms	1
	2. The Gouy Method	2
	3. The Quincke Method	6
	4. The Faraday Method	8
	5. The Curie-Chéneveau Balance	10
	6. The Rankine Balance	11
	7. Other Special Methods	12
	8. Measurement of Magnetic Anisotropy	15
	9. Measurement of Related Magnetic Quantities	17
	10. Measurements at Extremely Low Temperatures and at High Frequencies	21
	11. The *Ortho-Para* Hydrogen Method	24
	12. Production and Control of Large Magnetic Fields	25
	13. Calibration and Treatment of Data	28
II.	**Atomic Diamagnetism**	31
	1. Classical Theory of Diamagnetism	31
	2. Modern Theory of Diamagnetism	32
	3. Diamagnetism of Atoms	33
	4. Diamagnetism of Ions	34
	5. Diamagnetic Ionic Crystals	38
	6. Magnetic Anisotropy of Diamagnetic Ionic Crystals	40
	7. Diamagnetism of Atomic Crystals	42
III.	**Molecular Diamagnetism**	43
	1. Molecular Hydrogen	43
	2. Polynuclear Molecules	44
	3. Water	45
	4. Temperature Dependence of Molecular Diamagnetism	47
	5. Different Physical States	48
	6. Pascal's Constants	51
	7. Diamagnetism of Molecular Mixtures	55
	8. Magnetic Studies of Polymerization	58
	9. Miscellaneous Structural Problems	62
	10. Diamagnetic Anisotropy of Molecular Crystals	66
	11. Liquid Crystals	71
IV.	**Atomic Paramagnetism**	73
	1. Theories of Atomic Paramagnetism	73
	2. Monatomic Paramagnetic Gases	76
	3. The Stern-Gerlach Experiment	76
	4. The Rare Earths	78
	5. The "Molecular Field"	85

CHAPTER	*Chapter IV, contd*	PAGE
	6. Paramagnetic Anisotropy of Rare Earth Compounds	89
	7. Saturation, Relaxation, and Other Phenomena	92
	8. Non-Trivalent Rare Earths	94
	9. Transition Group Elements and Their Ions	97
	10. Copper, Silver, and Gold	100
	11. Titanium, Zirconium, Hafnium, and Thorium	103
	12. Vanadium, Columbium, Tantalum, and Protoactinium	103
	13. Chromium, Molybdenum, Tungsten, and Uranium	104
	14. Manganese and Rhenium	107
	15. Iron	109
	16. Cobalt and Nickel	112
	17. The Palladium and Platinum Groups	114
	18. Nuclear Magnetism	115
V.	**Molecular Paramagnetism**	116
	1. "Odd" Molecules	116
	2. Oxygen and Ozone	117
	3. Sulfur	120
	4. Oxides of Nitrogen and Their Derivatives	120
	5. Oxides of Chlorine	123
	6. Alkali Metal Polyoxides and Related Compounds	123
	7. Hexaarylethanes	124
	8. Organo-Metallic Free Radicals	128
	9. Hydrazyls	129
	10. Semiquinones and Related Compounds	129
	11. Metal Ketyls	133
	12. Highly Conjugated Systems, Biradicals	134
	13. Miscellaneous Structural Problems	138
VI.	**Complex Compounds**	142
	1. Introduction to Complex Compound Formation	142
	2. Complexes of Chromium and Related Elements	145
	3. Manganese and Rhenium	151
	4. Iron	154
	5. Cobalt	172
	6. Nickel	176
	7. Copper and Related Elements	181
	8. The Palladium and Platinum Groups	183
VII.	**Metallic Dia- and Paramagnetism**	185
	1. Introduction to Metallic Magnetism	185
	2. Alkali Metals	187
	3. Copper, Silver, and Gold	189
	4. Alkaline Earth Metals	191
	5. Zinc, Cadmium, and Mercury	192
	6. Group III Metals	193
	7. Graphite and Group IV Metals	196
	8. Group V Metals	200
	9. Chromium and Other Group VI Metals	202
	10. Manganese and Rhenium	203
	11. The Platinum Group Metals	204

Chapter		Page
VIII.	**Ferromagnetism** .	206
	1. Introduction to Ferromagnetism	206
	2. Iron . .	210
	3. Ferrous Alloys	212
	4. Nickel	215
	5. Nickel Alloys	216
	6. Cobalt and Cobalt Alloys	220
	7. Oxides and Hydroxides of Iron	220
	8. Other Ferromagnetic Compounds of Iron	226
	9. Non-Ferrous Ferromagnetic Substances	228
IX.	**Applied Magnetometric Analysis**. .	231
	1. Magnetometric Analysis of the Rare Earths	231
	2. Detection of Ferromagnetic Impurities	233
	3. Instruments Used in Metallurgical and Mineralogical Control	234
	4. Structure of Alloys	241
	5. Phase Ratios and Stoichiometry	245
	6. Magnetism and Catalysis	251
	7. Magnetism and Adsorption	260
	8. Miscellaneous Measurements	262
Author Index		267
Subject Index		277

CHAPTER ONE

MEASUREMENT OF MAGNETIC SUSCEPTIBILITY

1. Explanation and Definition of Terms

The intensity of a magnetic field is expressed in "oersteds," although the word "gauss" is often used in the same sense. A field of one oersted (or one gauss) is of such intensity that a unit magnetic pole placed in it is acted on by a force of one dyne.

If a substance is placed in a magnetic field of a certain intensity, then the intensity of the field within the substance may be either smaller or larger than the intensity in the surrounding space. (Fig. 1.) In the

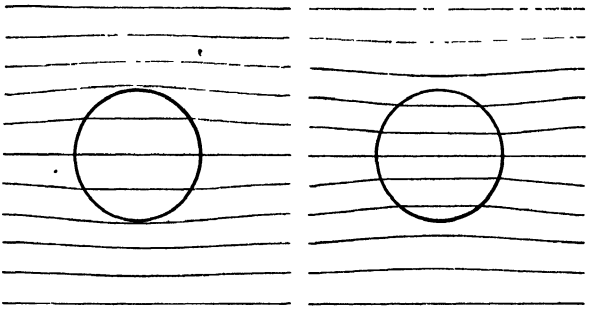


FIG. 1.—Diamagnetic bodies (*left*) are less permeable than a vacuum to magnetic lines of force. Paramagnetic bodies are more permeable than a vacuum.

first case the substance is called "diamagnetic," in the second "paramagnetic." There is also the case of "ferromagnetism" in which the intensity of field within the substance may be increased a million-fold or more. But ferromagnetism, although of great technological importance, is rare in nature. It occurs in only a few metals, alloys, and compounds. Paramagnetism is common in nature, especially among the transition group elements. Diamagnetism is a universal property of matter. All substances, even though paramagnetic, have at least an underlying diamagnetism that must be corrected for in precise determination of the per-

manent magnetic moment. A substance may be both diamagnetic and paramagnetic, but generally whenever paramagnetism is present it is so much larger that it hides the diamagnetism.

If a substance is placed in a field of intensity H, then the intensity within the substance is given by B, where

$$B = H + 4\pi\mathcal{J}$$

The quantity $\mathcal{J}$ is called the intensity of magnetization, and $\mathcal{J}/H = \kappa$ is the magnetic susceptibility per unit volume. The magnetic susceptibility per unit mass is obtained by dividing κ by the density. The symbol χ will be used throughout this book for the magnetic susceptibility per gram. The molar susceptibility, χ_M, is the magnetic susceptibility per gram-molecular weight.

In general the susceptibility of diamagnetic substances is independent of temperature and of field strength. The susceptibility of paramagnetic substances is often inversely proportional to the absolute temperature, and is independent of field strength. The susceptibility of ferromagnetic substances is dependent on both temperature and field strength in a rather complicated way.

There are many methods available for the measurement of magnetic susceptibility. The more important of these methods are described in detail in the following pages. Literature references are given to a number of other methods. A few highly specialized methods are described later. The given general references may be useful.[1–4]

2. The Gouy Method[5a]

If a cylindrical sample of matter is suspended between the poles of a magnet so that one end of the sample is in a region of large field intensity and the other end in a region of smaller field, then the sample will experience a force along its length. The magnitude of this force, f, is given by the expression

$$f = \tfrac{1}{2}(\kappa_1 - \kappa_2)(H_1^2 - H_2^2)A$$

where κ_1, κ_2 are the volume susceptibilities of sample and surrounding atmosphere respectively; H_1, H_2 are the maximum and minimum fields

[1] E. C. Stoner, *Magnetism and Matter*. Methuen and Company, Ltd., London 1934.

[2] S. S. Bhatnagar and K. N. Mathur, *Physical Principles and Applications of Magnetochemistry*. MacMillan and Company, Ltd., London 1935.

[3] W. Klemm, *Magnetochemie*. Akademische Verlagsgesellschaft, Leipzig 1936

[4] L. W. McKeehan, *The Measurement of Magnetic Quantities, J. Optical Soc. Am.*, 19, 213 (1929) Also B. Cabrera, *Dia- and Paramagnetism and the Structure of Matter*. Hermann, Paris 1937.

[5a] L. G. Gouy, *Compt. rend.*, 109, 935 (1889).

to which the sample is subjected; and A is the cross-sectional area of the sample.[5b] The arrangement is shown diagrammatically in Fig. 2. In practice H_2 may be made negligible, and, by using hydrogen or nitrogen for the surrounding atmosphere, κ_2 may also be made negligible. It is convenient to measure f by suspending the sample from a balance, in which case we may have

$$= \tfrac{1}{2}\kappa_1 H_1^2 A = g\Delta w$$

where g is the gravitational constant, and Δw the apparent change in weight of the sample on application of the magnetic field.

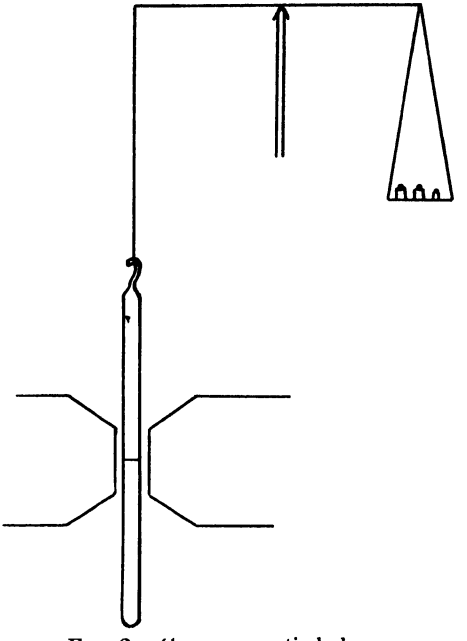


FIG. 2.—Gouy magnetic balance.

For many types of investigations it is convenient to use a magnetic field of from 5000 to 15,000 oersteds. For strongly paramagnetic samples Δw may then be of the order of several tenths of a gram. An ordinary analytical balance therefore gives a sufficient degree of accuracy for some purposes. But for more refined measurements, especially on solutions, it is necessary to use a microbalance.

Other methods are available for obtaining f. For instance the sample may be suspended from a spring, the extension of which, on application

[5b] Derivations of this and other formulas found in this section are given by Stoner (*op. cit.*[1]).

of the field, may be observed with a microscope, or interferometrically. Or the sample may be suspended horizontally from a torsion, or bifilar, suspension. The horizontal suspension methods lack nothing in sensitivity, but they become cumbersome when high or low temperature ranges are necessary.

Measurements on metals or alloys are very simple by the Gouy method. The sample has only to be cast or machined into the desired cylindrical shape. The accuracy of the magnetic measurement will generally be limited by the reproducibility of the sample. The Gouy method gives, of course, the volume susceptibility so that an independent determination of the density is necessary for calculation of the mass susceptibility.

Powdered samples may be measured by packing them into cylindrical glass sample tubes. Correction must be made for the susceptibility of the glass, which is generally diamagnetic with a slight temperature coefficient. The accuracy of measurements on powdered samples is severely limited by the uniformity and reproducibility of packing. It is difficult to exceed an accuracy of $\pm$ 1%. Theoretically there is no particular reason why the accuracy with powders should not be considerably greater.[6]

The susceptibility of pure liquids is also conveniently measured in glass sample tubes. As the difficulty of packing does not arise with liquids, the accuracy may be considerably greater.

Much magnetochemical research is done on solutions. Very accurate semi-differential methods are available for solutions. The glass sample tube may be double-ended, extending below the magnetic field just as far as above. The two ends are separated by a glass partition, in the region of which the magnetic field is applied. The solution under investigation is placed in one end of the sample tube, while the pure solvent is placed in the other. The arrangement is shown in Fig. 3. This sample

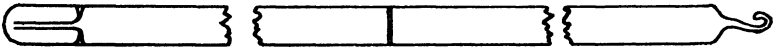


FIG. 3.—Sample tube used in the Gouy magnetic balance.

tube must be supplied with a reservoir for change in volume of the solvent in the lower compartment with temperature. Otherwise the tube would break whenever the temperature was raised, or, when the temperature was lowered a bubble of vapor would form at the partition. In the tube shown, solvent completely fills the lower half of the main tube, and half fills the reservoir. Then, as the solvent warms up, it expands through a

[6] B. Bleaney and R. A. Hull, *Proc. Roy. Soc. London*, **A178**, 86 (1941).

capillary tube into the reservoir, or if the solvent contracts, it sucks up more solvent from the reservoir without forming a bubble at the partition. For the most accurate measurements, it is necessary to use sample tubes of constant internal diameter. With all refinements, measurements to four significant figures are possible.

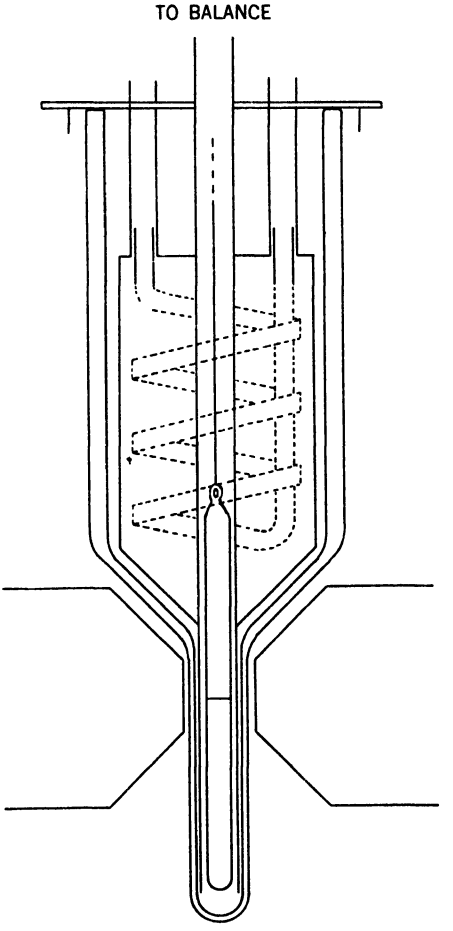


FIG. 4.—Temperature control arrangements for the Gouy balance. Thermocouples, heating coil, and other subsidiary equipment are not shown.

The Gouy method is not well adapted to the investigation of gases although rough measurements on oxygen and on other paramagnetic gases and vapors have been made.

Most magnetic measurements require a range of temperature and often a very accurate control of the temperature. During measurements

on solutions, using a microbalance, it is often necessary to control the temperature to within 0.1° C. This is not because of any very large temperature dependence of magnetic susceptibility but because the buoyancy effect of the surrounding atmosphere is markedly dependent on the temperature.

High temperatures are easily obtained by surrounding the sample tube with a tubular electric furnace. The only precautions necessary are to protect the balance from warm currents of air, and the magnet pole-pieces from extremes of temperature. Actual measurement of the temperature may be done with a thermocouple, or in some cases, the buoyancy effect of the surrounding atmosphere may be calibrated in terms of temperature.

Low temperatures may be achieved by surrounding the sample tube with a Dewar flask of appropriate design to go between the pole-pieces. Various low boiling liquids may be used as refrigerants. The author prefers to use a large lead block suspended by plastic tubes inside the Dewar flask. This block has a central cylindrical opening in which the sample hangs. It is also supplied with a spiral opening into which liquid air may be injected. A small heating coil is available as required. The apparatus is shown diagrammatically in Fig. 4. Temperatures are measured by a multi-junction thermocouple. This apparatus has proved very satisfactory for the temperature range − 190° to + 100° C.

A simple form of Gouy balance has recently been described by Wartman.[7]

3. The Quincke Method [8]

This method is similar in principle to the Gouy method except that the force on the liquid sample is measured in terms of the hydrostatic pressure developed when the liquid is placed in a capillary tube so that the meniscus stands in a strong magnetic field. The apparatus is shown diagrammatically in Fig. 5. On application of the field, the meniscus will rise if the liquid is paramagnetic or will fall if the liquid is diamagnetic. It is often possible and convenient to use fields of the order of 25,000 oersteds. For a diamagnetic liquid such as water the change in height of the meniscus may be several millimeters. When the reservoir is of large diameter compared with the capillary, and when the susceptibility of the vapor above the meniscus is negligible, the mass susceptibility of the sample is given by

$$\chi = \frac{2\Delta hg}{H^2}$$

[7] F. S. Wartman, *U. S. Bur. Mines, Repts. Investigations Tech. Papers*, **No. 3400**, 33 (1938).

[8] G. Quincke, *Ann. Physik.*, **24**, 347 (1885); **34**, 401 (1888).

where Δh is the change in vertical height of the meniscus, and the other terms have their usual significance. This method has, therefore, the advantage that independent measurement of the density is not necessary.

Sometimes rise or fall of the meniscus is observed directly. More frequently the meniscus is returned to its original position by changing the height of the reservoir, or by changing the gas pressure over the meniscus. Accuracy of the readings may be increased slightly by inclining the capillary.

The Quincke method is well adapted to the measurement of liquids, and the accuracy possible is at least as great as with the Gouy method. Unfortunately, arrangements for changing the temperature over a wide range are not convenient. For measurements near room temperature it is possible to control the temperature with a high degree of accuracy.

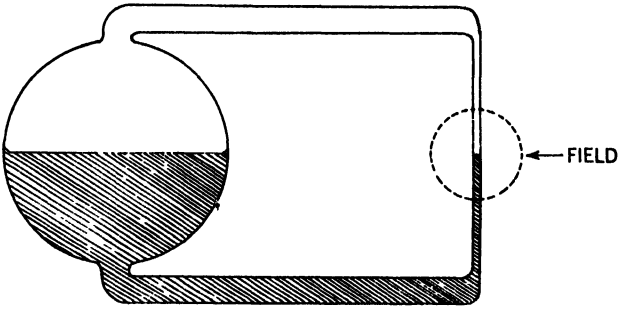


FIG. 5.—Diagrammatic representation of the Quincke magnetic balance. Many modifications have been described.

The method has recently been used by C. S. Marvel and co-workers in extensive studies of free radicals.

The Quincke method may also be used for gases. If the susceptibility of the vapor over the meniscus is not negligible, the hydrostatic pressure developed on application of the field is

$$p = \tfrac{1}{2}(\kappa - \kappa_0)H^2$$

where κ, κ_0 are the volume susceptibilities of the liquid and vapor, respectively.

Some very sensitive adaptations of the Quincke balance as applied to liquids and to gases are described by Wills and Hector,[9] Bauer and Piccard,[10] Bitter,[11] and Woodbridge.[12]

[9] A. P. Wills and L. G. Hector, *Phys. Rev.*, **23**, 209 (1924).
[10] E. Bauer and A. Piccard, *J. phys. radium*, **1**, 97 (1920).
[11] F. Bitter, *Phys. Rev.*, **33**, 389 (1929).
[12] D. B. Woodbridge, *ibid.*, **48**, 672 (1935).

4. The Faraday Method [13]

If the poles of a magnet are inclined toward each other (Fig. 6), there is produced a non-homogeneous field with an axis of symmetry. If a substance is now placed in a region where the strength of the field (H) changes rapidly with displacement along the axis of symmetry (x), then the substance will be subjected to a force along the axis

$$f = m\chi H \frac{dH}{dx}$$

where m is the mass of the sample, χ the mass susceptibility, H the field strength, and $\frac{dH}{dx}$ the rate of change of field strength along the x axis.

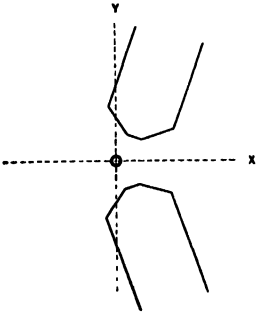


FIG. 6.—Faraday magnetic balance. The sample, shown here at the origin, is placed where the product $H_y \partial H_y/\partial x$ is a maximum. The sample is free to move along the x-axis and may be suspended on a torsion arm.

This method is convenient and sensitive. Small amounts of material are required, and no separate determination of density is necessary. The method was used extensively by Pierre Curie [14] in his classical measurements, and has been used by many investigators since then. The sample may conveniently be mounted on a torsion arm. Displacements may be observed directly, or by a mirror, lamp, and scale arrange-

[13] M. Faraday, *Experimental Researches*, **Vol. 3.** Taylor and Francis, London 1855, pp. 27 and 497.

[14] P. Curie, *Ann. chim. phys.*, **5**, 289 (1895).

ment. The sample is generally restored to its original position with the aid of a torsion head. The electrical torsion head is very satisfactory for this purpose.[15]

Although the torsion method is sensitive it becomes complicated when temperature control is necessary. Alternatively, the force may be measured as a horizontal force or as a vertical force. The horizontal force method, involving a bifilar suspension, has been developed by

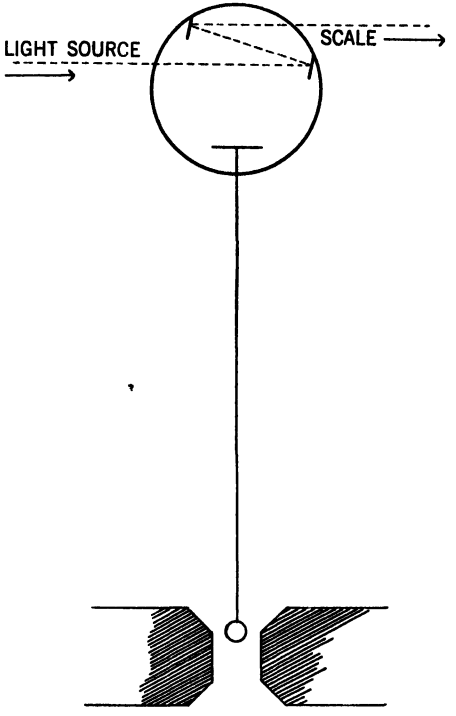


FIG. 7.—Sucksmith modification of the Faraday balance.

Weiss. A null method is used, the force being compensated by the attraction between two current-bearing coils. The method is described at length by Foëx.[16,17]

The vertical force method has been developed in a very useful piece of apparatus by Sucksmith.[18] Instead of using a balance as in the Gouy method, he suspends the sample from a ring of phosphor bronze

[15] A. N. Guthrie and L. T. Bourland, *Phys. Rev.*, **37**, 303 (1931).
[16] G. Foëx, *Ann. phys.*, **16**, 174 (1921).
[17] G. Foëx and R. Forrer, *J. phys. radium*, **7**, 180 (1926).
[18] W. Sucksmith, *Phil. Mag.*, **8**, 158 (1929).

which is fixed at its upper side. Two small mirrors are fixed to the ring at the optimum positions so that on a scale at one meter distance the image of a lamp filament may be observed. Movement of the filament image is at least 150 times the movement of the sample under investigation. A diagram of the apparatus is shown in Fig. 7. The method appears to combine some of the most valuable features of the Faraday and the Gouy methods. Recently, Sucksmith [19] has modified the balance in such a way that susceptibility determinations may be made in vacuum or in a controlled atmosphere up to 1500° C.

An interferometric adaptation of the Faraday method is described by Bhatnagar and Mathur.[20]

Many observations, using the Faraday method, have been made at high and at low temperatures. But for absolute measurements a careful and tedious mapping of the field is necessary. The method has its principal application in work on powders, for which small samples only are required, and for which the problem of uniform packing would otherwise arise. Cabrera has recently described refinements in which the accuracy reaches 1/1000.[21]

5. The Curie-Chéneveau Balance [22]

This balance is similar in principle to the Faraday method except that mapping of the field and careful setting of the sample are neatly avoided. The balance is shown diagrammatically in Fig. 8. It consists of a torsion arm suspended by a fine wire. One end of the torsion arm supports the sample which is free to move between the poles of a small permanent magnet. The magnet may be moved forward or backward with respect to the sample, and, because of its magnetic susceptibility the sample is either repelled or attracted. Movement of the torsion arm may be followed by a pointer or by a mirror, lamp, and scale. The sample automatically places itself in the region of maximum attraction or repulsion. The force acting on the sample is zero when the sample is between the poles. It is also zero when the sample is well removed from the poles. There are then two regions in which the force is a maximum as the magnet is moved from far on one side of the sample to far on the other side. The mass susceptibility of the sample is given by

$$\chi = \chi_0 \frac{m_0}{m} \left(\frac{\Theta - \Theta_t}{\Theta_0 - \Theta_t} \right)$$

[19] W. Sucksmith and R. R. Pearce, *Proc. Roy. Soc. London*, A167, 189 (1938).
[20] S. S. Bhatnagar and R. N. Mathur, *Phil. Mag.*, 8, 1041 (1929).
[21] B. Cabrera, *J. phys. radium*, 9, 209 (1938).
[22] C. Chéneveau, *Phil. Mag.*, 20, 357 (1910).

where χ_0, m_0 are the mass susceptibility and mass, respectively, of a substance of known susceptibility, m is the mass of the sample of unknown susceptibility, Θ is the difference in corresponding maximum deflections on either side of zero for the sample under investigation, Θ_0 the difference for the standard substance, and Θ_t the difference for the empty tube.

Various refinements have been suggested by Gray and Farquharson [23] and by others. Relatively small quantities of sample are required and the measurements may be made rapidly. On the other hand, it is difficult to introduce temperature control, and the sensitivity is not very

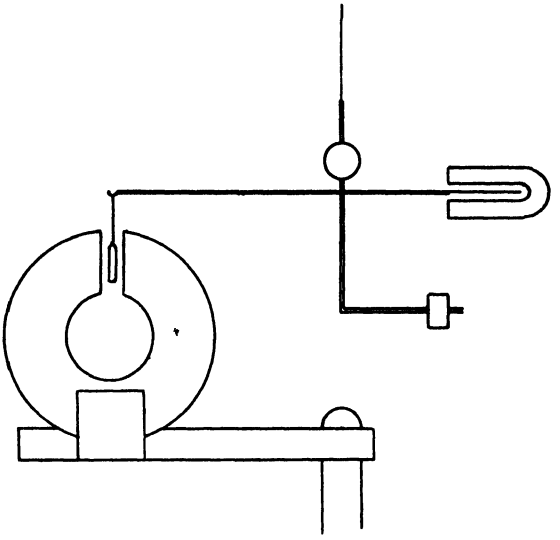


FIG. 8.—Curie-Chéneveau balance.

high. The Curie-Chéneveau balance is of most use in magnetochemical analyses such as are required in rare earth work. Useful elaborations of the Curie-Chéneveau balance are described by Wilson,[24] Oxley,[25] and Vaidyanathan.[26]

6. The Rankine Balance

If a bar magnet stands parallel to a plane surface, the induced polarity on the surface exerts a force on the magnet. This force is an attraction if the surface consists of a paramagnetic substance, a repulsion if the substance is diamagnetic. The magnitude of the force depends on the magnetic susceptibility of the substance. Use of this principle for

[23] F. W. Gray and J. Farquharson, *J. Sci. Instruments*, 9, 1 (1932).
[24] E. Wilson, *Proc. Roy. Soc. London*, A96, 429 (1920).
[25] A. E. Oxley, *Trans. Roy. Soc. London*, A214, 109 (1914); A215, 79 (1915).
[26] V. I. Vaidyanathan, *Indian J. Phys.*, 1, 183 (1926).

magnetic measurements was suggested by Rankine [27] and developed by Iskenderian.[28] The arrangement is shown diagrammatically in Fig. 9. The magnet is suspended by a quartz fiber from a horizontal beam supported by another quartz fiber. This arrangement minimizes the effects of the earth's magnetic field and of stray accidental fields. The relative magnetic susceptibilities of different materials can be deduced from the magnitudes of the torques produced in the torsion fiber.

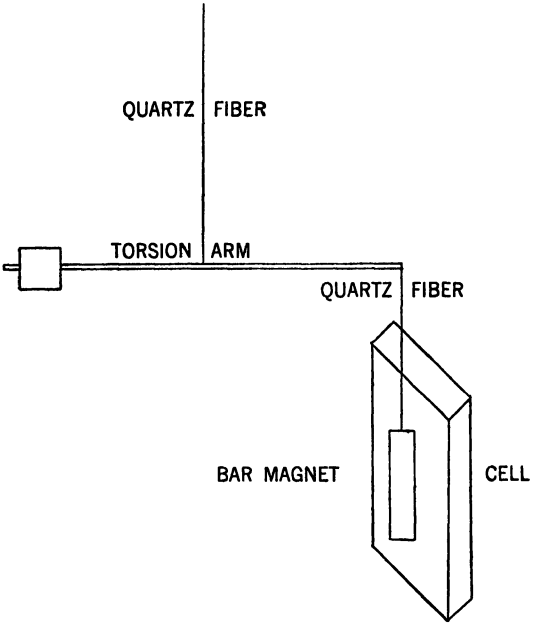


FIG. 9.—Rankine magnetic balance.

Owing to the effects of stray fields the method is rather difficult and it is necessary that all parts of the balance, other than the magnet, be constructed of non-ferromagnetic materials. The apparatus is capable of giving accurate results, with the interesting difference from other methods that very weak fields are used. The fields may be of the order of 100 oersteds.

7. Other Special Methods

There is an almost endless number of methods and modifications of methods which have been suggested for the measurement of magnetic susceptibility.

[27] A. O. Rankine, *Proc. Phys. Soc. London*, **46**, 1, 391 (1934).

[28] H. P. Iskenderian, *Phys. Rev.*, **51**, 1092 (1937) *et seq.*

If an elongated specimen is suspended by a fiber between the poles of a magnet, it will tend to take up an equilibrium position. A diamagnetic specimen will set itself at right angles to the field, a paramagnetic specimen parallel to the field. The force acting on the specimen depends on the difference in mass susceptibilities of specimen and surrounding atmosphere. This affords a convenient method for the investigation of liquids. The specimen may be made of glass or quartz, and the liquid takes the place of the surrounding atmosphere. The method was developed by Decker,[29] and has been used by the author.[30a] Reber and Boeker [30b] have recently adapted the method for use on vapors.

If the specimen is displaced from its equilibrium position, oscillations will occur, the period of which is a function of the magnetic susceptibilities of the specimen and of the medium. This method has been developed by Frazer and Long [31] by means of a device used in determination of the gyromagnetic effect. The specimen is suspended by a quartz fiber, and maintained in torsional vibration by the periodic imposition of a magnetic field of suitably adjusted intensity. Fields of the order of 300 oersteds may be used. The method is relative only, but gives the mass susceptibility with a fair degree of accuracy and uses a small (0.5 g.) sample.

A very sensitive balance for gases and vapors has been developed by Bitter [32] from a method originally suggested by Glaser.[33] This method is somewhat similar to that of Decker, but much more elaborate. A test body, made of pyrex glass, consists of a cylindrical vessel divided radially into four equal chambers. This vessel is suspended from a torsion fiber between the poles of an electromagnet. Two of the chambers, diametrically opposite one another, are open to the surrounding gas, the other two are evacuated and sealed off. On application of the field the test body turns through an angle which is a function of the magnetic susceptibility of the gas in the open chambers.

Salceanu [34] has developed a method of "magnetically neutral" solutions. If a paramagnetic substance is dissolved in a diamagnetic solvent, such as water, there must be a certain concentration, at a definite temperature, at which the susceptibility is zero. Salceanu determines this

[29] H. Decker, *Ann. Physik*, **79**, 324 (1926).
[30a] P. W. Selwood, *J. Am. Chem. Soc.*, **55**, 3165 (1933).
[30b] R. K. Reber and G. F. Boeker, *Phys. Rev.*, **59**, 938 (1941).
[31] J. H. Frazer and N. O. Long, *J. Chem. Phys.*, **6**, 462 (1938).
[32] F. Bitter, *Phys. Rev.*, **35**, 1572 (1930).
[33] A. Glaser, *Ann. Physik*, **75**, 459 (1924).
[34] C. Salceanu, *Z. Physik*, **108**, 439 (1938).

condition by the rotation of a glass float placed in the liquid under investigation, between the pole pieces of the magnet. The susceptibility of the solute may be calculated from a knowledge of the concentration at which $\chi = 0$. The method would appear to be of rather limited applicability.

Athenasiadis [35] has suggested an original method for liquids. As in the drop method for surface tension measurements, drops of the liquid fall from a tube, the orifice of which is placed in a non-homogeneous magnetic field. The relative susceptibilities of two liquids are a function of the mass of the drops and of the change in mass when the field is turned on or off. The method has been used by Abonnenc [36] to find the susceptibility of several inert gases. The basis of the method is determination of the concentration of a solution of $CuSO_4 \cdot 5H_2O$, the weight of a drop of which formed between the poles of an electromagnet remains unchanged whether the field is applied or not. This weight varies according to the susceptibility of the gas in which the drop is formed.

The problem of measurements on non-homogeneous systems has been studied by Bates, Baker, and Meakin,[37] particularly with reference to amalgams which separate on standing. One pole tip has a cylindrical surface and the other has a plane surface. When an amalgam is placed in a vertical tube, suspended in the field from a torsion balance, each portion of the amalgam is exposed to the same value of the gradient of H^2 in the direction along which motion of the tube is possible.

It may seem surprising that no reference has been made to the familiar methods used in determining intensity of magnetization, permeability, and related quantities of ferromagnetic bodies. Such methods are, with few exceptions, not adaptable to the determination of magnetic susceptibilities. The reason for this is that the susceptibilities of non-ferromagnetic substances are invariably extremely small in comparison with the susceptibility of, say, iron. Efforts have been made to develop methods depending on the change of inductance when a substance is inserted into a coil of wire. Some of these efforts are described by Stoner (*op. cit.*[1]), but none has been satisfactory. There are occasions when the ferromagnetic properties of a substance are of great value in determining the composition and structure of a chemical compound. Methods used for these determinations are described later under the heading "9. Measurement of Related Magnetic Quantities."

[35] G. Athenasiadis, *Ann. Physik*, **66**, 415 (1921).

[36] L. Abonnenc, *Compt. rend.*, **208**, 986 (1939).

[37] L. F. Bates, C. J. W. Baker, and R. Meakin, *Proc. Phys. Soc. London*, **52**, 425 (1940).

8. Measurement of Magnetic Anisotropy

The magnetic susceptibility of a solid depends not only on the nature of the molecules present but also on their orientation in the crystal. Measurement of susceptibility on a powdered specimen yields an average of the several different susceptibilities which exist along the different magnetic axes of the many crystals of which the powder is formed. Magnetic anisotropy is the variation of intensity of magnetization with direction in crystalline matter. Sometimes this is expressed as the difference of two principal susceptibilities, sometimes as the ratio. The magnetic axes of the crystal generally correspond with the optical axes. Gases, most liquids, and amorphous, highly powdered, or isotropic solids do not show magnetic anisotropy.

Within recent years, measurements of magnetic anisotropy have in many cases become complementary to x-ray structural studies of crystals, especially of aromatic compounds. The method has been reviewed by Mrs. Lonsdale.[38]

The most obvious method of measurement is to determine the magnetic susceptibility by one of the standard methods, but to have the crystal oriented in such a way so that the force of attraction, or repulsion, is exerted along one magnetic axis only. This method is not particularly accurate except for strongly paramagnetic substances, and some difficulty may be experienced in properly orienting the crystals. Jackson,[39] however, has had considerable success with crystals of rare earth compounds and other paramagnetic substances. The apparatus used is an adaptation of the Sucksmith modification of the Faraday magnetic balance. Measurements are reported down to the melting point of hydrogen.

An alternative method of high sensitivity has been described by Krishnan.[40] When any diamagnetic crystal is suspended by a thin fiber in a magnetic field, it will, of course, be subject to a lateral force tending to move it to the weakest part of the field. But there are also two different couples tending to rotate the crystal about the axis of suspension. First, there is a couple due to asymmetry of shape of the crystal and the non-homogeneity of the field. And second, there is a couple due to the magnetic anisotropy. The former effect may be eliminated by using a crystal cut into spherical shape, or more readily, by using a homogeneous field. A field of sufficient homogeneity may be found in a small region between relatively large plane pole faces.

[38] K. Lonsdale, *Science Progress*, **32**, 677 (1938).

[39] L. C. Jackson, *Proc. Roy. Soc. London*, **A140**, 695 (1933).

[40] K. S. Krishnan, B. C. Guha, and S. Banerjee, *Trans. Roy. Soc. London*, **A231**, 235 (1933).

If a crystal is suspended by a torsion fiber in such a field, it may be made to oscillate. The period of oscillation is related to the magnetic anisotropy as follows:

$$\chi_1 - \chi_2 = \frac{t_1^2 - t^2}{t^2} \cdot \frac{c}{H^2} \cdot \frac{M}{m}$$

where t and t_1 are the periods of oscillation with field on and off respectively; c is the torsional constant of the fiber; m is the mass of the crystal; M is the molecular weight; H is the field; and $\chi_1 - \chi_2$ is the difference between maximum and minimum molar susceptibilities along the magnetic axes lying in the plane of oscillation. A slight modification of this method for very small crystals is described by Krishnan and Banerjee.[41]

Krishnan's elegant method measures only the difference between principal susceptibilities, although it does so with great accuracy. If the absolute values are required, it is necessary to measure at least one of the principal susceptibilities directly. This may be done (in addition to the Jackson method) by a procedure due to Rabi.[42] The crystal to be investigated is suspended vertically in a non-homogeneous field. The crystal is then surrounded with a solution, the susceptibility of which is varied, and the orientation of the crystal adjusted, until there is no movement of the crystal due to the magnetic field. A diagram of the apparatus is shown in Fig. 10. The susceptibility of the solution is

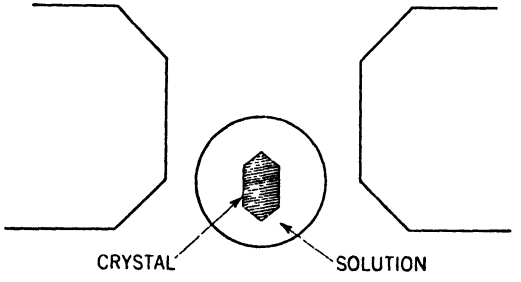


FIG. 10.—Rabi balance for measurement of magnetic anisotropy.

then measured by the Gouy (or other) method. Each axis of the crystal may be investigated in turn, if this is required. The method does not require preparation of crystal sections or measurement of the magnetic field. As many crystalline substances are soluble in water, the solutions used are first saturated with the substance under investigation. The method may, of course, be extended to include non-aqueous solutions.

[41] K. S. Krishnan and S. Banerjee, *Trans. Roy. Soc. London*, **A234**, 265 (1935).
[42] I. I. Rabi, *Phys. Rev.*, **29**, 174 (1927).

The Rabi method, with some modifications, has been extensively used by Krishnan and his co-workers.

9. Measurement of Related Magnetic Quantities

The relationship between several magnetic quantities is shown in Fig. 11. With increasing field strength, H, the intensity of magnetization, $\mathcal{J}$, decreases slightly for diamagnetic substances, and increases for paramagnetic substances. In both cases the slope of the straight line gives the magnetic susceptibility.

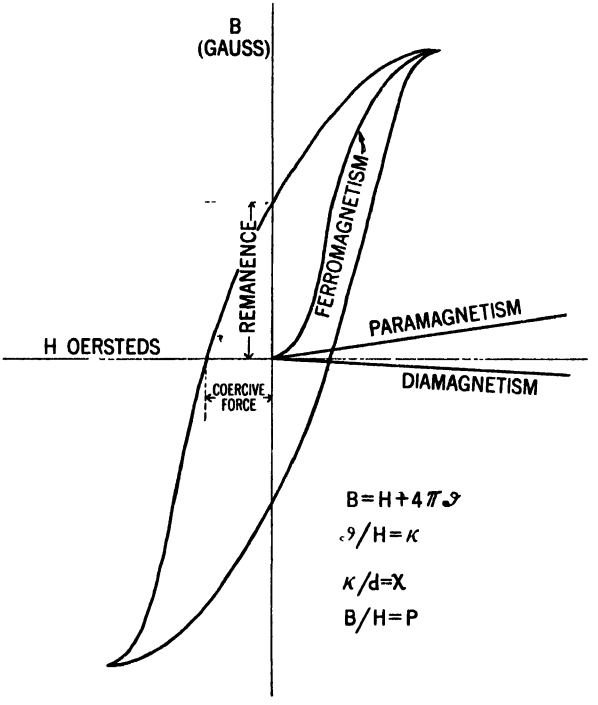


FIG. 11.—Relationships between various magnetic quantities.

For ferromagnetic substances the situation is quite different. The intensity of magnetization changes in a complicated, irreversible manner as H is changed, giving rise to the familiar hysteresis curves. Only at high fields, when the specimen is said to be saturated, does the intensity of magnetization become directly proportional to the field.

In the relationship $B = H + 4\pi\mathcal{J}$ (*cf.* Sec. 1) $\mathcal{J}/H$ is, of course, κ, the volume susceptibility. The quantity B/H is called the permeability, for which the symbol P will be used. The permeability is related to the

susceptibility by $P = 1 + 4\pi\kappa$. For dia- and paramagnetic substances both P and κ are independent of field strength, except that at extremely low temperatures and high fields paramagnetic substances approach saturation.

When a ferromagnetic body is placed in a magnetic field and then removed, B may not return to zero as H becomes zero. The body is then said to be permanently magnetized. The magnitude of B under such conditions of permanent magnetization is called the remanence. The field of opposite sign necessary to reduce B to zero is called the coercive force. *Specific* magnetization is the intensity of magnetization divided by the density, or $\mathcal{J}/d$. It is also given by the slope of the susceptibility plotted against reciprocal field strength.

Permeability, intensity of magnetization at saturation, remanence, and coercive force are all commonly measured magnetic quantities. But the methods used in determining the magnetic characteristics of a steel are often different from those used in magnetochemical analysis. A few of the more important methods will be described.

All ferromagnetic substances lose their ferromagnetism and become paramagnetic at a characteristic temperature called the Curie point. Determination of the Curie point has some analytical applications and will be described briefly. Reviews of this field are given by Bittel and Gerlach [43] and by Neumann.[44]

All treatises on experimental electricity and magnetism describe two fundamental methods used in "ferromagnetic" investigations, namely, induction methods and magnetometer methods.[45] The first implies the magnetization of a specimen by inserting it in a field produced by a solenoid. On removal or reversal of the primary current an induced charge is set up in a secondary coil which may be connected to a ballistic galvanometer. Innumerable modifications of experimental arrangement, frequency, and detection of the induced charge, have been described. The magnetometer method involves the use of a small permanent magnet suspended so as to turn, like a compass needle, under the influence of an external field. This method also has been subjected to many modifications. Both methods have some applications in magnetochemistry.

Elmore [46] has described an induction method designed by F. Bitter. This is an induction bridge consisting of two nearly identical mutual

[43] H. Bittel and W. Gerlach, *Physik regelmäss.*, **7**, No. 3, 119 (1939).

[44] H. Neumann, *Arch. Eisenhüttenw.*, **11**, 483 (1938).

[45] *Cf.*, Müller-Pouillets, *Lehrbuch der Physik*, 11th ed., edited by A. Eucken, O. Lummer, and E. Waetzmann. **Vol. IV**, Part 4: *Elektrische Eigenschaften der Metalle und Elektrolyte; magnetische Eigenschaften der Materie.* F. Vieweg und Sohn, Brunswick 1934.

[46] W. C. Elmore, *Phys. Rev.*, **54**, 1092 (1938).

inductances connected in opposition and through a calibrated mutual induction for restoration of balance. Balance is detected by a sensitive ballistic galvanometer connected to secondaries wound around each primary. The sample is placed inside one of the primaries. The method is suitable for susceptibilities of the order of 10^{-3}, and for fields from 0 to 400 oersteds.

Numerous attempts have been made to relate the carbon content of steels to magnetic properties. Most of these methods depend on an inductive type of measurement of permeability or of coercive force. Various instruments of this nature such as the "Carbometer," [47] "Carb-analyzer," [48] and "Coercimeter" [49] will be described later.

Observation of the hysteresis loop and measurement of other magnetic quantities may be achieved visually through use of a cathode-ray tube. A convenient apparatus, including temperature control, has been designed by Förster.[50]

Application of magnetometer methods to magnetochemical problems has been due chiefly to Tobusch [51a] and also to Bozorth.[51b] More recently a refined form of the Tobusch magnetometer has been described by Raychaudhuri.[52] This consists of an astatic magnetometer standing between two solenoids. Use of an astatic magnetometer greatly reduces the effect of external stray magnetic fields. The two solenoids exert equal and opposite torques on the magnetometer needles. If now a specimen, such as a ferromagnetic powder, is placed inside one of the solenoids, the effect on the magnetometer needles will no longer be balanced. Balance may be restored by use of a subsidiary solenoid or by placing an equivalent amount of magnetizable material in the second solenoid. The method has been used with success for measurement of ferromagnetic powders which are often difficult to place or to pack in the conventional Faraday or Gouy methods. A slightly different form of magnetometer is described by Grube and Winkler.[53] The instrument has considerable flexibility over a range of field strength and temperature.

Various adaptations of the Curie and Weiss modifications of the Faraday method have been used for determination of the magnetization

[47] G. Soler, *Metal Progress*, **31**, 159 (1937).

[48] H. K. Work and H. T. Clark, *Am. Inst. Mining Metal Engrs., Tech. Pub.*, **No. 1132** (1939).

[49] V. H. Gottschalk, *U. S. Bur Mines, Repts. Investigations Tech. Papers*, **No. 3400**, 21 (1938).

[50] F. Förster, *Z. Metallkunde*, **32**, 184 (1940).

[51a] H. Tobusch, *Ann. Physik*, **26**, 439 (1908).

[51b] R. M. Bozorth, *J. Optical Soc. Am.*, **10**, 591 (1925).

[52] D. P. Raychaudhuri, *Indian J. Phys.*, **9**, 417 (1935).

[53] G. Grube and O. Winkler, *Z. Elektrochem.*, **41**, 52 (1935).

curve and related properties. The Sucksmith modification, described in Sec. 4, has been adapted to ferromagnetic investigations with considerable success.[54] The force, exerted vertically on a few milligrams of specimen, is measured by Sucksmith's ring, which, however, may be made much less sensitive than when used for paramagnetic substances. In order to produce a field of high intensity and constant gradient the pole-pieces are planed as shown in Fig. 12. This arrangement is somewhat similar

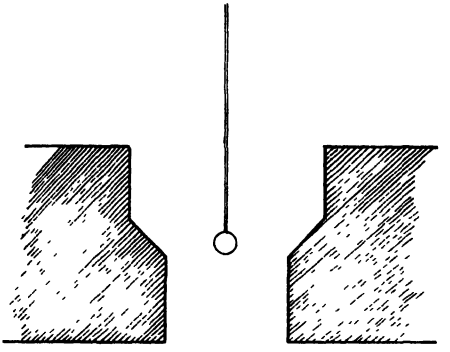


FIG. 12.—Special pole-pieces for uniform dH/dx.

to that described by Frantz [55] as an "isodynamic gap" which has the property that a particle of a given mass and magnetic susceptibility is acted upon by the same force regardless of its position in the gap. The force depends on the field H, the product of field and gradient $H\frac{dH}{dX}$, and the intensity of magnetization. For $H = 18{,}000$ oersteds, $\frac{dH}{dX} = 900$ oersteds per cm., the force on a 30 mg. sample of iron may be about 6 g. The method lacks nothing in sensitivity. The usual temperature controls are provided. Experimental details are given for temperatures up to 1500° C.[56]

A slightly more complicated balance of the same type is described by Lange and Mathieu,[57] who give many examples of measurements on different steels, carbides, and other ferromagnetic substances. A method in which the force is exerted horizontally is given by Rogers and Stamm.[58]

[54] W. Sucksmith, *Proc. Roy. Soc. London*, **A170**, 551 (1939).

[55] S. G. Frantz, U. S. Patent 2,056,426 (1936).

[56] W. Sucksmith and R. R. Pearce, *Proc. Roy. Soc. London*, **A167**, 189 (1938).

[57] H. Lange and K. Mathieu, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **20**, 239 (1938).

[58] B. A. Rogers and K. O. Stamm, *Am. Inst. Mining Metal Engrs., Tech. Pub.*, **No. 1133** (1939).

The method is of moderate sensitivity. Apparatus which permits a very wide range of field strength (up to 40,000 oersteds) and a wide range of temperature is described by Bitter and Kaufmann.[59] Other modifications are given by Franczak and Witkowski,[60] and by Dorfman and Sidorov.[61]

Almost any of the methods already described may be used to determine the Curie point. For instance, if a heated specimen is placed inside a solenoid, a change in self-induction may be observed as the specimen cools past the Curie point.[62] The Sucksmith method is well adapted to measurement of the Curie point. There are, however, other properties which change almost simultaneously with the magnetization. These are specific heat, electrical resistance, Thomson coefficient, thermal conductivity, elasticity, and thermal expansion. These properties are discussed by Gerlach.[63] The electrical resistance of nickel, for example, shows only a slight inflection at the Curie point, but the temperature coefficient of resistance shows a sharp peak. Unfortunately, for alloys the temperature coefficient of resistance reaches a maximum somewhat below the Curie point,[64a, 61b] and, in general, is not a very reliable substitute for magnetic measurements. A unique method for obtaining the Curie point has been suggested by Bryant and Webb.[65] This depends on the fact that the high frequency resistance of a ferromagnetic conductor is a function of its permeability. The method requires no special furnace and permits continuous observation of permeability variations with temperature. Limitations of the method are that it does not permit determinations over a very wide and definite range of flux densities, and the specimen must be in the form of a wire or long strip. The resistance of the specimen at about 400 kilocycles per second is measured with a high frequency resistance bridge or by the resistance substitution method.[66] The high frequency resistance drops sharply at the Curie point.

10. Measurements at Extremely Low Temperatures and at High Frequencies

Down to the temperature of boiling hydrogen, magnetic measurements by the Gouy or Faraday methods offer no unusual difficulties. But

[59] F. Bitter and A. R. Kaufmann, *Phys. Rev.*, **56**, 1044 (1939).
[60] W. Broniewski, S. Franczak, and R. Witkowski, *Ann. phys.*, **10**, 5 (1938).
[61] Y. G. Dorfman and S. Sidorov, *Compt. rend. acad. sci. U. R. S. S.*, **19**, 381 (1938).
[62] L. Bergmann, *Phys. Z.*, **37**, 547 (1936).
[63] W. Gerlach, *Z. Elektrochem.*, **45**, 151 (1939).
[64a] H. Bittel and W. Gerlach, *Ann. Physik*, **33**, 661 (1938).
[64b] A. Kussmann and A. Schulze, *Physik. Z.*, **38**, 42 (1937).
[65] J. M. Bryant and J. S. Webb, *Rev. Sci. Instruments*, **10**, 47 (1938).
[66] *Natl. Bur. Standards* (*U. S.*), *Circ.* No. 74, second edition, p. 178.

below about 14° K. the measurements present increasingly difficult experimental and theoretical problems. Most of the work in this field has come from the Leiden laboratory. An excellent description of magnetic, and other, phenomena at very low temperatures is given by Burton, Smith, and Wilhelm.[67]

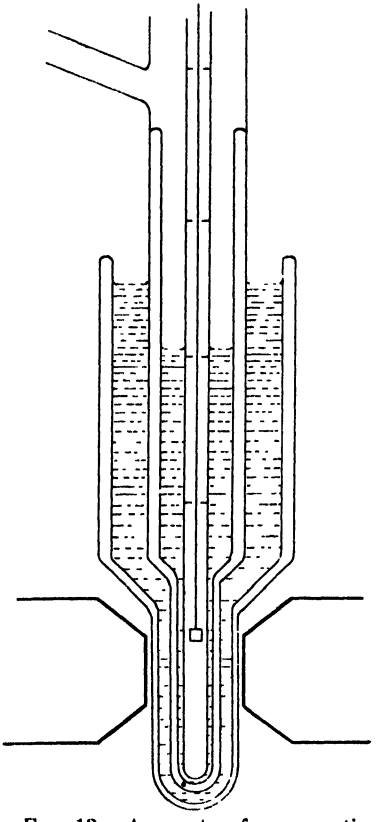


FIG. 13.—Apparatus for magnetic measurements at the temperature of liquid helium.

The Faraday method is preferred for such measurements because substances which are paramagnetic at ordinary temperatures often develop a field dependence of susceptibility at low temperatures. Consequently it is desirable to have the whole sample in a region of nearly constant field strength. The susceptibility of most paramagnetic substances is roughly inversely proportional to the absolute temperature. The forces at low temperatures are therefore often quite large. The sample may be suspended from a balance by a quartz rod. The sample is surrounded by two Dewar flasks, the outer of which contains liquid hydrogen or nitrogen, and the inner liquid helium. For the lowest temperatures the sample may be immersed directly in the cryostat liquid, but for temperatures at which the helium or hydrogen is boiling vigorously the sample is suspended in an atmosphere of helium or hydrogen gas inside a german silver tube. The arrangement is shown diagrammatically in Fig. 13. Various modifications will be found in the literature.[68–73]

[67] E. F. Burton, H. G. Smith, and J. O. Wilhelm, *Phenomena at the Temperature of Liquid Helium.* Reinhold Publ. Corp., New York, 1940.

[68] C. J. Gorter, W. J. de Haas, and J. van den Handel, *Proc. Acad. Sci. Amsterdam,* **34**, 1249 (1931); **36**, 158 (1933).

[69] W. J. de Haas and P. M. van Alphen, *Proc. Acad. Sci. Amsterdam,* **33**, 1106 (1930).

[70] H. K. Onnes and A. Perrier, *Proc. Acad. Sci. Amsterdam,* **16**, 689, 786 (1913).

[71] D. Shoenberg and M. Z. Uddin, *Proc. Roy. Soc. London,* **A156**, 687, 701 (1936).

[72] E. C. Wiersma and H. R. Woltjer, *Proc. Acad. Sci. Amsterdam,* **32**, 1046 (1929).

[73] H. R. Woltjer, *Proc. Acad. Sci. Amsterdam,* **32**, 759 (1929).

Measurements at still lower temperatures are of interest in connection with adiabatic demagnetization and the production of temperatures below 1° K. At such extremes of cold the variation of magnetic susceptibility with temperature was, for a time, the only method by which such temperatures could be estimated. In these experiments a paramagnetic substance is cooled as low as possible with hydrogen or helium while it is placed in a strong magnetic field. On removal of the field the substance cools itself still further, in some cases to a temperature only a few thousandths of a degree above the absolute zero. The susceptibility of the sample used to produce the low temperature may be measured directly by suspending it from a balance as previously described.[74] A more satisfactory method is to measure the susceptibility by induction,[75,76] either through the change in self-inductance of a test coil placed around the sample, or by the change of flux through a secondary coil when the current in the primary is reversed.

One further complication of magnetic measurements at extremely low temperatures may be mentioned. For all ordinary temperatures and readily attainable fields the intensity of magnetization of a paramagnetic substance is proportional to the field. In other words, the susceptibility is independent of the field. But at very low temperatures paramagnetic substances show saturation effects, in which the susceptibility falls as the field increases. The effect has been described for gadolinium sulfate by Woltjer and Onnes.[77] The effect is not to be confused with the field strength dependence shown by the susceptibility of some substances even at low fields.

A type of measurement related to that just described is the use of high frequency alternating fields at low temperatures. It is well known that polar substances exhibit anomalous dispersion and absorption when the dielectric constant is measured at very high frequencies. Analogous behavior is shown by paramagnetic substances at low temperatures, and frequencies of several megacycles.[78] The apparatus consists of an inductance bridge, the specimen being introduced into one of the two solenoids in the bridge. The phenomenon of paramagnetic absorption is greatly increased by making the high frequency measurements in a parallel constant magnetic field. The effect has been observed by

[74] W. J. de Haas, E. C. Wiersma, and H. A. Kramers, *Physica*, 1, 1 (1933).
[75] W. F. Giauque and D. P. Macdougall, *Phys. Rev.*, 43, 768 (1933).
[76] N. Kürti and F. Simon, *Proc. Roy. Soc. London*, A149, 152 (1935).
[77] H. R. Woltjer and H. K. Onnes, *Proc. Acad. Sci. Amsterdam*, 32, 772 (1923).
[78] C. J. Gorter and F. Brons, *Physica*, 4, 579 (1937).

Brons and Gorter.[79] A mutual inductance bridge suitable for this type of measurement is described by de Haas and du Pré.[80]

11. The *Ortho-Para* Hydrogen Method

The spin isomerization of hydrogen is catalyzed by inhomogeneous magnetic fields such as exist near paramagnetic ions or molecules. The effect is observed both for the heterogeneous and homogeneous catalysis.[81] The rate of conversion is a function of the magnetic moment of the paramagnetic ion or molecule, and hence may be used as a rough measure of the susceptibility. The theory of magnetic catalysis is given by Wigner [82] and by Kalckar and Teller.[83]

The method consists, in brief, of passing, say, 1,1 *ortho-para* hydrogen over the catalyst and then of analyzing the resultant mixture. The 1,1 *ortho-para* hydrogen may be prepared by passing tank hydrogen over charcoal or chromium oxide gel at liquid air temperature. Analysis of the mixture is done by the thermal conductivity method.[84] Modifications of this method, especially with reference to micro quantities of hydrogen are discussed by Farkas.[85]

This interesting method cannot compete in terms of accuracy with the more conventional methods for determining susceptibility. Furthermore, it is complicated by the fact that the low temperature conversion is strongly catalyzed by substances such as charcoal which are diamagnetic. This has been explained [86] as due to the existence of magnetic dipoles on the surface of the charcoal. In one or two instances direct evidence has been obtained for the existence of such "surface paramagnetism." [87, 88] Furthermore, the rate of conversion on paramagnetic surfaces is greatly influenced by the adsorptive properties of the catalysts.[89–91] Nevertheless, in favorable cases the change in catalytic

[79] F. Brons and C. J. Gorter, *Physica*, **5**, 60 (1938).

[80] W. J. de Haas and F. K. du Pré, *Physica*, **6**, 705 (1939).

[81] G. M. Schwab, H. S. Taylor, and R. Spence, *Catalysis*. D. Van Nostrand Co., New York, 1937, p. 213.

[82] E. Wigner, *Z. physik. Chem.*, **B23**, 28 (1933).

[83] F. Kalckar and E. Teller, *Proc. Roy. Soc. London*, **A150**, 520 (1935).

[84] K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **B4**, 113 (1929).

[85] A. Farkas, *Light and Heavy Hydrogen*. Cambridge Press, Cambridge, 1935.

[86] K. F. Bonhoeffer, A. Farkas, and K. W. Rummel, *Z. physik. Chem.*, **B21**, 225 (1933).

[87] G. F. Hüttig, *Naturwissenschaften*, **20**, 640 (1932).

[88] R. L. Haller and P. W. Selwood, *J. Am. Chem. Soc.*, **61**, 85 (1939).

[89] H. S. Taylor and A. Sherman, J. Am. Chem. Soc. **53**, 1614 (1931); *Trans. Faraday Soc.*, **28**, 247 (1932).

[90] J. Turkevich and P. W. Selwood, *J. Am. Chem. Soc.*, **63**, 1077 (1941).

[91] L. Farkas and L. Sandler, *J. Chem. Phys.*, **8**, 248 (1940).

activity between a diamagnetic surface such as that of lanthanum oxide, and a paramagnetic one such as gadolinium oxide, is very striking.[92]

In general the *ortho-para* hydrogen method is useful for detecting the presence of unstable paramagnetic molecules such as free radicals or compounds in which unpaired electrons are supposed to exist. For instance, Farkas and Sachsse [93] have shown by this method that boron hydride, B_2H_6, is diamagnetic. Application of the method to some structural problems in organic chemistry is discussed by Schwab and Schwab-Agallidis.[94]

12. Production and Control of Large Magnetic Fields

Most magnetochemical investigations are carried out in fields ranging from 5000 to 25,000 oersteds. Fields of this magnitude over several cubic centimeters of space are readily produced by large electromagnets drawing upwards of 1KW of electrical energy. Most such magnets are after the design of Weiss,[95] and at one time or another several models have been offered by manufacturers of scientific instruments both here and abroad. Most workers in the field seem to have had magnets of their own design made in local shops. Fig. 14 shows such a magnet used in connection with a Gouy balance in the author's laboratory. Actual design of the magnet depends so much on individual needs that no detailed plans need be given here. There are, however, a few general principles to be borne in mind. For most purposes a high degree of flexibility is to be preferred. The distance between the coils should be adequate for all temperature control mechanisms that may be necessary. The pole-pieces should be removable and the cores of the main coils should be drilled for possible experiments on the longitudinal Zeeman effect. It is useful to have the yoke mounted on a rotating platform, as this facilitates handling the magnet, and is useful in certain experiments on magnetic anisotropy. The magnet should preferably have little remanence. That is, the field should return as nearly as possible to zero after removal of the current through the coils. Soft iron and certain types of commercial steels are suitable for this purpose.

The shape and material of the pole-pieces are important. For the Gouy method flat cylinder faces, or truncated conical poles are most satisfactory. The plane face of the pole should not be less than two inches in diameter if a region of uniform field is to be produced. For maximum intensity conical pole-pieces may be used. Ferro-cobalt is

[92] H. S. Taylor and H. Diamond, *J. Am. Chem. Soc.*, **55**, 2613 (1933); **57**, 1251 (1935).
[93] L. Farkas and H. Sachsse, *Trans. Faraday Soc.*, **30**, 331 (1934).
[94] G. M. Schwab and E. Schwab-Agallidis, *Z. physik. Chem.*, **B49**, 196 (1941).
[95] P. Weiss, *J. phys.*, **6**, 353 (1907).

useful for the pole-tips because of its high saturation intensity. In the writer's experience, high intensity is less important than the ability to reach, at reasonable currents, a fairly flat region of the B/H curve for the pole interspace. The flatter this region is the less effect fluctuations of current will have on the accuracy of the results.

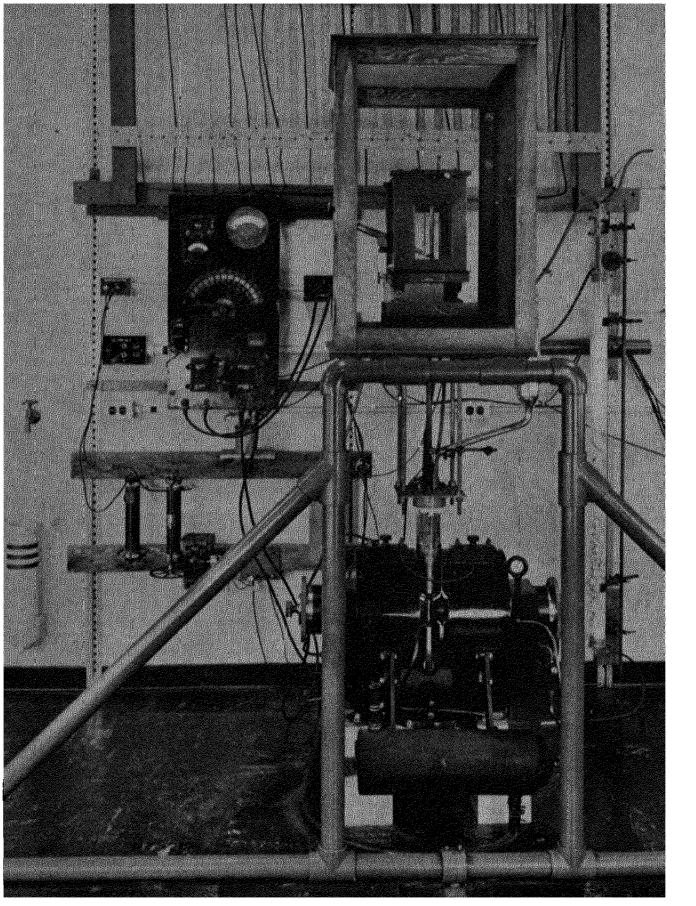


FIG. 14.—Gouy magnetic balance.

Many large magnets have cooling arrangements to dissipate the fairly large energies used. The coil windings may be made of tubing through which water circulates, or water jackets may be spaced between the coil layers. Alternatively, oil, cooled in an exchanger, may be pumped over the coil layers. There is no question that for very high fields and time-

consuming experiments some form of cooling is essential. This is true not only to protect the magnet from injury, but also because the strength of the field depends on the temperature of the iron core. But for many types of magnetochemical measurements the current is turned on intermittently and there is little danger of the core becoming warm. For such measurements it is probably a waste of money to introduce cooling.

Within recent years the technique of producing very large fields has been improved. A very large magnet of more or less conventional design has been built in Paris.[96] With this magnet, fields in excess of 70,000 oersteds have been produced over a much larger volume than is normally possible. Such magnets are of value in magnetoöptical experiments. For still larger fields there is nothing more to be gained by using iron cores, and the practice is to use coreless coils. Kapitza [97] has produced fields in excess of 300,000 oersteds by momentarily passing very large currents through specially constructed coils. Bitter [98] has described coreless magnets producing fields in excess of 40,000 oersteds over long periods. In such magnets the construction of the cooling system, and the cost of electricity and of cooling, become primary considerations.

In almost all magnetic measurements it is necessary to control the strength of the field, and in many the actual field strength must be known and be variable at will. For many cases, controlling the current through the coils is sufficient, provided the temperature of the magnet is reasonably constant. In the author's laboratory control is achieved by passing all the magnet current through a standard 0.01 ohm resistance. Leads from this resistance are connected to a potentiometer which in turn is connected to a galvanometer. Deviation of the galvanometer from a predetermined setting operates one of two photoelectric relays which are arranged to change the resistance in the field coils of the D.C. generator supplying the magnet. This apparatus has proved very satisfactory over a period of years. The sensitivity may be altered as desired. Other circuits for achieving the same purpose will suggest themselves.

Direct control of the field strength, rather than of the current, is more difficult. Use has been made of the fact that the electrical resistance of bismuth changes in a magnetic field.[99] A spiral of bismuth wire mounted in the field may serve as part of a controlling device. It is difficult to make the control sensitive enough, and temperature

[96] A. Cotton, *Report of the 6th Solvay Conference*. Gautier-Villars, Paris 1932.
[97] P. Kapitza, *Proc. Roy. Soc. London*, A115, 658 (1927).
[98] F. Bitter, *Rev. Sci. Instruments*, 10, 373 (1939).
[99] H. Decker, *Ann. Physik*, 79, 324 (1926).

fluctuations must be prevented. Stansfield [100] has suggested the anisotropy of calcite or sodium nitrate crystals as a means of controlling field intensities.

There are now available certain alloys [101] which combine very high remanence with high coercive power. Such alloys may be cast into permanent magnets which rival electromagnets in intensity of field. The fields produced are, of course, constant over indefinitely long periods. It is even possible to vary the fields by passing a suitable current through a magnetizing coil surrounding the magnet.[102] Permanent magnets have the obvious difficulty that the field may not readily be reduced to zero, so that the specimen being investigated must be removed mechanically from the neighborhood when the zero field readings are being taken. The cost of large permanent magnets is also high.[103]

Measurement of field intensity is commonly achieved by finding the force exerted on a current bearing wire in the field, or by use of an induction method such as the "fluxmeter." These are both described in all texts on electricity and magnetism. More frequently in magnetochemical investigations the field is estimated by use of a substance of known magnetic susceptibility such as water and one of the standard methods such as the Gouy balance. In certain instances where the whole field must be mapped, as in precise determinations by the Faraday method, this may be done with the aid of a bismuth spiral.

13. Calibration and Treatment of Data

Magnetic balances are most frequently calibrated with the aid of substances of known susceptibility. No single substance will serve as a calibrating agent for all types of measurements. The Gouy, Quincke, Faraday, and related balances are generally calibrated with water, provided the substance under investigation is one of low susceptibility. The magnetic susceptibility of water at 20° C. may be assumed to be -0.720×10^{-6} units per gram. The various measurements leading to this value, and the temperature coefficient of susceptibility of water (which is slight) will be discussed in a later chapter. Only one precaution is necessary in the use of water for this purpose, and that is that the water should be free from dissolved air. Oxygen dissolved in water has an appreciable susceptibility, but what is even more important

[100] R. G. Stansfield, *Proc. Cambridge Phil. Soc.*, **34**, 625 (1938).

[101] D. G. Fink, *Electronics*, **9**, 30 (1936).

[102] J. D. Cockcroft, C. D. Ellis, and H. Kershaw, *Proc. Roy. Soc. London*, **A135**, 628 (1932).

[103] W. A. Rawlinson, *Australian J. Biol. Med. Sci.*, **18**, 185 (1940), has used a permanent magnet for studies on hemoglobin and its derivatives.

is that no bubbles of air should come out of solution on the walls of the container during measurement.

A carefully prepared solution of nickel chloride is useful as a calibrating agent of somewhat higher susceptibility than water. This solution has been investigated by Miss Brant;[104] by Cabrera, Moles, and Guzman;[105] by Weiss and Bruins;[106] and by Nettleton and Sugden.[107] They agree that the molar susceptibility of nickel chloride at 20° C. is $(4433 \pm 12) \times 10^{-6}$, and that this value is independent of concentration in the neighborhood of 30% $NiCl_2$ by weight. There are cases in which the susceptibility of a mixture is not a linear function of the concentration, but for nickel chloride in water at 20° C. the susceptibility is given to a very fair degree of accuracy by the relationship

$$\chi = \left[\frac{4433}{129.6}p - 0.720(1 - p)\right] \times 10^{-6}$$

where p is the proportion of $NiCl_2$ present by weight.

Many substances have been suggested as calibration agents of high susceptibility. Probably as useful a compound as any is hydrated ferrous ammonium sulfate (Mohr's salt) for which the susceptibility per gram is given by $\chi = 9500 \times 10^{-6}/(T + 1)$ where T is the absolute temperature.[108]

A suitable gas for calibration purposes is oxygen,[109] the volume susceptibility of which at 20° C. and 760 mm. pressure is

$$\kappa = 0.1434 \pm 0.0004 \times 10^{-6}.$$

It not infrequently happens that substances subjected to magnetochemical investigation contain traces of ferromagnetic impurities. Such impurities may completely mask the true susceptibility of the substance. For instance, Fig. 15 shows the difference in Δw, the apparent change in weight by the Gouy method, before and after recrystallization to remove a few microscopic traces of ferromagnetic impurity from some triphenylgermanium, under investigation by the writer. Such impurities are readily detected by the apparent field strength dependence of the susceptibility, whether dia- or paramagnetic. If they cannot be removed by purification of the sample, there are two methods available for eliminating their effect. The first is to heat the substance and to make

[104] L. Brant, *Phys. Rev.*, 17, 678 (1921).

[105] B. Cabrera, E. Moles, and J. Guzman, *Arch. sci. phys. nat.*, 37, 324 (1914).

[106] P. Weiss and E. D. Bruins, *Proc. Acad. Sci. Amsterdam*, 18, 246 (1915).

[107] H. R. Nettleton and S. Sugden, *Proc. Roy. Soc. London*, A173, 313 (1939).

[108] L. C. Jackson, *Trans. Roy. Soc. London*, A224, 1 (1923).

[109] E. Bauer and A. Piccard, *J. phys. radium*, 1, 97 (1920). See also Stoner, (*op. cit.*[1]) for a discussion of this matter.

the measurements above the Curie point of the impurity. The second is to make the measurements over a range of field strength and to extrapolate the susceptibility to infinite field strength. One or other of these methods will generally suffice although the second has recently been criticized.[110]

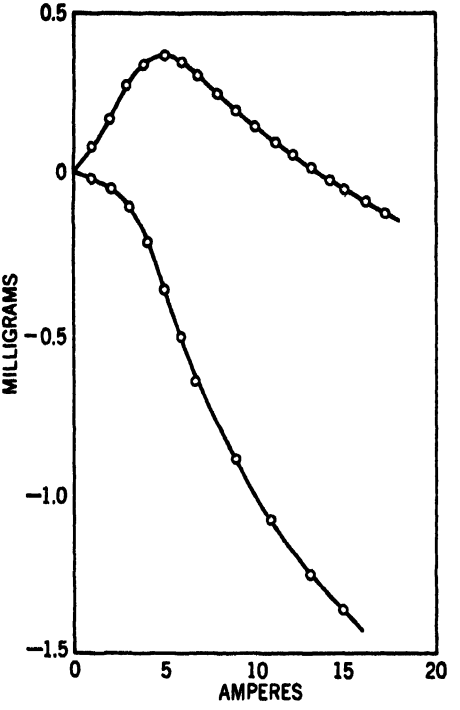


FIG. 15.—Apparent change in weight, Δw, plotted against current through the magnet. The upper curve indicates the presence of a trace of ferromagnetic impurity. The lower curve shows the same substance, hexaphenyldigermanium, after recrystallization.

The presence of paramagnetic impurities in a diamagnetic substance is also easy to detect and to correct for because the susceptibility of the former is nearly always inversely proportional to the temperature while that of the latter is independent of temperature.

In general, corrections for all types of impurities may be made provided the amounts present and susceptibilities are known, because the susceptibilities of mixtures are, at least to a first approximation, linear functions of the concentrations.

[110] A. Knappworst, *Z. physik. Chem.*, A188, 246 (1941).

CHAPTER TWO

ATOMIC DIAMAGNETISM

1. Classical Theory of Diamagnetism

It will be recalled that in diamagnetic substances the flux density is less than in the surrounding magnetic field, and that the susceptibility is independent of temperature. The classical theory of this phenomenon is due to Langevin.[1,2] A brief outline of Langevin's theory will be given here because it contributes greatly to an understanding of the effect.

An electron of mass, m, moving in a closed orbit is equivalent to a current in a wire. The magnitude of this equivalent current is $\frac{e}{c} \cdot \frac{\omega}{2\pi}$ electromagnetic units, where e is the electronic charge, c the velocity of light, and ω the angular velocity of the electron. Such a current will produce a magnetic field of the same intensity at a given distance as a magnet of moment μ, such that

$$\mu = \frac{e\omega S}{2\pi c} = \frac{e\omega\pi r_1^2}{2\pi c} = \frac{e\omega r_1^2}{2c}$$

where S is the area of the bounded surface around which the electron moves, and r_1 is the radius of the orbit. If the orbit is not circular, ωr_1^2 may be replaced by an average so that

$$\mu = \frac{e\overline{\omega r_1^2}}{2c}$$

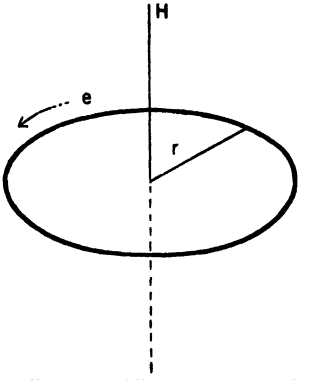


FIG. 16.—Electronic orbital motion subject to a vertical magnetic field.

It has been shown by Larmor[3] that the imposition of a perpendicular external field H on such a system superposes on the electronic motion an angular velocity of precession given by

$$l = -\frac{eH}{2mc}$$

[1] P. Langevin, *Ann. chim. phys.*, 5, 70 (1905); *J. phys.*, 4, 678 (1905).

[2] A good presentation of the theory will be found in E. C. Stoner's *Magnetism and Matter*. Methuen and Co., Ltd., London 1934.

[3] J. Larmor, *Aether and Matter*. Cambridge University Press, London 1900, p. 341.

The magnetic moment associated with the orbit will therefore be changed by

$$\Delta\mu = \frac{e\overline{r_1^2(\omega + 1)}}{2c} - \frac{e\overline{r_1^2\omega}}{2c}$$
$$= \frac{e\overline{r_1^2}l}{2c}$$
$$= -\frac{e^2\overline{r_1^2}H}{4mc^2}$$

For a system of n orbits oriented at random to the field, $\overline{r_1^2}$, the mean square radius of the projected orbit perpendicular to H becomes $\overline{r_1^2} = \frac{2}{3}\overline{r^2}$ where $\overline{r^2}$ is the mean square radius of the orbit. The change of magnetic moment per gram-atom will therefore be

$$\Delta\mu_A = -N\frac{e^2H}{6mc^2}\sum_n \overline{r^2}$$

where N is Avogadro's number. The susceptibility per gram-atom is then

$$\chi_A = \frac{\Delta\mu_A}{H} = -N\frac{e^2}{6mc^2}\sum\overline{r^2}$$
$$= -2.832\sum\overline{r^2} \times 10^{10}$$

It is clear that the negative character of diamagnetism is a consequence of the Larmor precession, and that diamagnetism will be found in all atoms regardless of whether or not they also possess permanent moments. Diamagnetism depends only on the radius of the electronic orbits and is therefore independent of temperature.

2. Modern Theory of Diamagnetism

The quantum-mechanical theory of magnetic susceptibilities has been treated by Van Vleck, and it will suffice here to state a few of the results.[4] The most interesting result is that the expression for diamagnetic susceptibilities is exactly the same as that already given in the classical theory. It is possible, however, to go much farther. For instance, the atomic diamagnetic susceptibility of hydrogen may be calculated directly from the expression

$$\chi_A = -2.832 \times 10^{10}\left\{\frac{h^2}{4\pi^2Ze^2m}\right\}\left[\frac{5}{2}n^4 - \frac{3}{2}n^2l(l+1) + \frac{1}{2}n^2\right]$$
$$= -0.790 \times 10^{-6}\left\{\frac{5n^4 - 3n^2l(l+1) + n^2}{2Z^2}\right\}$$

[4] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities.* Oxford University Press, Oxford 1932.

where n and l are the principal and subordinate quantum numbers respectively, and Z is the atomic number. The quantity h is Planck's constant, and m the electron mass. For atomic hydrogen $n = 1$, $l = 0$, and $Z = 1$, hence the gram-atomic susceptibility is -2.37×10^{-6}. Unfortunately, there is no direct method of measuring the magnetic susceptibility of atomic hydrogen. Furthermore, atomic hydrogen is highly paramagnetic and the diamagnetism would be concealed. An indirect method using Pascal's constants for combined hydrogen gives a value of -2.93×10^{-6}, which is about as good agreement as could be expected. Somewhat similar types of calculations have been made for helium and for heavier atoms.[5-8] With such atoms the principal difficulty is to find the effective nuclear charge $Z_{eff}e$ instead of Ze. The agreement with experiment is, on the whole, satisfactory. Complete details of calculations and of comparison with experiment are given by Van Vleck (*op. cit.*[4]).

3. Diamagnetism of Atoms

There are relatively few monatomic molecules known to chemists. Of these, the inert gases are diamagnetic and of sufficiently long life to be investigated by the methods described in the last chapter. Measurements on the inert gases are of considerable interest because these substances have relatively simple atomic systems, and the atoms are not greatly perturbed by the fields of adjacent atoms.

The most satisfactory determinations on the inert gases are probably those of Wills and Hector,[9a, 9b] and of Havens.[10] Their data and some others are summarized in the following table which includes a comparison with theoretical results obtained by the Slater, Pauling, and Hartree methods. These values and some others are discussed by Stoner (*op. cit.*[2]), and by Angus.[11]

Another diamagnetic substance for which data are available and which is believed to be monatomic is mercury vapor [12a, 12b] for which the susceptibility per gram is -0.389×10^{-6}, compared with -0.42×10^{-6} calculated by Slater's method.

[5] J. C. Slater, *Phys. Rev.*, **32**, 349 (1928).

[6] E. C. Stoner, *Proc. Leeds Phil. Lit. Soc., Sci. Sect.*, **1**, 484 (1929).

[7] L. Pauling, *Proc. Roy. Soc. London*, **A114**, 181 (1927).

[8] D. R. Hartree, *Proc. Cambridge Phil. Soc.*, **24**, 89 (1928).

[9a] A. P. Wills and L. G. Hector, *Phys. Rev.*, **23**, 209 (1924).

[9b] L. G. Hector, *Phys. Rev.*, **24**, 418 (1924).

[10] G. G. Havens, *Phys. Rev.*, **43**, 992 (1933). This paper gives references to previous work on gases.

[11] W. R. Angus, *Ann. Reports*, **38**, 44 (1941).

[12a] S. S. Bhatnagar and M. B. Nevgi, *Current Sci.*, **6**, 53 (1937).

[12b] S. Shur, *Nature*, **139**, 804 (1937).

TABLE I

GRAM-ATOMIC SUSCEPTIBILITIES OF THE INERT GASES
$-\chi_A \times 10^{-6}$

	Helium	Neon	Argon	Krypton	Xenon
Wills and Hector (obs.) [9a,9b]	1.88	6.66	18.13	—	—
Havens (obs.) [10]	1.91	7.65	19.23	—	—
Mann (obs.) [13]	—	6.75	19.54	28.02	42.40
Abonnenc (obs.) [14]	—	—	19.2	29.2	44.1
Gerlach and Roth (obs.)	—	—	19.72	—	—
Slater (calc.)	1.853	5.7	18.9	31.7	48.0
Pauling (calc.)	1.54	5.7	21.5	42	66
Hartree (calc.)	1.90	8.6	24.8		

4. Diamagnetism of Ions

Theoretical calculation of the diamagnetic susceptibility of ions is similar to that of atoms. Unfortunately, experiment gives $\chi_M = \chi_{\text{cation}} + \chi_{\text{anion}}$, assuming that the ionic susceptibilities are additive, and that no constitutive correction need be applied. The problem, therefore, of obtaining ionic susceptibilities from experimental data is similar to that involved in finding ionic refractivities and certain other properties. There are two important reasons for establishing a set of standard ionic susceptibility values; first, to compare with the various theoretical values for ions, and second, to obtain an accurate set of diamagnetic correction constants for paramagnetic substances.

This problem has been discussed by Miss Trew,[15] and by Klemm,[16a] but with rather discordant results. Reference to these papers should be made for the original literature. There are several methods by which ionic susceptibilities may be estimated. Miss Trew suggests a relation between the ionic susceptibility and the apparent atomic susceptibility of the element in a covalent compound. For instance, to calculate the ionic susceptibility of Cl^- she finds the molar susceptibility of chlorine gas, then divides by two to obtain the susceptibility for the covalent chlorine atom. This is called the Pascal constant for chlorine. This value is related to the ionic susceptibility by the expression $A/B = C/D$ where A is the theoretical susceptibility for the covalent atom, B is the

[13] K. E. Mann, *Z. Physik*, **98**, 548 (1936). This paper contains a review of earlier experimental and theoretical work.

[14] L. Abonnenc, *Compt. rend.*, **208**, 986 (1939).

[15] V. C. G. Trew, *Trans. Faraday Soc.*, **37**, 476 (1941).

[16a] W. Klemm, *Z. anorg. allgem. Chem.*, **244**, 377 (1940).

experimental value for the covalent atom, C is the theoretical susceptibility for the ion, and D the experimental ionic susceptibility. This whole procedure seems to the writer to be rather extraordinary, but it gives results in fair agreement with those obtained by other methods. The method is not applicable to elements which do not form diatomic covalent molecules.

Weiss has suggested that Pascal's constants for atoms may be corrected to ionic susceptibilities by the addition or subtraction of a constant factor $\pm$ 3.0 units of molar susceptibility to correct for the covalent bond. It should be pointed out that the magnitude of this bond effect is not constant, but varies with atomic number. But here, too, the results are in fair agreement with those obtained by other methods.

Weiss has also suggested that the susceptibility of the hydrogen halides may be used for calculating ionic susceptibilities because the hydrogen ion, H^+, has zero diamagnetism (having no electrons), and has an effective paramagnetism of 1.2 units of molar susceptibility owing to its nuclear moment.

Brindley has improved on a method suggested by Joos and used by Ikenmeyer. The total susceptibility of anion and cation are considered by Joos to be inversely as the square of the nuclear charge. Brindley showed that a more accurate estimate is given by the ratio $1/(Z - s)^2 : 1/(Z' - s')^2$ where Z, Z' are the respective nuclear charges, and s, s' are the respective screening constants given by Slater's method. The ionic susceptibility of, for instance, the cation is given by

$$\chi_{\text{cation}} = \chi_M \frac{\sum \overline{r^2}_{\text{cation}}}{\sum \overline{r^2}_{\text{cation}} + \sum \overline{r^2}_{\text{anion}}}$$

where

$$\sum \overline{r^2} = \frac{(n')(n' + \tfrac{1}{2})(n' + 1)}{(Z - s)^2}$$

$\sum \overline{r^2}$ represents the electron density distribution summed for each shell, n' is the effective quantum number of the shell.

Brindley and Hoare have suggested that as the susceptibility of Li^+ is small (-0.72×10^{-6}) the theoretical value may be assumed to be the same as the experimental value, because any small divergence would not appreciably influence values for other ions derived from this.

Kido has suggested the following method: From a large number of measurements of molar susceptibility on various salts he plots curves in which salts of metals in the same group of the periodic table, with a common anion, are compared. When the molar susceptibility is plotted against the number of electrons in the cation for the series, a group of straight lines results. For example, the alkali halides give a set of

parallel straight lines. By extrapolating to atomic number zero Kido deduces values for the anion. The method is open to theoretical objection but, like several other dubious methods, gives fairly satisfactory results.

There are available many experimental data from which to calculate ionic susceptibilities. The literature in this field is examined by Miss Trew and by Klemm. Among the most exact measurements are those of Hocart, and of Brindley and Hoare. Experimental test of the theoretical data is further complicated by the following considerations. *1.* The susceptibility of a dissolved salt is generally independent of concentration but this is not always true. *2.* The values for dissolved salts are generally somewhat different from those of water-free crystals. *3.* The susceptibility is changed by change of neighboring charge and of coordination number. These questions will be examined more fully later. Table II gives the standard values recommended by Miss Trew for the ions in solution. Some of these values have been obtained by the methods described above, some by use of the standard values so obtained. Klemm has given a somewhat similar tabulation of ionic susceptibilities, but the results do not agree with those of Miss Trew. There does not seem to be any way of reconciling the differences at the present time.[16b]

TABLE II

IONIC DIAMAGNETIC SUSCEPTIBILITIES AND DIAMAGNETIC CORRECTING CONSTANTS PER GRAM-ION

(Standard values)		(Derived values)	
Ion	$-\chi \times 10^{-6}$	Ion	$-\chi \times 10^{-6}$
Cl^-	23.4 ± 1.3	NO_3^-	18.9
Br^-	34.6 ± 1.6	ClO_3^-	30.2
I^-	50.6 ± 1.6	BrO_3^-	39.8
F^-	9.1 ± 1.8	IO_3^-	51.4
Li^+	1.0	ClO_4^-	32.0
Na^+	6.8	CN^-	13.0
K^+	14.9	CNO^-	19.8
Rb^+	22.5	CNS^-	31.0
Cs^+	35.0	$SO_4^=$	40.1
		$CO_3^=$	29.5
		NH_4^+	13.3
		Tl^+	35.7

[16b] W. Klemm, *Z. anorg. allgem. Chem.*, **246**, 347 (1941). This paper was not available to the writer.

As an example of the range of values found by other workers, Klemm suggests -28.0×10^{-6} as the ionic susceptibility of the chloride ion. Frivold and Olsen [17] have recently determined a number of susceptibilities from which they calculate ionic susceptibilities by the Joos method. The ionic susceptibilities for the cations are all higher, and for the anions, all lower than those given by Miss Trew. For instance, for Cl^- the ionic susceptibility is given as -21.9×10^{-6} for the ion in aqueous solution. Efforts have been made by several workers, for instance, by Frivold and Olsen, and by Klemm to correct the ionic susceptibility in aqueous solution to that for the free gaseous ion. The correction is not large.

The effect of concentration on diamagnetism of solutions has been studied by many investigators. Veiel [18] measured alkali and alkaline earth halides and in all cases found the susceptibility to be a linear function of the concentration as required by the Wiedemann additivity law. Similarly, Ranganadham and Qureshi [19] found the susceptibilities of sodium and of potassium nitrates to be linear with concentration from 1 to 20%. On the other hand Scott and Blair [20] found that while aqueous

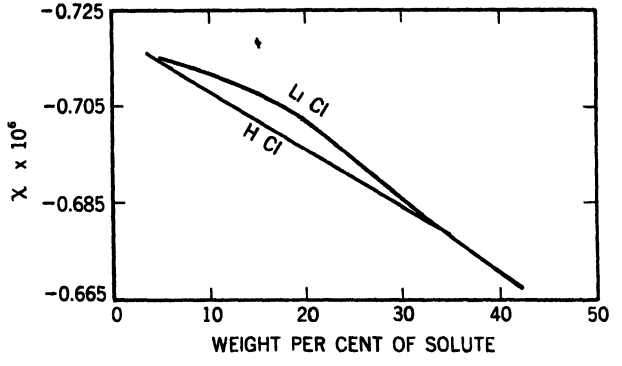


FIG. 17.—Susceptibility-concentration relationships for solutions of HCl and of LiCl in water.

solutions of hydrogen chloride show linearity between susceptibility and concentration, this is not true of lithium chloride solutions. But, in general, it may be said that the additivity law holds unless some rather obvious chemical change takes place with changing concentration.

[17] O. E. Frivold and N. G. Olsen, *Avhandl. Norske Videnskaps-Akad. Oslo, I. Mat.-Naturv. Klasse*, 1940, No. 2.

[18] U. Veiel, *Ann. Physik*, 24, 697 (1935).

[19] S. P. Ranganadham and M. Qureshi, *Indian J. Phys.*, 14, 129 (1940).

[20] A. F. Scott and C. M. Blair, *J. Phys. Chem.*, 37, 475 (1933).

The influence of hydrate formation on ionic diamagnetism has been studied by Rao and Varadachari.[21,22] At high concentrations the susceptibility of sulfuric acid is partly dependent on the particular hydrate formed, but for salts such as the alkali halides the effect is slight.

The effect of temperature on diamagnetic susceptibilities is generally negligible. But even water, which is often used as a standard, has a slight temperature coefficient of susceptibility. This question has been investigated by Bhatnagar, Nevgi, and Sharma,[23] particularly with reference to the Sn^{+4} ion. They find that the diamagnetism of salts of this ion increases slightly with increasing temperature.

Frivold and Sogn [24] have studied the susceptibilities of LiCl, LiBr, $CaCl_2$, $SrBr_2$, $NaClO_4$, $Ca(NO_3)_2$ and of $Ba(ClO_4)_2$ in water, ethyl alcohol, and for a few salts, in acetone. In most cases the susceptibilities are greater in aqueous solution than in the other solvents. In some cases the differences were within the experimental error. On the whole, susceptibilities in non-aqueous solvents have not been very thoroughly investigated.

A careful comparison of susceptibilities in the solid and dissolved states has been made by Flordal and Frivold,[25] and by Brindley and Hoare.[26] They find that the aqueous solution values are generally higher. The susceptibilities of large univalent ions in solution are comparable with their values in the crystalline state, whereas the susceptibilities of small and bivalent ions in solution are much smaller than in the crystalline state.

It is clear that a completely reliable method for calculating ionic susceptibilities from magnetic data remains to be found. Under these circumstances it is not surprising that purely theoretical estimates of ionic susceptibilities do not agree too well with experiment. Van Vleck (*op. cit.*[4], p. 225) gives a table of theoretical susceptibilities. It should be emphasized that the difficulty is not in measurement of susceptibility but rather in properly dividing the susceptibility between cation and anion.

5. Diamagnetic Ionic Crystals

Many, if not most, magnetic measurements have been performed on powdered ionic crystals, yet there is still much to be learned of the forces

[21] S. R. Rao and P. S. Varadachari, *Current Sci.*, **3**, 249 (1934).

[22] P. S. Varadachari, *Proc. Indian Acad. Sci.*, **2A**, 161 (1935).

[23] S. S. Bhatnagar, M. B. Nevgi, and R. L. Sharma, *J. Indian Chem. Soc.*, **13**, 273 (1936).

[24] O. E. Frivold and H. Sogn, *Ann. Physik*, **23**, 413 (1935).

[25] M. Flordal and O. E. Frivold, *Ann. Physik*, **23**, 425 (1935).

[26] G. W. Brindley and F. E. Hoare, *Trans. Faraday Soc.*, **33**, 268 (1937).

acting on the individual ions in such crystals. The relation between solid and dissolved ionic compounds has already been mentioned.

All the theoretical methods for calculating ionic susceptibilities deal with electronic systems subject to central forces such as isolated ions in field-free space. Since the only experimental data available refer to ions in crystals or solutions, there is always present the question of validity of such comparisons. Lithium hydride is cubic and is one of the simplest of all ionic lattices. This substance has been investigated by Freed and Thode.[27] They find the molar susceptibility of LiH to be $-4.60 \pm 0.09 \times 10^{-6}$ at 300° A. and at 78° A. Various theoretical computations indicate a diamagnetism of from 90 to 130 per cent higher. The discrepancy between experiment and theory is here unusually large. Freed and Thode suggest that the difference is due to a temperature independent paramagnetism which is present in all crystals but which is not included in the theoretical calculations. There is, of course, no experimental method of checking on such a suggestion. Temperature independent paramagnetism, however, is actually found experimentally in such compounds as $KMnO_4$, $K_2Cr_2O_7$, K_2MoO_4, and UO_2SO_4. The question has been considered by Van Vleck (*op. cit.*[4]). This effect may account for many discrepancies between theoretical and calculated susceptibilities.

Diamagnetic susceptibilities of solids might be expected to depend on crystalline form, and this is generally true. The problem may be investigated by measurements on closely related substances such as anhydrous and hydrated salts, or better on polymorphic compounds. Zimens and Hedvall[28] found little relation between crystal structure and magnetic susceptibility of titanium dioxide, selenium, zinc sulfide, sodium carbonate decahydrate, alum, and kaolin. On the other hand Duchemin[29] found definite susceptibility dependence on structure for hydrated and double magnesium sulfates, as did Mathur and Nevgi[30] for sulfur, and for oxides of lead.

The magnetic properties of solid solutions of ionic compounds are illustrated by the work of Bhatnagar and Kapur.[31] The susceptibility of a mechanical mixture follows Wiedemann's additivity law so far as is known. But the susceptibility-concentration curve of a true solid solution may follow a linear course, or it may pass through a maximum. In $KClO_4$-$KMnO_4$ which is a truly isomorphous system the relationship

[27] S. Freed and H. G. Thode, *J. Chem. Phys.*, **3**, 212 (1935).
[28] K. E. Zimens and J. A. Hedvall, *Svensk. Kem. Tid.*, **53**, 12 (1941).
[29] E. Duchemin, *Compt. rend.*, 199, 571 (1934).
[30] R. N. Mathur and M. B. Nevgi, *Z. Physik*, 100, 615 (1936).
[31] S. S. Bhatnagar and P. L. Kapur, *J. Indian Chem. Soc.*, 9, 347 (1932).

is almost strictly linear. But in solid solutions of KCl-KBr, of NaCl-KCl, and of NaBr-KBr the susceptibility concentration curve passes through a maximum. The maximum in the system KCl-KBr is at 70 mole per cent KBr, and in the systems NaCl-KCl and NaBr-KBr it is at 50 per cent. Solid solutions such as KCl-KBr show a minimum in the freezing point diagram, and the susceptibility shows a maximum

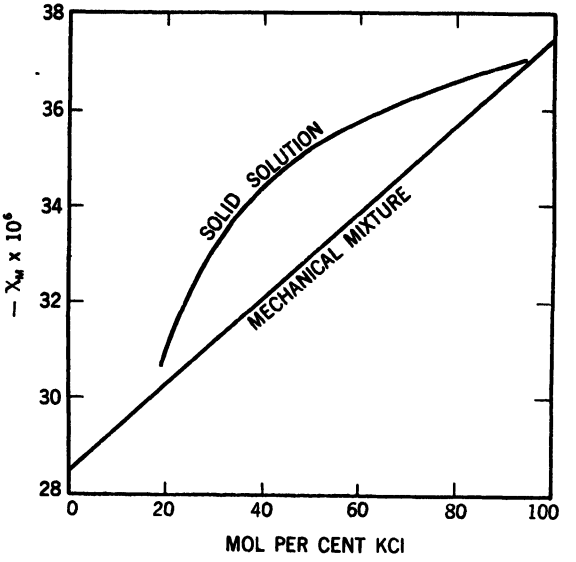


FIG. 18.—Deviation from linearity in a solid solution of KCl-NaCl.

deviation from linearity at the same concentration. This is also true of solid solutions of metals such as copper and gold. The deviation of the susceptibility from linearity is related to the heat of formation of the solution. When $\Delta H = 0$, the susceptibility concentration curve is linear. This effect might be developed into a method of estimating the heat of formation when other methods fail.

6. Magnetic Anisotropy of Diamagnetic Ionic Crystals

In general the susceptibilities along different crystalline axes are the same in diamagnetic ionic crystals, but there are some notable exceptions. For instance, the principal susceptibilities of zircon [32] are -0.170 and -0.732×10^{-6}. Raman and Krishnan [33] have measured the magnetic anisotropy of several inorganic salts. For sodium nitrate the molar susceptibility parallel to the trigonal axis is -29.5×10^{-6}, while perpen-

[32] W. Voigt and S. Kinoshita, *Ann. Physik*, 24, 492 (1907).

[33] K. S. Krishnan and C. V. Raman, *Proc. Roy. Soc. London*, A115, 549 (1927).

dicular to the axis it is -24.1×10^{-6}. The average molar susceptibility as determined on a powder is -25.9×10^{-6}. Nitrates, carbonates, and chlorates all exhibit large values of the magnetic anisotropy,[34] in contrast to the almost complete isotropy of sulfates. This is attributed to the intrinsic anisotropy of the NO_3^-, $CO_3^=$, and ClO_3^- ions, and their parallel arrangement in the crystals. A method is given for deriving the orientation of NO_3^- and other ions from the magnetic measurements. Raman and Krishnan have also derived a relationship between the magnetic and the optical anisotropy of crystals.

Tellurium probably is not to be considered an ionic crystal, but it may be worthwhile to mention the work of Rao and Govindarajan [35] on this substance. The principal susceptibilities of single crystals of tellurium were measured over a wide temperature range. At room temperature the susceptibility of a single crystal parallel to the trigonal axis is -0.329×10^{-6} and perpendicular, it is -0.296×10^{-6}, giving an anisotropy of 1.11. Increase in temperature does not affect the susceptibility perpendicular to the trigonal axis but decreases the susceptibility parallel to it. At 220° C. the two become equal. Addition of small amounts of tin, cadmium, bismuth, or lead produces a decrease in both principal susceptibilities and in the magnetic anisotropy, which approaches unity. The number of valence electrons in the added metal

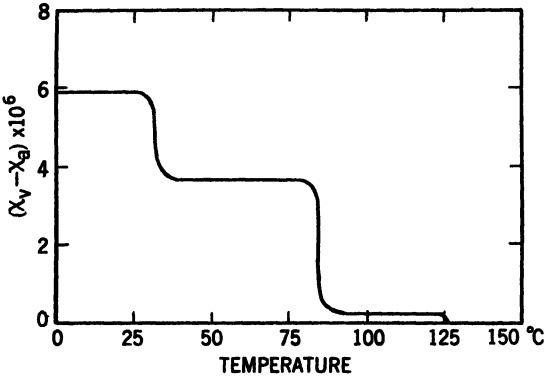


FIG. 19.—Temperature variation of diamagnetic anisotropy of ammonium nitrate.

does not seem to influence the magnitude of this effect, but the decrease in susceptibility is greater for elements of greater atomic radius. In respect to its susceptibility, tellurium behaves as a nonmetal, a conclusion

[34] K. S. Krishnan, B. C. Guha, and S. Banerjee, *Phil. Trans. Roy. Soc. London*, A231, 235 (1933).

[35] S. R. Rao and S. R. Govindarajan, *Proc. Indian Acad. Sci.*, 10A, 235 (1939).

which is supported by its large electrical resistance. It is interesting that the thermal conductivity, and the coefficient of linear expansion also have different values parallel and perpendicular to the trigonal axis.

The temperature dependence of magnetic anisotropy sometimes yields evidence which is supplementary to x-ray crystallographic studies. For instance, Nilakantan [36] has measured the temperature variation of the magnetic anisotropy of ammonium nitrate. Powder measurements [37] on this substance show only a slight and not very informative increase of susceptibility with increasing temperature. Nilakantan's work shows a marked step-wise change of magnetic anisotropy at 32°, 84°, and 125° C. corresponding to the x-ray findings of Hendricks, Posnjak, and Kracek.[38] At 125° C. the anisotropy falls to zero confirming Hendrick's postulate of free rotation and spherical symmetry of the nitrate ion above this temperature.

7. Diamagnetism of Atomic Crystals

The magnetic properties of atomic crystals such as diamond, aluminum nitride, etc., have generally been measured, but few intensive studies of such substances have been made. The mass susceptibility of diamond, -0.49×10^{-6}, is normal, and is of interest chiefly by comparison with that of graphite,[39] which is -3.5×10^{-6}. This great difference is due to the conduction electrons in graphite. Conduction electrons also contribute to the abnormal diamagnetism of silver subfluoride.[40]

[36] P. Nilakantan, *Phys. Rev.*, **52**, 383 (1937).
[37] G. E. R. Schulze, *Z. physik. Chem.*, **B40**, 308 (1938).
[38] S. B. Hendricks, E. Posnjak, and F. C. Kracek, *J. Am. Chem. Soc.*, **54**, 2766 (1932).
[39] M. Owen, *Ann. Physik*, **37**, 657 (1912).
[40] S. Freed, N. Sugarman, and R. P. Metcalf, *J. Chem. Phys.*, **8**, 225 (1940).

CHAPTER THREE

MOLECULAR DIAMAGNETISM

1. Molecular Hydrogen

The classical theory of diamagnetism has no solution for molecules containing more than one nucleus because the Larmor precession applies strictly to mononuclear systems. The quantum theory has, at least in principle, a complete solution to the problem, and one which for simple molecules like hydrogen yields a reasonably satisfactory result.

According to Van Vleck [1] the molar susceptibility of a polyatomic molecule with no resultant electron spin moment is given by

$$\chi_M = -\frac{Ne^2}{6mc^2}\sum\overline{r^2} + \frac{2}{3}N\sum_{n'\neq n}\frac{|m^0(n';n)|^2}{h\nu(n';n)}$$

where $m^0(n';n)$ is a non-diagonal element of the matrix for the angular momentum of the system, $\nu(n';n)$ is the frequency corresponding to $n';n$ transition, and the other terms have their usual significance. The susceptibility is, therefore, small and independent of temperature. The substance is either diamagnetic or feebly paramagnetic depending on which term is the larger.

Quantitative calculation of susceptibility by the above expression is difficult even for hydrogen because the wave functions are not accurately known. For hydrogen the first term is -4.71×10^{-6} and the second about $+0.51 \times 10^{-6}$, which gives a computed molar susceptibility of -4.20×10^{-6}. Experimental values range from about -3.9 to -4.0×10^{-6}, the most accurate being probably that of Havens,[2] -4.0051×10^{-6}. In view of the various uncertainties, the agreement is fairly satisfactory.

Making use of the James and Coolidge wave functions for hydrogen, Witmer [3a] has found that the average of the best calculated values lies between -3.78 and -3.90×10^{-6}. This is in slightly better agreement

[1] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*. Oxford University Press, Oxford 1932, p. 275.

[2] G. G. Havens, *Phys. Rev.*, **43**, 992 (1933).

[3a] E. E. Witmer, *Phys. Rev.*, **48**, 380 (1935); **51**, 383 (1937).

with experiment. A similar theoretical calculation [3b] for molecular deuterium gives $\chi_M = -3.93 \times 10^{-6}$.

2. Polynuclear Molecules

Theoretical calculation of susceptibilities of molecules more complex than hydrogen is in a rudimentary state. A very rough approximation may be made by a method similar to that already used for atomic hydrogen by use of appropriate screening constants and effective quantum numbers.[4]

The scarcity of theoretical results on diamagnetic susceptibility of molecules is due to the lack of knowledge about reliable wave-functions. For methane, the self-consistent field method has been explored by Buckingham, Massey, and Tibbs,[5] and the molecular-orbital and electron-pair approximate wave functions by Coulson.[6] The first method yields a molar susceptibility of -33.2×10^{-6} compared with an observed value of -12.2×10^{-6}. It is obvious that the calculated electron distributions are too diffuse. The authors believe that if the theory were extended to include exchange effects the gain would be worthwhile. The method can be applied to other molecules which possess tetrahedral or octahedral symmetry.

Coulson reports that the value found by the electron-pair method is close to that by the molecular-orbital method, and although both are less than the self-consistent field value, they are still twice the experimental value. The deviation is attributed to approximations in the wave functions. The largest influence is shown to come from the outer parts of the molecule in which the detailed form of the wave-function is known with least reliability.

Attempts to compare theoretical with experimental diamagnetic susceptibilities of even more complex molecules have led to some interesting anomalies. Farquharson [7] has, for instance, measured the susceptibilities of several sulfur compounds and compared the results with theoretical values obtained by the Pauling and Slater methods. In practically every case increasing complexity and decreasing symmetry are attended with a diminution of diamagnetism. The sum of the molar diamagnetism of water and sulfur trioxide is $-(12.96 + 28.54) \times 10^{-6}$

[3b] E. E. Witmer, *Phys. Rev.*, **58**, 202 (1940).

[4] E. C. Stoner, *Magnetism and Matter.* Methuen and Co., Ltd., London 1934, p. 467.

[5] R. A. Buckingham, H. S. W. Massey, and S. R. Tibbs, *Proc. Roy. Soc. London*, **A178**, 119 (1941).

[6] C. A. Coulson, *Proc. Phys. Soc. London*, **54**, 51 (1942).

[7] J. Farquharson, *Phil. Mag.*, (7) **14**, 1003 (1932).

$= -41.50 \times 10^{-6}$, but χ_M for sulfuric acid is -39.00×10^{-6}, a fall in diamagnetism of 2.5×10^{-6}.

An even more striking example is given by Henkel and Klemm,[8] who measured the magnetic behavior of some liquid fluorides. The experimental data are compared with Angus's [9] modification of Slater's theoretical susceptibilities in Table III. Starting with molybdenum

TABLE III

MAGNETIC SUSCEPTIBILITIES OF SOME LIQUID FLUORIDES

Compound	$\chi_M \times 10^6$	
	Observed	Calculated
SF_6	−44	−45
SeF_6	−51	−51
TeF_6	−66	−61
MoF_6	−26	−55
WF_6	−40	−66
UF_6	+43	∼−70

hexafluoride the observed susceptibilities become markedly less diamagnetic than the calculated, until with uranium hexafluoride the temperature independent paramagnetism becomes dominant and the susceptibility becomes positive. It should be pointed out that this paramagnetism is still quite small. For substances with a permanent magnetic moment the molar paramagnetism may be of the order of 5000×10^{-6}. Nevertheless the difficulty of calculating theoretical diamagnetic susceptibilities will be obvious. It should be emphasized that there is no essential difference between diamagnetic and weakly paramagnetic substances. The sign of the susceptibility depends simply on whether the negative or positive term is larger.

3. Water

Such frequent use is made of water for calibration purposes and as a solvent that some discussion of its susceptibility is justified. There have been several absolute determinations of the susceptibility of water. The two which seem to the writer to be most impressive are those of Piccard and Devaud,[10] and of Auer.[11] The former find $\chi_{20°} = -0.71992 \times 10^{-6}$ with an estimated error of 1.1 in 10,000. Auer finds $\chi_{20°}$

[8] P. Henkel and W. Klemm, *Z. anorg. allgem. Chem.*, 222, 70 (1935).

[9] W. R. Angus, *Proc. Roy. Soc. London*, A136, 569 (1932).

[10] A. Piccard and A. Devaud, *Arch. sci. phys. et nat.*, [5], 2, 455 (1920).

[11] H. Auer, *Ann. Physik*, 18, 593 (1933).

$= -0.7218 \times 10^{-6}$ with an estimated error of about 7 in 10,000. Unfortunately, the agreement is not quite as close as might be desired. But there are few cases in which susceptibilities must be known to four significant figures except for certain dilute solutions in which the relative susceptibility of solvent and solution should be known to at least four figures. Many workers arbitrarily set the gram susceptibility of water at 20° C. at -0.7200×10^{-6} for calibration purposes.

Most investigators agree that the susceptibility of water has a temperature coefficient, but there have been some astonishing disagreements as to the magnitude, and even to the sign, of the coefficient. At one time it was thought that the susceptibility of water depended on its thermal history, but this has been shown to be not true. Within the past twelve years the coefficient has been studied by Mathur,[12] Johner,[13] Cabrera and Fahlenbrach,[14] Auer,[11] Wills and Boeker,[15] and by Seely.[16] The work of Auer is particularly impressive. Using an elaborate modification of the Quincke method he obtains the following data.

TABLE IV

MASS SUSCEPTIBILITY OF WATER (AFTER AUER)

Temp. ° C.	$\chi \times 10^6$
1	−0.71896
5	.71982
10	.72067
15	.72131
20	.72183
25	.72224
30	.72258
40	.72286
50	.72361
60	.72406
70	.72454

The temperature coefficient $1/\chi_T \cdot d\chi/dT$ falls regularly from 2.9×10^{-4} at 5° C. to 0.62×10^{-4} at 70° C.

Wills and Boeker represent the susceptibility of water by the expression

$$\chi_T/\chi_{20} = 1 + (1.3 \times 10^{-4})(T - 20) - (0.7 \times 10^{-6})(T - 20)^2$$

[12] R. N. Mathur, *Indian J. Phys.*, **6**, 207 (1931).

[13] W. Johner, *Helv. Phys. Acta*, **4**, 238 (1931).

[14] B. Cabrera and H. Fahlenbrach, *Anales soc. españ. fis. quím.*, **31**, 401 (1933); *Z. Physik*, **82**, 759 (1933).

[15] A. P. Wills and G. F. Boeker, *Phys. Rev.*, **46**, 907 (1934).

[16] S. Seely, *Phys. Rev.*, **52**, 662 (1937).

The value of $1/\chi \cdot d\chi/dT$ at 20° is 1.30×10^{-4}, which is slightly higher than that reported by most others. They also suggest an anomalous region between 35° and 55° C. This is supported by Seely who finds a continuous, though irregular change of susceptibility, with temperature, with a marked change in slope at 45° C. His results agree with those of Wills and Boeker except at higher temperatures. Cabrera and Fahlenbrach [17] extend the susceptibility of water to 140° C. where $\chi = -0.727 \times 10^{-6}$, but this value is based on Cabrera's use of the rather high value -0.7220×10^{-6} for water at 20° C.

Reasons for the peculiar temperature coefficient of susceptibility for water have been examined by Cabrera and Fahlenbrach, Tammann,[18] and Sibaiya.[19] The consensus is that depolymerization of water molecules is responsible for the change. This view is supported by the observation that potassium iodide solutions all have diamagnetic susceptibilities slightly higher than those calculated by the additivity law.

Again using as standard the rather high value $\chi_{20} = -0.7220 \times 10^{-6}$, Cabrera and Fahlenbrach report the susceptibility of water at 0° C. as -0.7177×10^{-6} and of ice at the same temperature -0.7019×10^{-6}. There is considerable doubt as to the temperature coefficient of susceptibility for ice.

The diamagnetism of heavy water (D_2O) has been measured by several groups of investigators.[20–23] The susceptibility is -0.638×10^{-6} with thermal properties similar but not identical to those of ordinary water. Gray and Cruickshank claim that there is a time lag in the establishment of the correct susceptibility when either heavy or ordinary water is freshly formed from ice.

4. Temperature Dependence of Molecular Diamagnetism

Neither classical nor quantum theories suggest that diamagnetism should be anything but independent of temperature. But as has already been pointed out for water, the temperature coefficient of diamagnetism may sometimes be appreciable. Havens [2] has shown that the common diamagnetic gases such as hydrogen, helium, neon, argon, etc., have the same susceptibility at liquid air temperature as at 20° C. There is some

[17] B. Cabrera and H. Fahlenbrach, *Anales soc. españ. fís. quím.*, **32**, 525 (1934).
[18] G. Tammann, *Z. Physik*, **91**, 410 (1934).
[19] L. Sibaiya, *Current Sci.*, **3**, 421 (1935).
[20] B. Cabrera and H. Fahlenbrach, *Naturwissenschaften*, **22**, 417 (1934); *Anales soc. españ. fís. quím.*, **32**, 538 (1934).
[21] F. W. Gray and J. H. Cruickshank, *Nature*, **135**, 268 (1935).
[22] F. E. Hoare, *Nature*, **137**, 497 (1936).
[23] V. C. G. Trew and J. F. Spencer, *Nature*, **137**, 706, 998 (1936).

divergence of opinion regarding the temperature dependence of susceptibility for liquids and solids. Johner [13] and Mathur [24] report positive though small temperature coefficients for aliphatic alcohols, and negative coefficients for several alkyl and aryl iodides. Some of these results are supported by Bhatnagar, but Cabrera and Fahlenbrach [25] show that the temperature coefficient is practically zero for a large group of aliphatic alcohols, excepting *n*-octyl, dodecyl, and especially cetyl alcohol. Slight changes are observed for nitrobenzene and for *m*-cresol. Rather marked changes are observed on going from liquid to solid. These changes will be discussed in the next section. The susceptibility of super-cooled liquids has been examined by Cabrera and Fahlenbrach who find that for *o*- and for *p*- cresol the diamagnetism follows a normal extension of the susceptibility-temperature curve for the liquid.

One of the most careful examinations in this field was conducted by Boeker [26] who found no temperature dependence of susceptibility exceeding ½ per cent for carbon tetrachloride, benzene, and toluene over the temperature range 10° to 50° C. The liquids were not subjected to special purification and the writer's experience is that dissolved water may appreciably alter the apparent temperature coefficient of susceptibility for non-polar organic solvents. Boeker's work, however, is supported by that of Bhatnagar, Nevgi, and Khanna [27] on the susceptibilities of diamagnetic aromatic liquids.

The situation regarding temperature dependence of diamagnetism may be summed up about as follows: In diamagnetic gases there is no dependence. In non-polar liquids the coefficient is very small except possibly near the melting and boiling points. In polar liquids and in solids, so far as is known, the temperature coefficient is generally positive but it seldom exceeds one per cent change over a fifty degree temperature change. Such changes as are observed probably do not indicate any fault in the modern theory of magnetism but rather that slight redistributions of electron density occur, attendant on the formation of polymers and addition compounds.

5. Different Physical States

Very considerable success has been achieved in calculating susceptibilities additively from what are known as Pascal's constants. The fact that such calculations are possible suggests that diamagnetism is inde-

[24] R. N. Mathur, *Indian J. Phys.*, **6**, 207 (1931).

[25] B. Cabrera and H. Fahlenbrach, *Z. Physik*, **85**, 568 (1933); **89**, 682 (1934); B. Cabrera, *J. chim. phys.*, **37**, 86 (1940).

[26] G. F. Boeker, *Phys. Rev.*, **43**, 756 (1933).

[27] S. S. Bhatnagar, M. B. Nevgi, and M. L. Khanna, *Z. Physik*, **89**, 506 (1934).

pendent of physical state. Oxley [28] has measured the susceptibilities of a large number of organic compounds over a temperature range and finds for many substances a decrease in diamagnetism of from 3 to 13 per cent on crystallization. Mere supercooling, even to the vitreous state, did not produce any comparable diminution of diamagnetism. If Oxley's results are correct then it becomes difficult to understand the success of Pascal's constants. Cabrera and Fahlenbrach, however, support Oxley's results and in some cases find even greater changes on crystallization. They show that for many diamagnetic substances the susceptibility-temperature relation may be represented by a curve of the form shown in Fig. 20.[25] The susceptibility of the solid is substantially independent

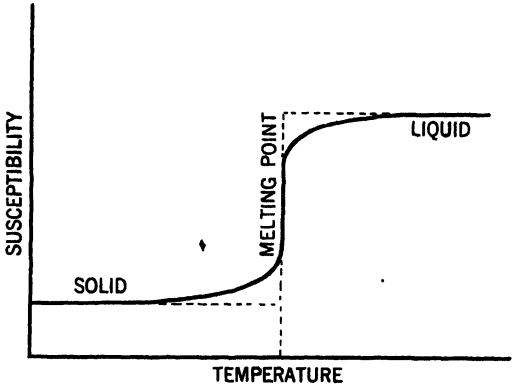


FIG. 20.—General relationship between susceptibility and temperature for a diamagnetic substance in the neighborhood of the melting point. The change in susceptibility may amount to 5 per cent or more.

of temperature until near the melting point where it begins to rise increasingly sharply as the substance melts. Finally, the susceptibility of the liquid does not reach its full value until several degrees above the melting point. This surprising effect has apparently been observed both with rising and with falling temperatures, but it is reminiscent of Trew and Spencer's claim that there is a time lag in the establishment of the correct susceptibility when water is freshly formed from ice. The effect, however, is not inconsistent with what is known of the structure of certain substances, notably water, near their freezing points. According to all workers in the field the liquids are invariably more diamagnetic than the solids, provided any change occurs. Cabrera and

[28] A. E. Oxley, *Phil. Trans. Roy. Soc. London*, **A214**, 109 (1914); **A215**, 79 (1915); **A220**, 247 (1920).

Fahlenbrach [25] suggest that there is a relationship between the dipole moment of the compound and the magnitude of the change on melting.

The change of susceptibility on melting is also supported for benzophenone and *p*-nitrotoluene,[29] but Bose [30] has reached just the opposite conclusion. He has measured susceptibilities of several organic compounds in the molten and dissolved states. The data are compared with crystal powder data of Pascal, with average susceptibilities calculated from the known principal susceptibilities, and with additive values from Pascal's constants. Bose reaches the surprising conclusion that, within the limits of experimental error (about 1 per cent) the diamagnetism of a compound is independent of its physical state, that is, whether it is a single crystal, molten liquid, or in solution. This is directly contradictory to Oxley and to some others. It should be pointed out that Bose did not actually measure both liquid and solid states himself, but relied on Pascal's measurements for the solids. Also, in those cases where Bose actually compared liquid and solution values, data are given for only seven of the twenty-seven compounds investigated, and in these seven cases the differences of susceptibility amount to over 3 per cent.

A possible explanation of Oxley's results may be that owing to the diamagnetic anisotropy of most organic crystals, preferential orientation of the micro-crystals may have taken place. Such orientation would naturally result in the smallest principal diamagnetic susceptibility lying along the lines of force. Taking everything into consideration, the writer feels that a change of diamagnetism on crystallization probably does occur. What the magnitude of that change may be we are not yet ready to state.

The question of possible changes in magnetization on vaporization has been poorly studied. Vaidyanathan,[31] with the aid of a sensitive torsion balance, investigated the vapors of a number of organic compounds. In all but two cases, carbon disulfide and benzene, the susceptibility of the vapor is the same as that for the liquid, within the rather large experimental error. Yanus and Shur [32,33] express the opinion that Vaidyanathan's anomalous results for carbon disulfide and benzene are due to experimental error. So far, therefore, as is known, there is no significant change of susceptibility on the vaporization of a diamagnetic liquid.

[29] K. C. Subramanian, *Proc. Indian Acad. Sci.*, **3A**, 420 (1936).
[30] A. Bose, *Phil. Mag.*, **21**, 1119 (1936).
[31] V. I. Vaidyanathan, *Phys. Rev.*, **30**, 512 (1927).
[32] R. I. Yanus and J. Shur, *Nature*, **134**, 101 (1934).
[33] J. Shur, *Physik. Z. Sowjetunion*, **11**, 194 (1937).

It should perhaps be mentioned that there is some evidence for decrease of diamagnetism with decreasing particle size. This seems to be true of quartz.[34] This may possibly be due to "surface paramagnetism."

6. Pascal's Constants[35]

From measurements on a very large number of compounds Pascal concluded that the susceptibilities could be represented by the expression

$$\chi_M = \sum n_A \chi_A + \lambda$$

where n_A is the number of atoms of susceptibility χ_A in the molecule, and λ is a constitutive correction depending on the nature of the bonds between the atoms. In this expression, χ_A is not the theoretical atomic susceptibility, but is a purely empirical constant derived from the measured susceptibility. At first glance this whole procedure looks rather dubious, especially in connection with λ. It cannot be denied, however, that considerable success has been achieved by use of Pascal's constants and they often afford means of estimating susceptibilities where no other methods are available. For instance, in free radicals such as the triarylmethyls, there is a substantial diamagnetic correction to be made but there is no very direct way to measure this correction.

Basic values for Pascal's constants are derived from the halogens. The constant for Cl is half the molar susceptibility of Cl_2. All of Pascal's original data refer to the susceptibility of water as -0.75×10^{-6} as standard. Values given here are therefore multiplied by 72/75 to correct his data to the modern value for water.

The method will be illustrated by a simple example: for ethyl bromide, C_2H_5Br, the molar susceptibility is given by $2\chi_C + 5\chi_H + \chi_{Br} + \lambda$. In this case λ is the constitutive correction for the $-\overset{|}{\underset{|}{C}}-Br$ bond. The magnitude of these quantities is as follows:

$$\{-[(2 \times 6.00) + (5 \times 2.93) + 30.6] + 4.1\} \times 10^{-6} = -53.1 \times 10^{-6}$$

The observed molar susceptibility is -53.3×10^{-6}. Pascal's constants are most useful for organic compounds and the values for the metals are probably doubtful. A partial list of constitutive corrections is given in Table VI.

[34] Y. Shimizu and N. Takatori, *Science Repts. Tôhoku Imp. Univ.*, K. Honda Anniversary Vol., First Ser., **1936**, 306.

[35] P. Pascal, *Ann. chim. phys.*, **19**, 5 (1910); **25**, 289 (1912); **29**, 218 (1913). *Compt. rend.*, **147**, 56, 242, 742 (1908); **148**, 413 (1909); **150**, 1167 (1910); **152**, 862, 1010 (1911); **156**, 323 (1913); **158**, 37 (1914); **173**, 144 (1921); **176**, 1887 (1923); **177**, 765 (1923); **180**, 1596 (1925).

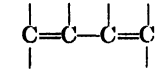
TABLE V

PASCAL'S CONSTANTS FOR THE ELEMENTS

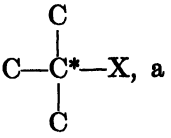
H		−2.93	P	−26.3
C		−6.00	As	−43
N	open chain	−5.57	Sb^{+3}	−74
N	ring	−4.61	Bi	−192
N	monoamide	−1.54	Li	−4.2
N	diamide, imide	−2.11	Na	−9.2
O	alcohol,.ether	−4.61	K	−18.5
O	aldehyde, ketone	+1.73	Mg	−10
O	carboxyl group	−3.36	Ca	−15.9
F		−11.5	Al	−13
Cl		−20.1	Zn	−13.5
Br		−30.6	Hg^{+2}	−33
I		−44.6	Si	−20
S		−15.0	Sn^{+4}	−30 ?
Se		−23.0	Pb	−46
Te		−37.3		

TABLE VI

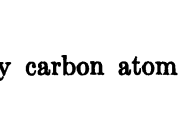
CONSTITUTIVE CORRECTION CONSTANTS

		+5.5
		+10.6
		+0.8
cyclohexane		+3.0
		+1.8
		+8.2
	(each carbon atom as a member of one aromatic ring)	−0.24
	(each carbon atom as a member of two aromatic rings)	−3.1
		+3.1
		+4.1
		+4.1

Pascal also found that the position of oxygen with respect to carbon atoms in the molecule introduced another constitutive correction. He referred to "tertiary" and "quaternary" (C_3 and C_4) carbon atoms as those in which three or four valences respectively are attached to carbon, regardless of the actual number of surrounding carbon atoms. For instance, a tertiary carbon atom is the one designated in the group,



, a quaternary carbon atom

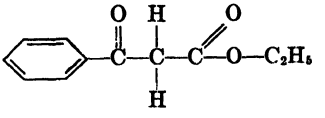


. A tertiary carbon atom in the alpha position with respect to an oxygen group is designated C_3^{α}. This notation is not common to organic chemistry. The magnitude of these constitutive corrections is shown in Table VII.

TABLE VII

Group	Correction
C_2^{α}, C_3^{γ}, C_3^{δ}, C_3^{ϵ}	−1.29
C_4^{α}, C_4^{γ}, C_4^{δ}, C_4^{ϵ}	−1.54
C_3^{β}, C_4^{β}	−0.48

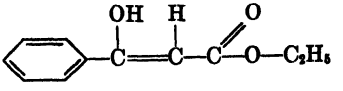
A somewhat more complicated application of Pascal's constants will now be given. Ethyl benzoyl acetate may exist in either keto or enol forms. The susceptibility of the keto form is as follows:



$$\chi_M \times 10^6 = 11\chi_C + 12\chi_H + \chi_{O(ket.)} + \chi_{O(carbox.)} + \chi_{O(alc.)} + 6\lambda_{C(aro.)} + \lambda_{C_4^{\alpha}} + \lambda_{C_4^{\gamma}}$$

$$= (11 \times 6.00) + (12 \times 2.93) - 1.73 + 3.36 + 4.61 + (6 \times 0.24) + 1.54 + 1.54 = 111.9$$

The susceptibility of the enol form is:



$$\chi_M \times 10^6 = 11\chi_C + 12\chi_H + \chi_{O(carbox.)} + 2\chi_{O(alc.)} + 6\lambda_{C(aro.)} + \lambda_{C=C} + \lambda_{C_4^{\alpha}} + \lambda_{C_4^{\gamma}} + \lambda_{C_3^{\beta}} + \lambda_{C_3^{\alpha}} + \lambda_{C_3^{\alpha}}$$

$$= (11 \times 6.00) + (12 \times 2.93) + 3.36 + (2 \times 4.61) + (6 \times 0.24) - 5.5 + 1.54 + 1.54 + 0.48 + 1.29 + 1.29 = 115.8$$

The measured molar susceptibility for ethyl benzoyl acetate is − 115.2

$\cdot \times 10^{-6}$. The magnetic evidence, therefore, supports the view that this compound is largely enolic.

An extensive discussion of Pascal's constants is given by Bhatnagar and Mathur.[36] Tables and critical discussion are also given by Gray and Farquharson.[37]

It may be predicted that a homologous series of organic compounds should have a susceptibility which is a linear function of the number of methylene groups. This is approximately true as found for many such series by Pascal, and more recently by Woodbridge [38] for a group of alkyl acetates, and by Bhatnagar and Mitra [39] for fifteen hydrocarbons, and for twenty-nine oxygenated, thirteen halogenated, nineteen nitrogenous, and five acetylenic compounds. Farquharson and Sastri [40a] have measured the susceptibilities of butyric, valeric, caproic, heptylic, and caprylic acids. Pascal's original constant for the CH_2 group was -11.86×10^{-6}, but Bhatnagar and Mitra favor -11.36×10^{-6}, while Farquharson and Sastri recommend $(-11.64 \pm 0.026) \times 10^{-6}$. The true value for the —CH_2— increment is probably close to -11.68×10^{-6}.[40b] It is perhaps scarcely valid to draw such conclusions from measurements on one particular homologous series or even from one class of compounds. For instance Nevgi [41] finds that the susceptibilities of the sodium and potassium salts of higher fatty acids are all lower than those calculated by Pascal's law. He ascribes this to the formation of micelles consisting of large particles of colloidal dimensions built of a large number of monomeric anions of the fatty acid containing alkali metal ions as well.

Organic isomers might be expected to have identical molar susceptibilities and certainly this is true to a first approximation. Some small differences have been reported from time to time and their significance is discussed by Bhatnagar and Mathur. A possible slight difference is reported by Byerly and Selwood [42a] for *cis* and *trans* decalin (decahydronaphthalene). The *cis* compound has a gram susceptibility of -0.744 and the *trans* -0.779×10. The results suggest that the second term in Van Vleck's expression for molecular diamagnetism may be slightly larger in the *cis* form in which the atomic orbits are slightly

[36] S. S. Bhatnagar and K. N. Mathur, *Physical Principles and Applications of Magnetochemistry*. MacMillan and Co., Ltd., London 1935, p. 67.

[37] F. W. Gray and J. Farquharson, *Phil. Mag.*, **10**, 191 (1930).

[38] D. B. Woodbridge, *Phys. Rev.*, **48**, 672 (1935).

[39] S. S. Bhatnagar and N. G. Mitra, *J. Indian Chem. Soc.*, **13**, 329 (1936).

[40a] J. Farquharson and M. V. C. Sastri, *Trans. Faraday Soc.*, **33**, 1472 (1937).

[40b] W. R. Angus, *Ann. Repts.*, **1941**, 32.

[41] M. B. Nevgi, *J. Univ. Bombay*, **7**, Part 3, 74 (1938).

[42a] W. Byerly and P. W. Selwood, *J. Am. Chem. Soc.*, **64**, 717 (1942).

more distorted than in the *trans* form. Similar measurements on the isomeric butyl alcohols have been made by Cabrera and Colson.[42b]

Pascal's data have given many indications of their reliability. They fit well together into a system and in many cases have been confirmed by experimental methods entirely different from those of Pascal. The usefulness of the constants is undeniable, and yet the whole system is empirical. It is not surprising therefore that efforts have been made to put the constants on a theoretical basis. Such an attempt has been made by Gray and Cruikshank[43a] who relate Pascal's constants to Pauling's theoretical atomic susceptibilities, and the constitutive correction in part to Van Vleck's temperature independent high frequency paramagnetism. The method gives promise and has been applied successfully to certain structural problems which will be discussed in section 9 of this chapter. It is to be hoped that this or analogous methods will be developed to the point where they can be used by chemists with the same confidence and ease with which molar refractivities are used.

7. Diamagnetism of Molecular Mixtures

It is well known that the dielectric polarization of polar liquids is greatly modified by association and other effects, and it might be concluded that similar phenomena would be found in the magnetic analog. This matter is reviewed up to 1934 by Stoner (*op. cit.*,[4] p. 474), and it must be admitted that, in spite of considerable research, the outlook has not been clarified much in the past nine years.[43b] Investigators seem to be divided into three groups, those who find wide positive deviations, those who find wide negative deviations, and those who find the susceptibility to be a strictly linear function of the concentration, all, of course, working with the same solutions. Garssen,[44] working with solutions of acetone-nitrobenzene, and acetone-*p*-nitroaniline found deviations from additivity amounting to as much as 17 per cent. On the other hand Rao and Varadachari[45] measured the susceptibilities of binary solutions of acetone mixed with benzene, chloroform, and nitrobenzene, all over the temperature range 15° to 50° C. In all cases the susceptibility was

[42b] B. Cabrera and H. Colson, *Compt. rend.*, **213**, 108 (1941). See also W. R. Angus, ref. 40*b*.

[43a] F. W. Gray and J. H. Cruikshank, *Trans. Faraday Soc.*, **31**, 1491 (1935).

[43b] F. v. Rautenfeld and E. Steurer, *Z. physik. Chem.*, **B51**, 39 (1941). This paper on "Intermolecular forces and diamagnetism of organic molecules" was unfortunately not available to the writer.

[44] J. E. Garssen, *Compt. rend.*, **196**, 541 (1933).

[45] S. R. Rao and P. S. Varadachari, *Proc. Indian Acad. Sci.*, **1A**, 77 (1934).

strictly additive. Further work by Rao,[46] who used a different method, shows strict linearity within the experimental error (0.2%) for solutions of acetone with benzene, chloroform, acetic acid, and aniline, and benzene with acetic acid and with nitrobenzene. He discusses possible reasons for the discrepancies between results of various investigators. Salceanu and Gheorghiu [47] also find the susceptibility of acetone-nitrobenzene mixtures to be additive.

One of the most accurate studies of this problem has been reported by Seely [48] who investigated binary combinations of carbon tetrachloride, benzene, and nitrobenzene. His results seem accurate to at least 0.1 per cent, that is, somewhat better than those of Rao. The mixture benzene-nitrobenzene shows no deviations within the experimental error, but the other two mixtures show deviations amounting to over 0.5 per cent. (Fig. 21). Reasons for these departures from linearity are ob-

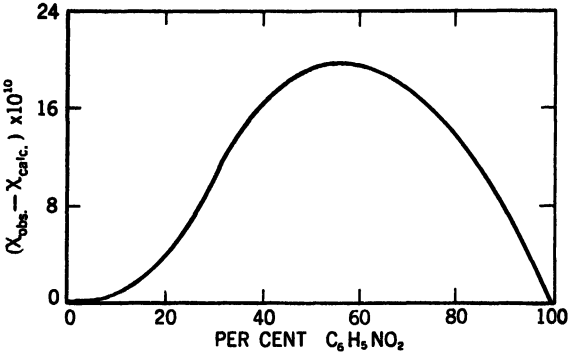


FIG. 21.—Deviation from linearity of the susceptibility-concentration relationship for a mixture of nitrobenzene and carbon tetrachloride.

scure. Seely points out that the temperature coefficient of susceptibility for nitrobenzene is zero, consequently molecular association cannot account for the effects he observes.

Trew and Spencer [49] have studied the magnetic susceptibility, density, refractive index, heat of mixing, and specific heat of several binary mixtures of organic compounds. The mixtures and magnetic results are shown in Table VIII. They point out that molar susceptibilities are more nearly additive than any other property investigated.

[46] S. R. Rao, *Indian J. Phys.*, **8**, 483 (1934).
[47] C. Salceanu and D. Gheorghiu, *Compt. rend.*, **200**, 120 (1935).
[48] S. Seely, *Phys. Rev.*, **49**, 812 (1936).
[49] V. C. G. Trew and J. F. Spencer, *Trans. Faraday Soc.*, **32**, 701 (1936).

TABLE VIII

ADDITIVITY OF SUSCEPTIBILITY FOR BINARY MIXTURES

Mixture	Maximum % deviation from additivity
benzene—toluene	0.1
benzene—*m*-cresol	0.1
toluene—*m*-cresol	0.1
aniline—nitrobenzene	0.1(5)
aniline—*m*-cresol	<0.1
nitrobenzene—*m*-cresol	<0.1

There is good evidence that formic acid-water mixtures show deviations from linearity. Rao and Sriraman [50] find a deviation of 5 per cent at a concentration of approximately 70 per cent acid. They suggest that the deviation is due to formation of a monohydrate, or possibly to breaking up of double molecules of acid. The question is further reported on by Rao and Narayanaswamy [51a] who measured binary mixtures of formic and of acetic acids with water, methanol, ethanol, acetone, and diethyl ether. For each combination a series of mixtures was used in which the concentration of acid varied from 0 to 100 per cent in ten or fifteen steps. Refractive indices and relative densities were also determined. These two properties show greater deviations from the simple additivity law than does the magnetic susceptibility, although it, too, is not strictly additive. Deviations from additivity are also found for solutions of nitric acid,[51b] and of iodic acid,[51c] in water.

The susceptibility of pyridine-acetic acid mixtures has been studied by Venkataraman.[52] Maximum deviation occurred in a mixture containing 60 mol per cent acetic acid where the calculated susceptibility was -0.569×10^{-6} and the observed -0.588×10^{-6}. He accounts for this deviation by the fact that both acetic acid and pyridine are polar, associated, and asymmetrical, and suggests that a complex is formed containing three molecules of acetic acid and one of pyridine.

About the only conclusion to be drawn from these varied reports is that the deviations from additivity among mixtures of diamagnetic liquids are not large; that where obvious chemical changes take place some deviations may occur; and that there is no parallel between the dielectric and magnetic properties of binary liquid mixtures. Perhaps the latter conclusion is not a fair one because the marked deviations in

[50] S. R. Rao and S. Sriraman, *J. Annamalai Univ.*, **7**, 187 (1938).
[51a] S. R. Rao and A. S. Narayanaswamy, *Proc. Indian Acad. Sci.*, **9A**, 35 (1939).
[51b] S. P. Ranganadhan and M. Qureshi, *Current Sci.*, **4**, 404 (1935).
[51c] M. R. Nayar and N. K. Mundle, *Current Sci.*, **10**, 76 (1941).
[52] S. Venkataraman, *J. Indian Chem. Soc.*, **17**, 297 (1940).

the dielectric case occur only for molecules with a permanent moment. But, as will be shown later, even mixtures of paramagnetic molecules are approximately linear with concentration in this respect.

8. Magnetic Studies of Polymerization

The dimerization of free radicals and of other paramagnetic molecules is one of the most fruitful fields for magnetochemical research. But another promising field, the polymerization of diamagnetic molecules, has received comparatively little attention. Most of the work that has been done is due to Farquharson [53] who shows that under favorable circumstances magnetic measurements may be used to determine the degree of polymerization.

When polymerization takes place between two molecules $2B \rightarrow B_2$, the molar susceptibility of the dimer $\chi_M = 2\chi_B + \lambda$, where λ is Pascal's constitutive constant for the formation of a new bond. If n molecules react to form B_n, then $\chi_M = n\chi_B + (n - 1)\lambda$, and the relationship between χ_M and n will be a straight line. The mass susceptibility of the complex is

$$\chi = \frac{n\chi_B + (n - 1)\lambda}{nM_B}$$

where M_B is the molecular weight of the monomer. The curve for change of χ with n will then be a hyperbola. For certain compounds, notably

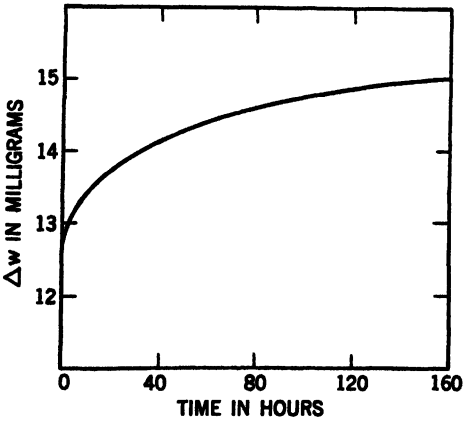


FIG. 22.—Polymerization of 2,3-dimethylbutadiene. The figure shows the apparent change in weight, Δw, as measured on a Gouy balance, plotted against time.

2,3-dimethylbutadiene, this is actually the case. If something is known regarding the mode of formation of the polymer, λ may be estimated from

[53] J. Farquharson, *Trans. Faraday Soc.*, 32, 219 (1936).

Pascal's data. Hence by measurements of susceptibility it is possible to find n, the number of molecules in the polymer. Where n is not large its value may be found with considerable accuracy. Farquharson's results for 2,3-dimethylbutadiene are shown in Fig. 22. The initial susceptibility, of the monomer, is -0.670×10^{-6} and the final, after polymerization, -0.7305×10^{-6}. The general shape of the curve is consistent with other evidence as to the course of polymerization. Another compound investigated is cyclopentadiene the susceptibility of which changes from -0.717×10^{-6} to -0.680×10^{-6} after 41.5 hours of heating. Whether the change of diamagnetism on polymerization is positive or negative depends, of course, on the nature of the bonds ruptured and formed during the reaction. Results are also given for cyanogen chloride and for nitrosobenzene.

A further investigation by Farquharson[54] has been made on the mechanism of formation of polyoxymethylenes. The formula previously given

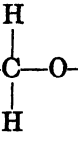
$$\chi = \frac{n\chi_B + (n-1)\lambda}{nM_B}$$

may also be written

$$\chi = \frac{\chi_B + (n-1)\chi_C}{nM_B}$$

where χ_C is the susceptibility of the group which is added each time to give the next higher polymeride. This is true because λ, the constitutive bond correction, is simply $\chi_C - \chi_B$. In a homologous series nM_B becomes $M_B + (n-1)M_C$ where M_B is the molecular weight of the first member of the series, and M_C the molecular weight of the added group. The mass susceptibilities of a homologous series are then given by

$$\chi = \frac{\chi_B + (n-1)\chi_C}{M_B + (n-1)M_C}$$

Hence for polymerization proceeding by regular addition of a known group it should be possible to estimate n from magnetic data. Farquharson has determined the Pascal constant of the  group as -14.9×10^{-6} from measurements on the oxymethylene diacetates. It is worth mentioning that this value is different from the value, -16.6×10^{-6}, for the group, although Pascal's method would give the same sus-

[54] J. Farquharson, *Trans. Faraday Soc.*, **33**, 824 (1937).

ceptibility for each group. The mass susceptibility of the —CH_2O— group is then -0.496×10^{-6}.

If the polyoxymethylenes are long chains of the form

$$H—O—CH_2—O—CH_2—O—CH_2—O-------CH_2OH$$

made up of many —CH_2O— units, then with increasing polymerization the susceptibility should approach the value -0.496×10^{-6}. Good (referred to by Farquharson) has measured the magnetic susceptibilities of several polyoxymethylenes and obtains the values shown in Table IX.

TABLE IX

MAGNETIC SUSCEPTIBILITIES OF POLYOXYMETHYLENES

	$-\chi \times 10^6$
α polyoxymethylene	0.503
β "	.501
γ "	.467
δ "	.417

Farquharson therefore concludes that only the α and β polyoxymethylenes are long chain compounds of this type and that the others are probably fundamentally different. Estimates of the number of molecules in the polymer give for the α-polyoxymethylene $n = 32$; for the β, $n = 44$.

Bhatnagar, Nevgi, and Mathur [55] have investigated several dimers and condensation polymers. Their results are summarized in Table X.

TABLE X

MAGNETIC SUSCEPTIBILITIES OF SOME POLYMERS

	$-\chi \times 10^6$
anthracene	0.726
dianthracene	.574
acetone	.583
diacetone alcohol	.539
benzaldehyde	.591
benzylbenzoate	.566
benzoin	.554
furfural	.498
furoin	.456
acetylcyanide	.481
diacetylcyanide	.46

In all the above cases the diamagnetism of the polymer is smaller than that of the monomer. The polymerization of anthracene has also been

[55] S. S. Bhatnagar, M. B. Nevgi, and R. N. Mathur, *Z. Physik*, 100, 141 (1936).

investigated by Farquharson and Sastri,[56] and by Bhatnagar, Kapur, and Kaur.[57]

A magnetic study of the polymerization of styrene has been made by the latter group.[58] After 16 hours of heating in vacuum the diamagnetism rose from -0.6575 to -0.7112×10^{-6}. In the presence of oxygen the

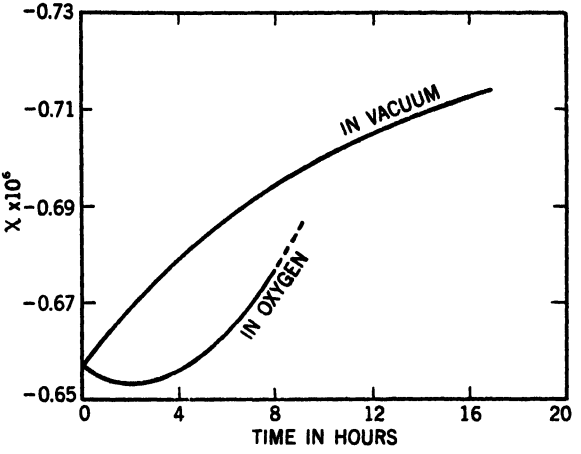


FIG. 23.—Polymerization of styrene, in vacuum and in the presence of oxygen.

diamagnetism first falls for a few hours then rises again. The authors interpret this behavior in terms of formation of peroxides which have a rather low diamagnetism. The results are discussed in connection with various theories of polymerization.

The polymerization of thiocyanogen has been studied by Bhatnagar, Kapur, and Khosla.[59] Fresh 0.5 *N* solutions in carbon disulfide and in bromoform are diamagnetic indicating dimerization to $(SCN)_2$, but solutions in carbon disulfide and in cyclohexane become paramagnetic, suggesting the existence of SCN molecules, or at least of $(SCN)_n$ groups where n is an odd number.

It is well known that uncatalyzed polymerizations are often preceded by an induction period, and it has been suggested that the polymerization nuclei are free radicals. As free radicals are paramagnetic they should

[56] J. Farquharson and M. V. C. Sastri, *Current Sci.*, 9, 135 (1940).

[57] S. S. Bhatnagar, P. L. Kapur, and Miss Gurbaksh Kaur, *J. Indian Acad. Sci.*, 10A, 468 (1939).

[58] S. S. Bhatnagar, P. L. Kapur, and Miss Gurbaksh Kaur, *J. Indian Chem. Soc.*, 17, 177 (1940).

[59] S. S. Bhatnagar, P. L. Kapur, and B. D. Khosla, *J. Indian Chem. Soc.*, 17, 529 (1940).

be easily detected provided the concentration is high enough. Farquharson and Ady [60] have repeated the examination of 2,3-dimethylbutadiene both in the presence and absence of benzoyl peroxide as an accelerator. In the complete absence of accelerator there is an induction period of about 3 hours during which the diamagnetic susceptibility falls about 13.6 per cent. The susceptibility then rises in the normal fashion. In the presence of sufficient accelerator the susceptibility curve rises smoothly throughout the experiment.

If the induction period actually involves formation of free radicals it should be possible to estimate their concentration. Assuming that each free radical has one unpaired electron, it may be shown (Chap. V) that the molar paramagnetism produced is about 1270×10^{-6} at room temperature. The susceptibility of dimethylbutadiene is about -0.75×10^{-6}, with χ_M = about -61.5×10^{-6}. The molar susceptibility of the free radical will therefore be $(1270 - 61.5) \times 10^{-6}$, and the mass susceptibility about 14.7×10^{-6}. Hence the concentration of free radical necessary to produce a 13.6 per cent fall in diamagnetism is about 0.7 per cent by weight. Farquharson and Ady, using the same data, reach a somewhat smaller concentration of free radical by a method which the writer must admit he cannot follow. It is interesting that the concentration of accelerator necessary to produce a smooth curve of susceptibility *vs.* time is about the same as the calculated concentration of free radical.

It would seem that a valuable extension of this work would be to prepare a polymerizing quantity of dimethylbutadiene and to cool it down to liquid air temperature. If any free radicals are actually present their greatly enhanced paramagnetism at $-190°$ C. should make them very easy indeed to detect.

9. Miscellaneous Structural Problems

In an earlier section it was pointed out that Gray and Cruikshank [43a] had attempted a theoretical interpretation of Pascal's constants. They have elaborated this into a rather useful tool for determination of structure. In brief, the method consists of comparing experimental susceptibilities with those derived theoretically from different possible structures. Most of the applications of this method are due to Clow.[61] The nature of the calculations will be indicated by reference to urea and its derivatives. It is first necessary to estimate the residual charges on the atoms due to unequal sharing of bond electrons. This may be done as described

[60] J. Farquharson and P. Ady, *Nature*, **143**, 1067 (1939).

[61] A. Clow, *Trans. Faraday Soc.*, **33**, 381 (1937).

by Sidgwick.[62] For the carbamide structure of urea, the atoms are found

$$H_2N : \underset{\cdot\cdot}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{C}}}} : NH_2$$
$$\quad\quad\quad

Clow and his co-workers [64, 65] have also used this method to study the resonance structures of carbon dioxide, carbon oxysulfide, carbon disulfide, several thioureas, and a rather large number of sulfur compounds.[66, 67]

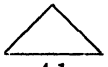
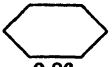
Farquharson and Sastri [68] have investigated the effect of ring closure on magnetic susceptibility. Constitutive corrections for various rings are given by Pascal but for one reason and another are not particularly accurate. The difference in diamagnetism between saturated cyclic compounds and corresponding saturated open chains must be due to:

(*1*) loss of two H atoms
(*2*) loss of two C—H bonds
(*3*) formation of one C—C bond
(*4*) possible distortion of tetrahedral symmetry, change of C—C bond distance, etc.

The change may be represented

$$\chi_{\text{cyclic}} = \chi_{\text{open}} - 2\chi_{\text{H}} + \lambda$$

Measurements were made on *n*-hexane, cyclopropanecarboxylic acid, cyclobutanecarboxylic acid, cyclopentanecarboxylic acid, cyclohexanecarboxylic acid, cyclohexane, cyclohexanol, cyclohexanone, and cycloheptanone. The following constitutive corrections are calculated.

Ring				
λ	4.1	3.05	− 0.98	0.86

A somewhat similar problem is ring closure by hydrogen bonding. A preliminary report on diamagnetism and the hydrogen bond has been made by Angus and Hill.[69a] It should be mentioned, of course, that the slight temperature coefficient of susceptibility found for water may be due to breaking up of hydrogen bonds. Angus and Hill have measured various concentrations of benzoic, salicylic, *p*- and *m*-hydroxybenzoic acids, and nitrophenol in benzene, chloroform, ethanol, and ethyl acetate. The results are rather inconclusive but seem to indicate that ring-formation is attended with a decrease of diamagnetism, while open-chain addition compounds are formed with an increase of diamagnetism. The interpretation is criticized by Mrs. Lonsdale, and by Venkataramiah.[69b]

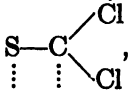
[64] A. Clow and J. M. C. Thompson, *Nature*, **138**, 802 (1936).
[65] A. Clow, *Trans. Faraday Soc.*, **34**, 457 (1938).
[66] A. Clow and J. M. C. Thompson, *Trans. Faraday Soc.*, **33**, 894 (1937).
[67] A. Clow, H. M. Kirton, and J. M C. Thompson, *Trans. Faraday Soc.*, **36**, 1018 (1940).
[68] J. Farquharson and M. V. C. Sastri, *Trans. Faraday Soc.*, **33**, 1474 (1937).
[69a] W. R. Angus and W. K. Hill, *Trans. Faraday Soc.*, **36**, 923 (1940).
[69b] H. S. Venkataramiah, *J. Mysore Univ.*, Sect. B, Contrib. 10 in Phys. **3**, Part 4, 19 (1942). This paper was not available to the writer.

Dharmatti [70–72a] has examined the structure of a rather large number of sulfur, selenium, and tellurium compounds. The method is to compare experimental susceptibilities with theoretical values obtained by modifications of the Slater and Angus methods. Compounds investigated are: sulfur monochloride, monoiodide, dichloride, thionyl chloride, sulfuryl chloride, chlorsulfonic acid, selenium monobromide, chloride, selenous acid, silver selenite, selenium oxychloride, tellurous acid, tellurium dichloride, dibromide, telluric acid dihydrate, dimethyl tellurium diiodide, and dimethyl tellurium dichloride.

Similar studies on basic beryllium acetate and on beryllium acetylacetonate have shown the absence of single electron bonds in such compounds.[72b]

The diamagnetism of phosphorus has been studied by Rao and Aravamudachari.[73] They examined solid white phosphorus and solutions of phosphorus in carbon disulfide ranging from 3 to 22 per cent by weight. The susceptibility of the solutions is greater than that calculated from the additivity law. The difference is nearly constant at lower concentrations and somewhat less at higher. This deviation is ascribed to the disappearance on solution of forces assumed to act between P_4 molecules in the solid.

The diamagnetic susceptibilities of mercury in various states of combination are given by Bhatnagar, Nevgi and Ohri.[74] Theoretical implications regarding different types of linkage are described at length.

The question of phototropy and photochemical isomerism has been studied from the magnetic standpoint by Bhatnagar, Kapur and Hashmi.[75a] They investigated twenty-three organic compounds which undergo reversible phototropic changes on exposure to light. In most cases there was no change of magnetic susceptibility, but thiophosgene and cinnamylidenemalonic acid showed definite changes. For the former, for instance, the original red substance has a susceptibility of -0.4401×10^{-6}, while after exposure to light the white compound had a susceptibility of -0.3914×10^{-6}. No evidence was obtained, however, for a paramagnetic free biradical,  , as an intermediate product. As a matter

[70] S. S. Dharmatti, *Proc. Indian Acad. Sci.*, **13A**, 359 (1941).

[71] M. Prasad and S. S. Dharmatti, *Proc. Indian Acad. Sci.*, **12A**, 185 (1940).

[72a] S. S. Dharmatti, *Proc. Indian Acad. Sci.*, **12A**, 212 (1940).

[72b] W. R. Angus and J. Farquharson, *Proc. Roy. Soc. London*, **A136**, 579 (1932).

[73] S. R. Rao and S. Aravamuthachari, *Proc. Indian Acad. Sci.*, **12A**, 361 (1940).

[74] S. S. Bhatnagar, M. B. Nevgi, and G. L. Ohri, *Proc. Indian Acad. Sci.*, **9A**, 86 (1939).

[75a] S. S. Bhatnagar, P. L. Kapur, and M. S. Hashmi, *J. Indian Chem. Soc.*, **15**, 573 (1938).

of fact, from what we now know regarding biradicals, the formation of such a compound as that above is most improbable. The authors lean to the "change of aggregation" theory as responsible for the change of color. Other theories are discussed.

Other magnetic studies of reversible phototropic change have been made on 4-hydroxy-α-naphthyliminocamphor,[75b] and on *p*-dimethylamino- and *p*-diethylaminophenyliminocamphor.[75c]

The diamagnetism of different-colored solutions of iodine has been studied by Courty [76a] who finds that violet and brown solutions of iodine in organic solvents obey the additivity rule, while red and red-brown solutions do not. This difference is proposed as a method of determining the purity of solvents. Iodine dissolved in cyclohexane has a much smaller diamagnetism than it has in other solvents such as benzene.[76b] This appears to be true of the other halogens as well.[76c]

Bhagavantam [77] has investigated a possible relationship between electric polarizability and diamagnetic susceptibility.[78]

The change of diamagnetism on the death of living cells is discussed by Bauer and Raskin.[79] Bauer has suggested that life depends on an excited state of protein molecules in the protoplasm. Hence on death the paramagnetic component of susceptibility should diminish. Actually in yeast cells and in certain bacteria, (*B. coli* and *B. proteus*) an increase of diamagnetism amounting to 4 per cent was found. This change is independent of the way the cells are killed. Cooling with liquid air produced the same effect. Denaturation of native protein did not affect the magnetic susceptibility. If these observations can be substantiated they suggest an approach to a very fundamental problem.

10. Diamagnetic Anisotropy of Molecular Crystals

Within the past few years determination of principal susceptibilities in the crystal has become a useful tool in structural chemistry. This is particularly true for aromatic compounds which often show striking magnetic anisotropy. The information obtainable from magnetic data sometimes greatly simplifies determination of crystal structure by x-ray methods. The anisotropy which is observed experimentally is due, first,

[75b] M. Singh and A. Singh, *J. Indian Chem. Soc.*, 17, 604 (1940).

[75c] M. Singh and T. R. Datt, *J. Indian Chem. Soc.*, 19, 130 (1942). This paper was not available to the writer.

[76a] C. Courty, *Bull. soc. chim. Mém.*, 5, 84 (1938).

[76b] S. S. Bhatnagar and C. L. Lakra, *Indian J. Phys.*, 8, 43 (1933).

[76c] S. R. Rao and S. R. Govindarajan, *Proc. Indian Acad. Sci.*, 15A, 35 (1942).

[77] S. Bhagavantam, *Indian J. Phys.*, 7, 617 (1933).

[78] J. P. Vinti, *Phys. Rev.*, 41, 813 (1932).

[79] E. Bauer and A. Raskin, *Nature*, 138, 801 (1936).

to the anisotropy of the individual molecules, and second, to their orientation in the crystal. If any two of these properties is known, or can be estimated, the third can be found.

A semi-technical review of this field is given by Mrs. Lonsdale.[80] A theory of magnetic anisotropy of cubic crystals at the absolute zero is given by van Peype,[81] and a theory of diamagnetic anisotropy of acyclic molecules by Neugebauer.[82] But, as mentioned before, the chief application is to aromatic compounds.

It was observed by Raman and Krishnan [83] that the principal susceptibility of benzene normal to the plane of the ring is more than twice that in the plane. The phenomenon appears to be general in aromatic compounds and is sometimes developed to a pronounced degree. It will be recalled that classical theory of diamagnetism permits a reasonably accurate calculation of atomic radius from susceptibility. Even for polyatomic molecules a fair estimate of molecular radius may be made by application of the Langevin formula. This is definitely not true, however, for aromatic compounds. Failure of the theory to hold, even approximately, for aromatic compounds is related to the strong magnetic anisotropy shown by these substances.

Reasons for this behavior on the part of aromatic molecules have been stated qualitatively by Hückel,[84] and by Ubbelohde,[85] and quantitatively by Pauling,[86] by London,[87] and Brooks.[88] In aromatic compounds the probability is that certain electrons are not restricted to individual atoms, but flow all around the ring. According to Pauling one (p) electron per aromatic carbon atom is free to move between adjacent carbon atoms under the influence of the impressed field. Molecules containing several condensed aromatic rings show an increase of principal susceptibility normal to the plane of the rings. It might be expected, therefore, that the effect would reach a maximum with graphite, and such is the case. Krishnan [89] reports the two principal molar susceptibilities of graphite as -5×10^{-6} in the plane, and -275×10^{-6} normal to the plane. Ubbelohde points out the relation between this effect and the theory of

[80] K. Lonsdale, *Science Progress*, **32**, 677 (1938).
[81] W. F. van Peype, *Physica*, **5**, 465 (1938).
[82] Th. Neugebauer, *Z. Physik*, **115**, 678 (1940).
[83] C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc. London*, **A113**, 511 (1927).
[84] E. Hückel, *Z. Physik*, **83**, 632 (1933).
[85] A. R. Ubbelohde, *Nature*, **132**, 1002 (1933).
[86] L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).
[87] F. London, *Compt. rend.*, **205**, 28 (1937); *J. phys. radium*, **8**, 397 (1937); *J. Chem. Phys.*, **5**, 837 (1937).
[88] H. Brooks, *J. Chem. Phys.*, **8**, 939 (1940); **9**, 463 (1941).
[89] K. S. Krishnan, *Nature*, **133**, 174 (1934).

metallic conduction, which is, of course, shown by graphite. It is interesting that the anisotropy and the average susceptibility of graphite are reported to decrease with decreasing size of crystal grain.[90, 91]

Further theoretical work on the diamagnetic anisotropy of aromatic molecules is reported by Squire [92] and by König.[93]

Interpretation of magnetic anisotropy in terms of crystal structure is due to Krishnan.[94–96] The actual computations are complex and reference should be made to the original literature for details. A few remarks will be made on certain of the interpretations.

It is unfortunately true that the higher the symmetry of the crystal, the less information may be found. A rather favorable case is hexamethylbenzene which is triclinic and is shown by x-ray methods to have the molecules lying in layers parallel to a natural cleavage face. One of the principal magnetic axes, for which the molar susceptibility (χ_3) is -163.8×10^{-6}, is perpendicular to this face and hence to the plane of the benzene ring. This is a result which is typical of plane aromatic molecules. The susceptibility χ_3 is numerically much larger than either of the other two susceptibilities χ_1 and χ_2, which are perpendicular to χ_3 and therefore lie in the plane of the ring. Surprisingly χ_1 and χ_2 are not quite equal, $\chi_1 = -101.1$ and $\chi_2 = -102.7 \times 10^{-6}$, and their directions do not bear any simple relationship to the geometric form of the benzene nucleus. An angle of about 10° is made by χ_1 with the line of centers of one pair of carbon atoms and the methyl groups. This direction is at right angles to χ_2. It seems probable that even benzene itself may not possess magnetic symmetry in the plane of the ring because the two principal susceptibilities in the plane of the ring are not quite equal for any benzene derivative investigated. There is as yet no explanation for this peculiar phenomenon.

Chains of conjugated double bonds show effects similar to aromatic compounds. The increase of susceptibility is always normal to the plane of the molecule, indicating a concentration of electron density in that plane. In sharp contrast is the anisotropy of diphenyldiacetylene [97] for which there is an abnormal increase of susceptibility along the carbon chain axis.

[90] S. Paramasivan, *Indian J. Phys.*, **4**, 139 (1929).
[91] K. S. Krishnan and N. Ganguli, *Current Sci.*, **3**, 472 (1935).
[92] C. F. Squire, *Compt. rend.*, **206**, 665 (1938).
[93] H. König, *Z. Physik*, **108**, 391 (1938).
[94] K. S. Krishnan, *Nature*, **130**, 313, 698 (1932).
[95] K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. London*, **A156**, 597 (1936).
[96] K. Lonsdale, *Proc. Roy. Soc. London*, **A159**, 149 (1937).
[97] K. Lonsdale, *Nature*, **145**, 148 (1940).

Some of the many compounds which have been studied by the method of principal susceptibilities are listed below. These are arranged in chronological order of their published appearance. Naphthalene, anthracene, biphenyl, dibenzyl, stilbene, benzophenone, benzil, azobenzene, hydrazobenzene, β-naphthol, acenaphthene, and salol;[98] *p*-benzoquinone, catechol, hydroquinol, hexamethylbenzene, durene, hexachlorobenzene,

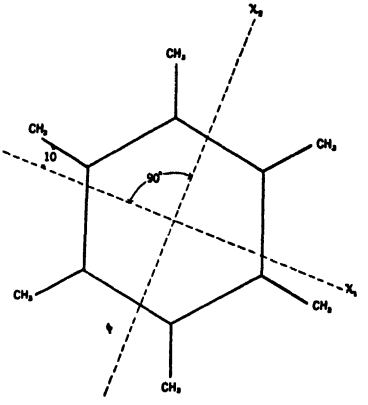


FIG. 24.—Diamagnetic anisotropy of hexamethylbenzene. χ_1 is not quite equal to χ_2, and there is no simple relation between the magnetic axes and the crystal axes.

1,2,4,5-tetrachlorobenzene, *p*-dichlorobenzene, *p*-dibromobenzene, *p*-dinitrobenzene, *m*-nitroaniline, terphenyl, quaterphenyl, 1,3,5-triphenylbenzene, triphenylcarbinol, 4,4-dichlorodiphenyl, 4,4-dibromodiphenyl, dimesityl, diphenic acid, *o*-toluidine, 1,4-naphthoquinone, α-naphthol, α-naphthylamine, fluorene, fluorenone, phenanthrene, chrysene, pyrene, and fluoranthrene;[99] 1,2,5,6-dibenzanthracene;[100] hexaethylbenzene;[101]

[98] K. S. Krishnan, B. C. Guha, and S. Banerjee, *Phil. Trans. Roy. Soc. London*, **A231**, 235 (1933).

[99] K. S. Krishnan and S. Banerjee, *Phil. Trans. Roy. Soc. London*, **A234**, 265 (1935).

[100] K. S. Krishnan and S. Banerjee, *Z. Krist.*, **91**, 173 (1935).

[101] N. Ganguli, *Z. Krist.*, **93**, 42 (1936).

resorcinol;[102] 1,2-diphenylbenzene;[103] wood, lignin and wood cellulose;[104a] sulfur;[104b] acenaphthene;[105] quinhydrone, resorcinol, phloroglucinol dihydrate, *s*-tetrabromobenzene, chloranil, bromanil, *p*-toluidine, *p*-acetotoluide, *m*-dinitrobenzene, *s*-trinitrobenzene, α-benzenehexachloride, γ-biphenol, benzidine, fluorene alcohol, stilbene, tolane, azobenzene, diphenylamine, triphenylmethane, naphthazarin, naphthalene tetrachloride, anthraquinone, alizarin, dihydroanthracene, thianthrene, dianthracene, retene, naphthacene, dimethyldibenzphenanthrene, 1,2-benzpyrene, perylene, and duodecahydrotriphenylene;[106] metal-free phthalocyanine, oxalic acid dihydrate, stilbene, tolane, and *trans*-azobenzene;[107] guanidine carbonate, *o*-dinitrobenzene, *m*-dinitrobenzene, benzamide, and artostenone;[108] nonacosane, stearic acid, stearolic acid, behenolic acid, cyclodiketone (2), pentaerythritol, pentaerythritol tetraacetate, pentaerythritol tetranitrate, pentaerythritol tetraphenylether, *i*-erythritol, *d*-mannitol (β), succinic acid, maleic acid, succinic anhydride, maleic anhydride, *trans*-cinnamic acid, benzophenone, dibenzyl, stilbene, tolane, *trans*-azobenzene, and *cis*-azobenzene;[109] benzil;[110] urea, urea nitrate, urea oxalate, cyanuric acid dihydrate, and anhydrous cyanuric acid;[111] and sorbic acid.[112]

It will be recalled that a method is available for calculating magnetic susceptibilities from magneto-optical data. This method has been used for some of the compounds listed above. Piekara[113] has so determined the principal susceptibilities of acetic, propionic, butyric, and isobutyric acids. Salceanu[114] has discussed similar computations for the naphthalene molecule.

The problem of temperature variation of magnetic anisotropy of organic crystals has received little attention. Nilakantan[115] reports that

[102] K. Lonsdale, *Nature*, **137**, 826 (1936).

[103] C. J. B. Clews and K. Lonsdale, *Proc. Roy. Soc. London*, **A161**, 493 (1937).

[104a] P. Nilakantan, *Proc. Indian Acad. Sci.*, **7A**, 38 (1938).

[104b] P. Nilakantan, *Proc. Indian Acad. Sci.*, **4A**, 419 (1936).

[105] J. Shanker and M. Prasad, *Current Sci.*, **6**, 554 (1938).

[106] S. Banerjee, *Z. Krist.*, **100**, 316 (1938).

[107] K. Lonsdale, *J. Chem. Soc.*, **1938**, 364.

[108] K. Banerjee and J. Bhattacharjya, *Science and Culture*, **4**, 60 (1938), also (including decahydro-β-naphthol) in *Z. Krist.*, **100**, 420 (1939).

[109] K. Lonsdale, *Proc. Roy. Soc. London*, **A171**, 541 (1939).

[110] I. E. Knaggs and K. Lonsdale, *Nature*, **143**, 1023 (1939).

[111] K. Lonsdale, *Proc. Roy. Soc. London*, **A177**, 272 (1941).

[112] K. Lonsdale, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc. London*, **A178**, 43 (1941).

[113] A. Piekara, *Compt. rend.*, **199**, 527 (1934).

[114] C. Salceanu, *Bull. sect. sci. acad. roumaine*, **16**, 5 (1933).

[115] P. Nilakantan, *Nature*, **140**, 29 (1937).

the anisotropy of resorcinol decreases slowly from 26° to 95°, then rapidly to zero at the melting point 110° C. A few other examples are mentioned in the following section.

11. Liquid Crystals

So far as the writer is aware Foëx [116] is the only investigator who has reported on the magnetic properties of substances in the mesomorphic state. There have, of course, been several studies of the phenomenon discovered by Mauguin [117] that the optic axis of substances in this state tends to set itself parallel to the lines of force of a magnetic field of sufficient intensity. Foëx finds that a typical substance such as *p*-

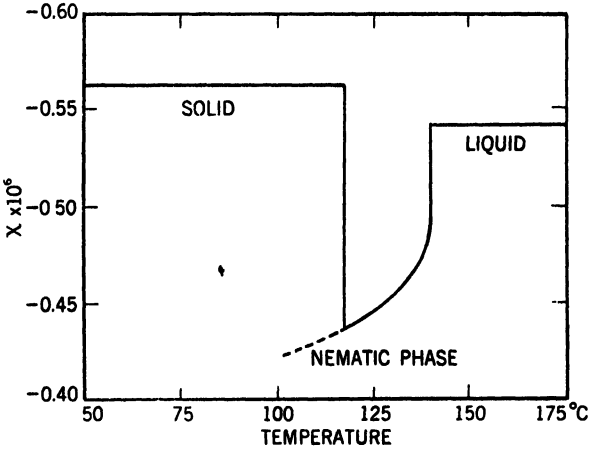


FIG. 25.—Susceptibility of *p*-azoxyanisole in the neighborhood of the "liquid crystal" transition.

azoxyanisole has, in the crystalline state the following principal sucepti-bilities per gram, $\chi_1 = -0.665$, $\chi_2 = -0.634$, and $\chi_3 = -0.408$ all time 10^{-6}. This anisotropy is not particularly large, in fact it is much less intense than for substances such as naphthalene which do not occur in the mesomorphic state. The average susceptibility of powdered *p*-azoxyanisole is -0.565×10^{-6}, the nematic phase is formed at 116° C. during which change the susceptibility falls rapidly to -0.457×10^{-6}. As the temperature rises the diamagnetism also rises slowly until, above 133° C., the substance becomes an isotropic liquid for which $\chi = -0.545 \times 10^{-6}$. If now the temperature is lowered the reverse change occurs except that the nematic phase may persist considerably

[116] G. Foëx, *J. phys. radium*, **10**, 421 (1929); *Trans. Faraday Soc.*, **29**, 958 (1933).
[117] C. Mauguin, *Compt. rend.*, **152**, 1680 (1911).

below 116° C. These changes are shown in Fig. 25. Analogous curves are followed by azoxyphenetol, azoxyanisolephenetol, and by anisaldazine. The reason for these peculiar curves is that the long dimension of the molecule is the least diamagnetic and hence orients to lie in the lines of force. If the substance is crystallized in a magnetic field a strong anisotropy exists, with the smallest diamagnetism along the lines of force. Foëx also reports on measurements of principal susceptibilities over a temperature range.

Substances such as ethylazoxybenzoate which occur in the smectic phase show, in general, only a small and irregular increase of diamagnetism on passing from solid to liquid. If, however, a field is present during cooling to the smectic state, orientation sets in with a strong decrease of diamagnetism.

CHAPTER FOUR

ATOMIC PARAMAGNETISM

1. Theories of Atomic Paramagnetism

An atom may or may not have a permanent magnetic moment. In the first case, application of a magnetic field to the atom leads to an induced moment of sign opposite to that of the applied field and the atom is said to be diamagnetic. But if the atom has a permanent magnetic moment application of a field leads to orientation of the moment and the atom is said to be paramagnetic. An atom will have a permanent magnetic moment if it has an odd number of electrons, or if all the electrons are not paired off. All atoms are, of course, subject to induced magnetization, but when paramagnetism is present it is nearly always at least 10 times greater, numerically, than the diamagnetism.

The classical theory of paramagnetism was developed by Langevin [1] on the assumptions that each atom is a little permanent magnet, and that these atomic magnets tend to line up parallel to an applied magnetic field, but that the alignment is resisted by the thermal agitation of the atoms. There is an obvious identification of the hypothetical atomic magnets with the magnetic moments induced by orbital electronic motion.

The expression deduced by Langevin for the molar paramagnetism is

$$\chi_M = \frac{N\mu^2}{3kT}$$

where N is Avogadro's number, μ is the permanent moment, k the Boltzmann constant, and T the absolute temperature. A precise expression will also include a term for the relatively small diamagnetic part of the susceptibility. The above expression is applicable only to cases where molecular interactions are negligible. It will be seen that paramagnetism, in sharp contrast to diamagnetism, is inversely proportional to the absolute temperature. This theoretical prediction is fulfilled experimentally for a very large number of substances. In fact the experimental discovery of what is known as Curie's Law,[2] $\chi = C/T$, preceded Langevin's work by some years. This expression is approximately true for many solids and liquids, as well as for at least one of the two common para-

[1] P. Langevin, *J. phys.*, [4] 4, 678 (1905); *Ann. chim. phys.* [8] 5, 70 (1905).

[2] P. Curie, *Ann. chim. phys.*, [7] 5, 289 (1895), *et seq.*

magnetic gases, oxygen and nitric oxide. Unfortunately, the more accurate magnetic measurements become the more deviations from Curie's law are discovered.

The quantum mechanics in the hands of Van Vleck [3] yields the analogous expression

$$\chi_M = \frac{N\bar{\bar{\mu}}^2}{3kT} + N\bar{\alpha} \tag{1}$$

where $\bar{\bar{\mu}}^2$ is the square of the low frequency part of the magnetic moment vector, averaged over time, and this average being itself averaged over the various normal states appropriately weighted according to the Boltzmann factor. $N\bar{\alpha}$ is the combined temperature independent contribution of the high frequency elements of the paramagnetic moment, and of the diamagnetic part.

A convenient unit of atomic magnetic moment is the Bohr magneton, the magnitude of which is given by

$$\beta = \frac{eh}{4\pi mc} = 0.917 \times 10^{-20} \text{ erg oersted}^{-1}$$

Equation (1) then becomes

$$\chi_M = N\left(\frac{\beta^2\bar{\bar{\mu}}_B^2}{3kT} + \bar{\alpha}\right) \tag{2}$$

where $\bar{\bar{\mu}}_B$ is the low frequency part of the magnetic moment expressed in Bohr magnetons.

In general the magnetic moment of an atom consists of two parts, the orbital contribution, and the electron spin contribution. In different normal states of the atom the inclination of the orbital and spin contributions may be different. Hence, while we speak of the "permanent" magnetic moment, we must remember that it may not be invariant with temperature although for many cases it appears to be so. Also in most if not all cases of "molecular" paramagnetism as contrasted with "atomic" paramagnetism, the orbital contribution appears to be quenched out. This fact aids greatly in the interpretations to be given in the following chapter.

In evaluating $\bar{\bar{\mu}}^2$ and $\bar{\alpha}$ in terms of experimentally determinable quantities there are three cases for which different equations are required. First there are the two limiting cases of spin multiplets very narrow or very wide compared to kT, and then there is the general case of multiplet intervals comparable to kT.

[3] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*. Oxford University Press, Oxford 1932. This book covers the whole field of classical and modern theory in a most thorough and admirable fashion.

a. Multiplet intervals small compared to kT:

The high-frequency elements of the paramagnetic moment are absent (neglecting the diamagnetic part). Equation (2) then becomes

$$\chi_M = \frac{N\beta^2}{3kT}[4S(S+1) + L(L+1)] \tag{3}$$

where S and L are the resultant spin and orbital moments respectively.

b. Multiplet intervals large compared to kT:

$$\chi_M = \frac{Ng^2\beta^2 J(J+1)}{3kT} + N\alpha \tag{4}$$

where, following the usual spectral notation, J is the vector sum of L and S; g, the Landé splitting factor is given by

$$g = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)}$$

The term α no longer has the value zero (neglecting the diamagnetic part) but is given by

$$N\alpha = \frac{N\beta^2}{6(2J+1)}\left[\frac{F(J+1)}{h\nu(J+1;J)} - \frac{F(J)}{h\nu(J+1;J)}\right]$$

where

$$F(J) = \frac{1}{J}[(S+L+1)^2 - J^2][J^2 - (S-L)^2]$$

Equation (4) is used for most ions of the rare earth elements as will be shown in a later section.

c. Multiplet intervals comparable to kT:

This case involves summation of the contributions of atoms with different values of J. The number N_J, that is the number of atoms in a mole with a given value of J, is determined by the Boltzmann temperature factor

$$\chi_M = \frac{N\sum_{J=|L-S|}^{L+S}\{[g_J^2\beta^2 J(J+1)/3kT] + \alpha_J\}(2J+1)e^{-W^0_J/kT}}{\Sigma(2J+1)e^{-W^0_J/kT}} \tag{5}$$

It is clear from the above that when the multiplet intervals are small or large compared to kT the Curie law should be obeyed, except for the relatively small temperature independent high frequency elements. But where the multiplet intervals are comparable to kT we get a Boltzmann distribution of the various "normal" states together with some rather striking departures from the Curie law.

The modern theory of paramagnetism, by far the greater part of which is due to Van Vleck, is, in the main, very satisfactory. A few new phenomena have been discovered, and the theory has undergone considerable elaboration especially in the field of complex compounds. But on the whole Van Vleck's contributions have suffered little or no fundamental modification during the past ten years.

2. Monatomic Paramagnetic Gases

Unfortunately direct experimental test of the equations given above is very difficult. The theory applies to substances in which mutual molecular interactions are negligible, namely to gases. But the only common monatomic gases are diamagnetic. There are, of course, substances whose vapors should be monatomic and paramagnetic but these are extremely difficult to handle. The alkali metal vapors ought to be paramagnetic because their molecules contain an odd number of electrons. But the vapor pressures are not high at any reasonably attainable temperature, the paramagnetism of such substances is not large at high temperature, a certain degree of association to double molecules must occur, and it is difficult to find suitable containers for these vapors. Gerlach [4] has reported on the susceptibility of potassium vapor between 600° and 800° C., corresponding to vapor pressures of from 0.5 to 30 mm. Within the rather large experimental error the susceptibility obeys the Curie law and is of about the correct magnitude. As Van Vleck (*op. cit.*, p. 239) points out it would be of interest if Gerlach's measurements could be refined and extended to other alkali metals. Such measurements would also serve as a sensitive test for molecular association, as magnetic measurements do for free radicals. But so far the experimental difficulties have proved insurmountable.

Another possibility is thallium vapor which has been reported to be paramagnetic.[5] Probably, however, precise measurements on this vapor would be subject to the same or even greater difficulties than those on the alkali metals. Similarly, measurements on the rare earth metal vapors would be of great interest.

3. The Stern-Gerlach Experiment

Although monatomic paramagnetic gases are difficult to obtain, there is ample evidence that many atoms have magnetic moments, and that these are often integral multiples of the Bohr magneton. The most direct experimental proof of this condition is known as the Stern-Gerlach experiment, a brief description of which will be given.

[4] W. Gerlach, *Atti congresso intern. fisici*, 1, 119 (1927).

[5] M. B. Nevgi, *J. Univ. Bombay*, 7, Part 3, 19 (1938).

If a magnet is placed in a uniform magnetic field it will be oriented but it will suffer no lateral force either parallel or perpendicular to the field. But if the field be made non-homogeneous then the magnet will not only be oriented but will be deflected toward the region of maximum intensity. Similarly, if an atom possessing a permanent magnetic moment is placed in a non-homogeneous field it will be deflected, although the nature of the deflection is rather complicated.

The Stern-Gerlach experiment consists of passing an atomic (or molecular) beam through a non-homogeneous magnetic field. The beam is deflected and from the magnitude of the deflection it is possible to compute the magnitude of the magnetic moment. A non-homogeneous field may be produced with the aid of two specially prepared pole-pieces, one wedge-shaped, the other slotted. The apparatus is shown diagrammatically in Fig. 26. The atomic beam, after deflection, impinges on a target from which an image may be developed. The image so formed consists generally of a bow-shape, that is, atoms are deflected both toward and away from the region of maximum intensity. This effect is due to space quantization, or the ability of the atoms to take up only certain discrete orientations in space.

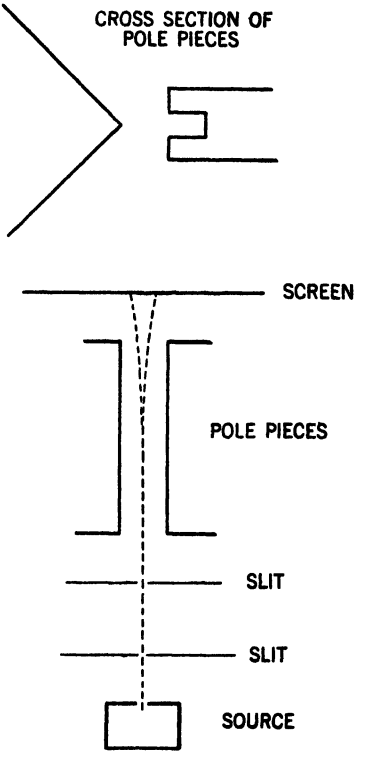


FIG. 26.—Stern-Gerlach Experiment.

The theory of the Stern-Gerlach experiment lies outside the scope of this book. It must suffice to say that for atoms such as those of hydrogen or of silver the atomic magnetic moment is shown to be one Bohr magneton. An authoritative account of the technique and applications of the molecular ray method is given by Fraser.[6] The method is by no means limited to atomic beams.[7] Stern [8] has more recently described a new method for the measurement of the Bohr magneton. The magnetic force acting on the molecular beam is compensated by the force of gravity.

[6] R. G. J. Fraser, *Molecular Rays*. Cambridge University Press, Cambridge 1931.
[7] R. Schnurmann, *J. phys. radium*, 6, 99 (1935).
[8] O. Stern, *Phys. Rev.*, 51, 852 (1937).

4. The Rare Earths

Failing to find monatomic paramagnetic vapors with which to test Van Vleck's equations we turn now to paramagnetic salts and their solutions. It is to be hoped that in at least some cases the mutual interactions of the ions will be negligible. In most cases this is not true but the rare earth elements are unique in this respect, that the electrons responsible for the paramagnetism are to a great degree shielded from external influence. The electronic configuration for the rare earth elements is

$$\cdots 4f^{0-14}5s^2 5p^6 5d^2 6s$$

These elements are generally trivalent, losing their 6s and two 5d electrons. Evidence that the 4f electrons, responsible for the paramagnetism, are relatively free from external influence is given by the facts that the rare earths are astonishingly alike chemically, and that their absorption bands and magnetic susceptibilities are but little affected by change of ionic environment as by change of compound or of solvent. As will be seen these fortunate circumstances lead to very satisfactory confirmation of the Van Vleck theory.

The relation

$$\chi_M = \frac{Ng^2\beta^2 J(J+1)}{3kT}$$

which is, of course, the first part of equation (4) was obtained in the old quantum theory. As we realize now this is simply equivalent to assuming the multiplets all very wide compared to kT. This relationship was used by Hund [9] in his calculation of the magnetic moments of the rare earths, in which with some exceptions, good agreement with experiment was obtained. As Hund had available no direct spectroscopic evidence as to the spectral terms of the rare earth ions, it may be of interest to show how he evaluated L, S, and J.

Whenever there are several equivalent electrons, the Pauli exclusion principle severely limits the possible spectral terms. It was assumed by Hund that the lowest energy is possessed by the spectral term of highest multiplicity. If, when the multiplicity $2S + 1$ has its maximum value, there are several possible values of L, then the least energy is assumed to be given by the greatest L consistent with this S. Other possible states are assumed to be not normal, because they have so much more energy. For instance, for praseodymium with two equivalent f electrons, the following terms are admitted by the Pauli exclusion principle, ^1S, ^3P, ^1D, ^3F, ^1G, ^3H, ^1I, and to exclude the ^3S, ^1P, ^3D, ^1F, ^3G, ^1H, and ^3I states.

[9] F. Hund, *Z. Physik*, **33**, 855 (1925).

Under Hund's assumptions, of the first group of terms, only the ^3H term is a normal state. The correctness of Hund's assumptions is demonstrated by the magnetic theory itself.

It is, of course, necessary to know whether equation (3), (4), or (5) should be used for calculating the susceptibilities. This is done by supposing that the normal state is the one whose component has a minimum or maximum J, depending on whether the multiplet is "regular" or inverted. For less than seven 4f electrons the multiplet is "regular," for more, inverted. The trivalent ion of gadolinium, with seven 4f electrons, is in an S state. For europium, samarium, and to a slight degree neodymium, the general equation (5) must be used as will be described below.

A convenient comparison of theoretical with observed susceptibilities is made by the aid of "effective Bohr magneton numbers" instead of susceptibilities. These are defined as

$$\mu_{eff} = \sqrt{\frac{3k\chi_M T}{N\beta^2}} = 2.83\sqrt{\chi_M T}$$

This quantity, so defined, is, of course, a function of temperature unless Curie's law is obeyed.

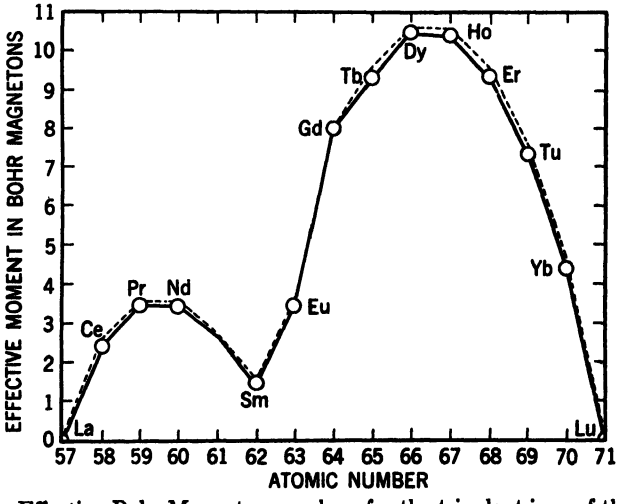


FIG. 27.—Effective Bohr Magneton numbers for the trivalent ions of the rare earths at room temperature. The dotted line shows theoretical numbers calculated from the appropriate equations of Van Vleck.

Theoretical effective Bohr magneton numbers calculated from the appropriate equations of Van Vleck are in extraordinarily good agreement with observed values. In Fig. 27 the averages of all recent experimental

values at room temperature have been shown. This figure represents by no means the least of the many triumphs of theoretical physics during the past few years.

Some remarks may be made concerning the experimentally determined susceptibilities of the trivalent rare earth ions. Although there has been a vast accumulation of data in this field it must be remembered that most of the material used has come from only two or three laboratories where fractional crystallization of rare earths is carried on. Interpretation of experimental results should therefore be weighted somewhat by considerations of source and purity of material. Furthermore, as will be shown later, the ionic environment is not without influence on the susceptibility of rare earth ions, in spite of the shielding of the 4f electrons. Most weight should probably be given to measurements on hydrated, "magnetically dilute" crystals, or even better on solutions. By "magnetically dilute" crystals is meant crystals in which the paramagnetic ions do not form a large proportion of the whole, that is, they are so dispersed that their magnetic interactions are relatively small. There is a final difficulty and that is that no uniform method has been adopted for reporting ionic susceptibilities. Most workers properly correct for the diamagnetism of solvent and of anion and water of hydration. Few correct for the underlying diamagnetism of the paramagnetic ion itself.

In spite of these difficulties the agreement between theory and experiment is very satisfactory. Lanthanum and lutecium are diamagnetic. The susceptibilities of the other rare earth trivalent ions lie on two curves, the oxides Dy_2O_3 and Ho_2O_3 being the most powerfully paramagnetic compounds known. A bottle full of even neodymium oxide, Nd_2O_3, is quite strongly attracted to a powerful magnet. The susceptibilities of these ions follow the Curie law with a fair degree of accuracy except for samarium and europium which are entirely different.

It may be mentioned that some observers have reported magnetic moments in terms of "Weiss magnetons" which were at one time believed to be significant. The Bohr magneton, which is of course based on sound theory, is equal to 4.95 Weiss magnetons.

In addition to the reviews given by Van Vleck and by Stoner a good summary of experimental work on the rare earths up to 1932 is given by Gorter.[10] Some of the more important papers which have appeared since that date will be mentioned here, together with a few earlier papers.

Dilute solutions of rare earth salts would appear to be the most favorable case for obtaining ionic moments free from complication by mutual interaction. But there have been relatively few measurements

[10] C. J. Gorter, *Arch. du Musée Teyler*, 7, 183 (1932).

made on solutions, and very few over a temperature range. The most extensive work in this field is that of Decker [11] who measured the susceptibilities of aqueous solutions of nitrates or sulfates of all the rare earth elements. A good bibliography is included. The writer [12] measured the susceptibility of neodymium nitrate solutions over a range of concentration. The susceptibility decreases slightly with increasing concentration. It may be mentioned that the rare earth nitrates are anomalous in several respects such as their absorption spectra and their tendency to dissolve in some organic solvents such as acetone. The writer has also measured the susceptibility of neodymium nitrate in ethyl alcohol solution over a range of temperature.[13] Some unpublished work suggests that the magnetic susceptibilities of rare earth salts in dilute non-aqueous solvents show marked deviations from additivity. Salts of trivalent cerium in aqueous and in alcoholic solution have been studied over a temperature range by Haenny and Dupouy,[14] and by Liquier-Milward.[15] The susceptibility is roughly inversely as the absolute temperature but there are some irregularities yet to be cleared up. Cabrera, Espurz, and Menéndez [16] report on neodymium chloride solutions over a temperature range, while Dupouy gives data on aqueous solutions of praseodymium, neodymium, samarium, europium, and gadolinium over a temperature range.[17]

Next to dilute solutions, the octahydrated sulfates of the rare earths are probably most satisfactory. They are fairly easy to prepare in stoichiometrically accurate form. They crystallize well and are readily handled, and they are magnetically dilute. Some of the classical low temperature work has, for instance, been done on $Gd_2(SO_4)_3 \cdot 8H_2O$. Woltjer [18,19] and Onnes measured the susceptibility of this compound down to 1.48° K. over a large range of field strength, and were the first to show that the Langevin formula is obeyed at extremes of cold, even though the fundamental assumptions of the Langevin theory may be shown to be inapplicable. Zernike and James [20] have measured the

[11] H. Decker, *Ann. Physik*, 79, 324 (1926).

[12] P. W. Selwood, *J. Am. Chem. Soc.*, 53, 1799 (1931).

[13] P. W. Selwood, *J. Am. Chem. Soc.*, 55, 3161 (1933).

[14] C. Haenny and G. Dupouy, *Compt. rend.*, 199, 843 (1934).

[15] J. Liquier-Milward, *Proc. Phys. Soc. London*, 47, 559 (1935).

[16] B. Cabrera, A. Espurz, and N. Menéndez, *Bol. acad. cienc. Madrid*, I, No. 2, 2 (1935).

[17] G. Dupouy, *Compt. rend.*, 202, 646 (1936).

[18] H. R. Woltjer and H. K. Onnes, *Proc. Acad. Sci. Amsterdam*, 26, 626 (1923).

[19] H. R. Woltjer, *Proc. Acad. Sci. Amsterdam*, 26, 613 (1923).

[20] J. Zernike and C. James, *J. Am. Chem. Soc.*, 48, 2827 (1926).

temperature coefficient of susceptibility of all the octahydrated rare earth sulfates except europium, dysprosium, and thulium. De Haas, Wiersma, and Capel [21] report on erbium sulfate octahydrate from 14° to 285° K. Kürti [22] gives magnetic and other data on $Gd_2(SO_4)_3 \cdot 8H_2O$ in the liquid helium region. The susceptibilities of several compounds of praseodymium, neodymium, samarium, and ytterbium at room temperature are given by Rodden.[23] Williams [24] reports on $Gd_2(SO_4)_3 \cdot 8H_2O$ over a temperature range and states that the susceptibility-temperature curve is a broken line. Velayos [25] gives temperature coefficients of susceptibility for the octahydrated sulfates of terbium, dysprosium, holmium, and erbium, while Cabrera, Velayos, and Cabrera [26] give the same for thulium and neodymium. Jackson [27a] reports on the susceptibilities of octahydrates of ytterbium, dysprosium, erbium, and neodymium over a wide temperature range. Some of the data and conclusions in this paper are later corrected.[27b] Some very painstaking researches of Cabrera [28,29] especially on gadolinium, dysprosium, holmium, erbium, and terbium are probably among the most accurate yet performed. He points out that many discrepancies and differences from theoretical values of the magnetic constants are due not to the difficulty of separating them but to the presence of water.

Many magnetic measurements have been done on rare earth oxides. These compounds are, of course, easy to prepare once the rare earth itself has been obtained in a state of purity. Because of their high magnetic concentration and the rapidity with which some of them take up carbon dioxide from the air, their susceptibilities are less reliable than those of some other compounds. Amongst the many reports on rare earth oxides, those of Velayos [30] on Gd_2O_3, Dy_2O_3, Er_2O_3, Pr_2O_3 and Nd_2O_3, and of Sucksmith on Yb_2O_3, Nd_2O_3, Sm_2O_3, and Eu_2O_3 may be mentioned. Measurements are also reported on cerous ortho-

[21] W. J. de Haas, E. C. Wiersma, and W. H. Capel, *Proc. Acad. Sci. Amsterdam*, **32**, 739 (1929).

[22] N. Kürti, *Z. physik. Chem.*, **B20**, 305 (1933).

[23] C. J. Rodden, *J. Am. Chem. Soc.*, **56**, 648 (1934).

[24] E. H. Williams, *Phys. Rev.*, **46**, 133 (1934).

[25] S. Velayos, *Anales soc. españ. fis. quím.*, **33**, 297 (1935).

[26] B. Cabrera, S. Velayos, and N. Cabrera, *Bol. acad. cienc. Madrid*, **I**, **No. 2**, 1 (1935).

[27a] L. C. Jackson, *Proc. Phys. Soc. London*, **48**, 741 (1936).

[27b] L. C. Jackson, *Proc. Roy. Soc. London*, **A170**, 266 (1939).

[28] B. Cabrera, *J. phys. radium*, **9**, 209 (1938); *J. chim. phys.*, **36**, 237 (1939).

[29] B. Cabrera, *Anales. soc. españ. fis. quím.*, **35**, 207 (1937); *Compt. rend.*, **297**, 1077 (1938); *J. chim. phys.*, **36**, 117 (1939).

[30] S. Velayos, *Anales españ. fis. quím.*, **31**, 597 (1933); **33**, 5 (1935).

phosphate,[31] cerous fluoride,[32] the rare earth borides,[33] cerous chloride,[34] and the rare earth cobalticyanides.[35] Further reports are indicated below.[36–40a]

As previously mentioned, compounds of trivalent samarium and europium have temperature coefficients of susceptibility quite different from those of the other rare earths. At one time it was suggested that these elements had "electron isomers" in which the number of 4f electrons might be different from five and six respectively. Also, until recently it has been a matter of several years work to purify europium and it was thought that impurities might be responsible for the anomalous temperature coefficients. These suggestions have been shown by Van Vleck to be unnecessary. The real reason is that the multiplet levels for these elements are comparable to kT, hence the general expression (5) must be used. The over-all multiplet width is given in wave-numbers by a theoretical expression

$$\frac{1}{c}\Delta\nu_{\text{total}} = \frac{5.82(2L+1)}{n^3 l(l+1)(2l+1)}(Z-\sigma)^4 cm^{-1}$$

where the factor 5.82 comes from substituting numerical values for h, e, m, and c; l is the azimuthal quantum number for a single electron, Z is the atomic number and σ the screening constant. Use of this expression soon shows the necessity for the general expression for the susceptibilities of samarium and europium, and to a smaller degree for element 61 and for neodymium. There are, of course, no experimental measurements on element 61. In samarium and europium the temperature independent term α_J becomes quite large and at some temperatures contributes practically all the paramagnetism.[40b]

[31] R. Brunetti, *Nuovo cimento*, 6, 85 (1929).

[32] W. J. de Haas and C. J. Gorter, *Proc. Acad. Sci. Amsterdam*, 33, 949 (1930).

[33] W. Klemm, W. Schüth, and M. von Stackelberg, *Z. physik. Chem.*, B19, 321 (1932).

[34] C. J. Gorter, W. J. de Haas, and J. van den Handel, *Proc. Acad. Sci. Amsterdam*, 34, 1249 (1931).

[35] T. Karantassis, K. Basileiados, and N. Perakis, *Compt. rend.*, 208, 1720 (1939).

[36] H. A. Kramers, *Proc. Acad. Sci. Amsterdam*, 35, 1272 (1932).

[37] L. Abonnenc, *Compt. rend.*, 198, 2237 (1934).

[38] G. Foëx and C. Fehrenbach, *Compt. rend.*, 203, 857 (1936).

[39] L. F. Vereshchagin, L. V. Shubnikov, and B. G. Lazarev, *Physik. Z. Sowjetunion*, 10, 618 (1936).

[40a] B. Cabrera, *Compt. rend.*, 205, 400 (1937).

[40b] Very recently Van Vleck has shown that it is no longer necessary to use the screening constant formula for this calculation, because the multiplet widths for samarium are now available [W. Albertson, *Phys. Rev.*, 47, 370 (1935)]. With a very slight extrapolation these data may be applied to europium. The results so obtained are in excellent agreement with the observed values. The writer is indebted to Professor

The striking feature about the susceptibilities of samarium and europium is that that of the former is nearly independent of temperature above about 400° C. while that of europium is nearly independent of temperature below about 100° K. There is a slight uncertainty in the theoretical calculations regarding use of 33 or of 34 as the screening constant. Fig. 28 shows theoretical values calculated for both screening

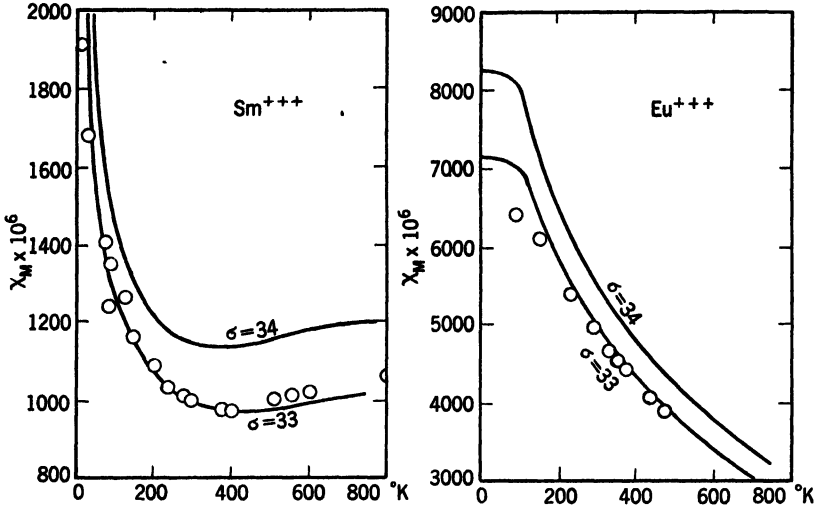


FIG. 28.—Ionic susceptibilities for Sm^{+++} and Eu^{+++}. The solid lines are theoretical curves for screening constants 33 and 34. The points are averages of such experimental data as are available. The results seem to indicate that a screening constant of 33 is correct but if consideration is given to the molecular field constant, Δ, the correct value for σ may be 34.

constants, and average experimental values taken from several of the most authoritative publications. For samarium the experimental values [41–45] have been calculated simply from the observed susceptibilities by the expression

$$\mu_{eff} = \sqrt{\frac{3k\chi_M T}{N\beta^2}}$$

Van Vleck for letting him see these results before publication. They will appear in the *Proceedings of the Strasbourg Congress on Magnetism* and in the published form of Dr. Van Vleck's lectures for the Institut Henri Poincaré.

[41] S. Freed, *J. Am. Chem. Soc.*, **52**, 2702 (1930).

[42] F. H. Spedding, *J. Am. Chem. Soc.*, **54**, 2593 (1932).

[43] E. C. Wiersma and B. H. Schultz, *Physica*, **13**, 171 (1933).

[44] P. W. Selwood, *J. Am. Chem. Soc.*, **56**, 2392 (1934).

[45] O. E. Frivold and L. Lunde, *Physik. Z.*, **39**, 571 (1938).

and it will be noticed that there is some deviation from the theoretical especially at low temperatures. For europium [46–48a] a set of values has been obtained by using

$$\mu_{eff} = \sqrt{\frac{3k\chi(T + \Delta)}{N\beta^2}}$$

where $\Delta = 22$ and these results are in extremely good agreement with the theoretical for $\sigma = 34$. It would be interesting to have magnetic measurements on europium down to liquid helium temperatures. Some recent measurements [48b] indicate that the susceptibility of europium sulfate is the same at 20° K. as at 80° K. This is good confirmation of the theory. The paper referred to, however, does not state whether the anhydrous or the hydrated sulfate was used, and gives only relative values for the susceptibility at different temperatures. It is impossible, therefore, to estimate the effective moment of the Eu^{+++} ion from this work. The reader may wonder about the apparently arbitrary inclusion of the quantity Δ in the expression for μ_{eff} for europium. So far, it has not been possible to justify this quantitatively, but it may be shown that $\Delta = 22$ is not unreasonable. This brings us, however, to consideration of the so-called "molecular field."

5. The "Molecular Field"

It is an illuminating fact that the magnetic susceptibility of many substances may be represented by the relation $\chi = C/(T + \Delta)$ much better than by the simple Curie law $\chi = C/T$. On classical grounds Weiss [49] obtained this expression theoretically by consideration of the mutual interaction of the elementary magnets or molecular magnetic fields. Although Δ is no longer identified with this supposed field, the name has been retained, and Δ will be referred to as the "molecular field constant." This constant has been discussed at length by Van Vleck,[50] Gorter,[51] Kramers,[52] and by many others. In fact it has received attention out of all proportion to its importance. The significance of Δ in the light of our present knowledge is threefold.

[46] W. Sucksmith, *Phil. Mag.*, 14, 1115 (1932).

[47] G. Hughes and D. W. Pearce, *J. Am. Chem. Soc.*, 55, 3277 (1933).

[48a] P. W. Selwood, *J. Am. Chem. Soc.*, 55, 4869 (1933). Earlier values for europium are given by Van Vleck.

[48b] H. Fritsch, *Ann. Physik*, 39, 31 (1941).

[49] P. Weiss, *J. phys.*, 6, 661 (1907).

[50] C. J. Gorter and W. J. de Haas, *Proc. Acad. Sci. Amsterdam*, 34, 1243 (1931).

[51] C. J. Gorter, *Phys. Rev.*, 42, 437 (1932).

[52] H. A. Kramers, *Proc. Acad. Sci. Amsterdam*, 35, 1272 (1932); 36, 17 (1933); *Physica*, 1, 182 (1934).

First, Δ may appear as an empirical constant from the fact of the multiplet intervals being neither very large nor very small compared with kT. In this case the Curie constant, C, will itself change with temperature, and Δ will therefore have no real significance and probably will not remain constant over a very large temperature interval. This is precisely the case that arises with samarium and europium as has just been described. But for neodymium, calculation shows that neglect of the multiplet levels adds only 3 per cent to the susceptibility at room temperature. Gadolinium has also received attention in this connection but here, of course, we are not bothered with multiplet structure as the Gd^{+++} ion is in an S state.

The second source of the molecular field constant is the effect of inhomogeneous electric fields produced by neighboring ions or oriented solvent dipoles on the orbital moment of the 4f electrons. Measurements at low temperatures are of special interest because they indicate the size of the interatomic forces tending to orient the 4f orbits. Penney and Schlapp [53] have examined theoretically the influence of crystalline fields on the susceptibilities of praseodymium and neodymium as well as certain other rare earths whose experimental examination has been less thorough. Assuming cubic symmetry for the octahydrated sulfates they find that the field causes a splitting of the multiplet levels and consequent redistribution of the magnetic moment. At ordinary temperatures kT is of the same order as the energy separations produced by the field and the susceptibility actually appears to follow the Weiss law over a wide temperature range, although here again Δ has no real significance. At low temperatures the $1/\chi$, T relationship should bend away from the temperature axis for praseodymium and toward it for neodymium. Of course, for gadolinium, as before, the question does not arise. The theory of Penney and Schlapp is in remarkably good agreement with Gorter's experimental results as may be seen from Fig. 29. Further studies of the crystalline field and its effect on magnetic properties of the rare earths have been made by Penney,[54] Jordahl,[55] Spedding,[56] and Fritsch.[57]

The third, and final, source of Δ lies in the Heisenberg exchange interaction. When magnetic atoms or ions are very close together this interaction has the effect of introducing a very strong coupling between the respective spins. This is the effect responsible for ferromagnetism

[53] W. G. Penney and R. Schlapp, *Phys. Rev.*, **41**, 194 (1932).
[54] W. G. Penney, *Phys. Rev.*, **43**, 485 (1933).
[55] O. Jordahl, *Phys. Rev.*, **45**, 87 (1934); **46**, 79 (1934).
[56] F. H. Spedding, *J. Chem. Phys.*, **5**, 316 (1937).
[57] H. Fritsch, *Ann. Physik*, **38**, 555 (1940).

in Heisenberg's theory of that subject. In this discussion we are interested only in behavior above the Curie point, that is, above the temperature at which ferromagnetism turns into paramagnetism. As a matter of fact, for rare earth compounds the Curie point lies below 0° K. and so is

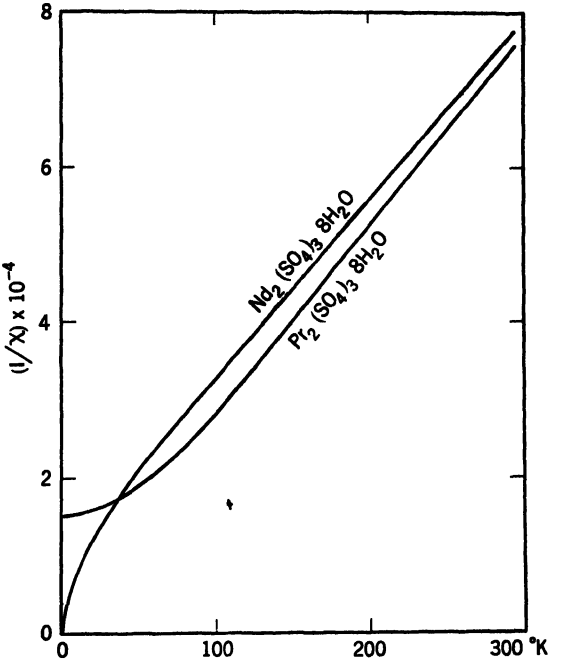


FIG. 29.—Susceptibility-temperature relationships for Pr^{+++} and Nd^{+++}. The lines represent both theoretical values, and Gorter's experimental values. It should be mentioned that some other experimental data do not agree quite so well with the Penney and Schlapp theory.

imaginary. We have the relationship

$$\chi_M = \frac{4N\beta S(S+1)}{3k(T - T_C)} \tag{6}$$

where

$$T_C = \frac{2Jz}{3k} S(S+1) \tag{7}$$

J (following Van Vleck's notation) is here the exchange integral, z is the number of equidistant neighbors with which the atom has exchange coupling. For example, for a linear chain $z = 2$, for a simple cubic system $z = 6$. The other terms have their usual significance. Equation (6) is equivalent to $\chi = C/(T + \Delta)$.

Turning now to the pertinent experimental data,[13,48a] we have the information given in Table XI.

TABLE XI

MOLECULAR FIELD CONSTANTS FOR SOME COMPOUNDS OF GADOLINIUM

Compound	Δ in ° C.
Gd_2O_3	18 ± 2
$GdCl_3$	14
$Gd_2(SO_4)_3.8H_2O$	2 (or zero)

For gadolinium there is no multiplet structure so that Δ must here be due solely to exchange forces. Few will deny that the order of compounds written down is the order of increasing "magnetic dilution," that is, the Gd^{+++} ions are getting farther apart. It is, therefore, gratifying to see Δ decreasing until in the octahydrated sulfate the exchange forces are presumably negligible. Gadolinium is the only trivalent paramagnetic rare earth in which Δ approaches zero in any compound, and is the only one in an S state.

Neodymium is somewhat more complicated. Here we have to contend both with exchange forces and with the crystalline field effect.

TABLE XII

MOLECULAR FIELD CONSTANTS FOR SOME COMPOUNDS OF NEODYMIUM

Compound	Δ in ° C.
Nd_2O_3	59
NdF_3	54
$Nd(NO_3)_3$	49
$Nd(ClO_4)$	48
$Nd_2(SO_4)_3.8H_2O$	45
Nd^{+++} in solution	45

Obviously, while the exchange forces become negligible, the crystalline field splitting produced by oriented water dipoles remains constant and fairly large even at the highest magnetic dilution.

As the crystalline field can scarcely be constant in all the compounds used, it would be of interest to know precisely what part of the change from 45° to 59° is produced by each effect. This has been done simply by holding the crystalline field constant while the magnetic dilution is increased. Solid solutions were made of neodymium oxide in the diamagnetic and isomorphous lanthanum oxide. It was formerly thought that even diamagnetic atoms would have strong mutual magnetic interactions but both Van Vleck and Slater have shown that atoms or ions with closed shells, and hence diamagnetic, have no exchange interaction. The results obtained are shown in Table XIII.

Of course, the experimental error is quite large in these measurements but they show that practically all the change in Δ in the various compounds is due to exchange forces. It would be of interest to extend these measurements to other rare earths. They suggest also a possibility of measuring the rate of diffusion of one rare earth ion into the crystal lattice of another.

TABLE XIII

MOLECULAR FIELD CONSTANT IN SOLID SOLUTIONS OF NEODYMIUM OXIDE IN LANTHANUM OXIDE

$\%Nd_2O_3$ in La_2O_3	Δ in ° C.
50	55
10	32
2	30

Returning for a moment to europium, it will be recalled that some qualitative reason was promised for putting $\Delta = 22$ in the expression $\mu_{eff} = \sqrt{\frac{3k\chi_M(T+\Delta)}{N\beta^2}}$ for europium. The crystalline field must be much the same for $Eu_2(SO_4)_3 \cdot 8H_2O$ as for $Nd_2(SO_4)_3 \cdot 8H_2O$ (the compounds are isomorphous), and the ion Eu^{+++} is certainly not in an S state. Therefore, after what has been said with respect to Δ for neodymium and the other rare earths, surely no one will claim that $\Delta = 22$ is unreasonable for europium.

It will be observed that equation (7) suggests a means of calculating the Curie temperatures. Such calculations have been made by Néel.[58] The agreement with experimental results is good.

6. Paramagnetic Anisotropy of Rare Earth Compounds

Van Vleck points out that paramagnetic crystalline matter may be divided into three groups:

a. Crystals in which the electrical fields have little influence on the coupling between the orbital and spin moments.

b. Crystals in which the fields are strong enough to break down the spin-orbital coupling but not the Russel-Saunders coupling between electrons.

c. Crystals in which the fields are large enough to break down the Russel-Saunders coupling.

Compounds of the rare earth elements belong to the first group, but even here the influence of the crystalline field is by no means negligible. The result of presence of a local orienting field will be:

[58] L. Néel, *Compt. rend.*, 206. 49 (1938).

1. A value for the effective moment which will bear no simple relation to the spin and orbital moments. As will be seen in a later section, this effect is marked for those ions in which the electrons responsible for paramagnetism are not so well shielded as they are in the rare earths.

2. A complicated deviation from the Curie law. Even for the magnetically dilute rare earth sulfate octahydrates the deviations, as has been seen, are appreciable.

3. Magnetic anisotropy will appear unless the crystal has cubic symmetry. For many rare earth crystals the anisotropy is somewhat greater than might have been anticipated.

There have not been very many investigations of the paramagnetic anisotropy of the rare earths, but the above conclusions are verified by Krishnan and Mookherji [59] and by others. A good introduction to both theory and experiment is given by Jackson.[60]

Fereday and Wiersma [61] have examined the principal susceptibilities of some rare earth ethylsulfates over a considerable temperature range. The ions of cerium, neodymium, and erbium have an odd number of electrons. Their ethylsulfates show the highest principal susceptibility along the principal axis of the hexagonal crystal. The difference increases rapidly as the temperature is lowered. For instance, for cerium ethylsulfate the difference in principal susceptibilities is small at room temperature, but at 20.45° K. the susceptibilities are 61.2 and 20.7×10^{-6} respectively, along and perpendicular to the main axis. The parallel susceptibility follows the simple Curie law, but the perpendicular has a molecular field constant (Δ) of about 17.4°. It is a general rule that where paramagnetic anisotropy exists, not only the Curie constant, but the molecular field constant as well, are different along different axes. The ion of praseodymium has an even number of electrons and this fact seems to be responsible for a somewhat different type of anisotropy. The susceptibility along the principal axis is still the highest at room temperature, but at about 130° K. the principal susceptibilities are equal, and at still lower temperatures the susceptibility along the binary axis is highest.

Measurements on neodymium and other rare earth sulfate octahydrates have been made by Krishnan and Mookherji [62,63] and by

[59] K. S. Krishnan and A. Mookherji, *Phil. Trans. Roy. Soc. London*, **A237**, 135 (1938).

[60] L. C. Jackson, *Proc. Roy. Soc. London*, **A140**, 695 (1933).

[61] R. A. Fereday and E. C. Wiersma, *Physica*, **2**, 575 (1935). See also: J. van den Handel and J. C. Hupse, *Physica*, **9**, 225 (1942); J. van den Handel, *Nederland. Tijdschr. Natuurkunde*, **8**, 397 (1941).

[62] K. S. Krishnan and A. Mookherji, *Nature*, **140**, 549 (1937).

[63] K. S. Krishnan, A. Mookherji, and A. Bose, *Phil. Trans. Roy. Soc. London*, **A238**, 125 (1939)

Jackson.[64] For very pure crystals of $Nd_2(SO_4)_3 \cdot 8H_2O$ all three principal susceptibilities obey the Weiss law above 120° K. but at lower temperatures the anisotropy increases very rapidly being 11 per cent at room temperature and 70 per cent at 14° K. This large anisotropy, implying that the rare earth sulfate octahydrates do not have cubic symmetry, is surprising because spectroscopic and other evidence suggests that they do. The implications of this phenomenon are discussed by Penney and Kynch.[65] Large anisotropies are reported also for the hexahydrated chlorides of neodymium, samarium, and europium. With crystals in which the paramagnetic ions are in S states it might be expected that the anisotropy would be very small, but Krishnan reports an appreciable anisotropy for $Gd_2(SO_4)_3 \cdot 8H_2O$. For such substances the anisotropies vary inversely as the square of the absolute temperature. Krishnan suggests that the bulk of the anisotropy in $Gd_2(SO_4)_3 \cdot 8H_2O$ arises from magnetic interaction between Gd^{+++} ions, but this explanation seems difficult to reconcile with the fact that this compound obeys the Curie law down to extremely low temperatures.

Mention should be made of a unique method for obtaining the principal susceptibilities of rare earth crystals. Van Vleck and Hebb [66] have shown that the temperature variation of the magneto-optical rotation is, apart from an additive constant, the same as that of the magnetic susceptibility. Hence at any given temperature

$$V = A\chi + K$$

where V is the Verdet constant (rotation per unit length divided by field strength), and A and K are constants.

TABLE XIV

MAGNETIC AND MAGNETO-OPTICAL PRINCIPAL SUSCEPTIBILITIES OF DYSPROSIUM ETHYLSULFATE

Temp. ° K.	μ_{eff} parallel to principal axis	
	Magnetic	Magneto-optical
14.1	5.63	5.478
77.4	6.41	6.476
205	6.37	6.355
289	6.17	6.293

[64] L. C. Jackson, *Proc. Roy. Soc. London*, A170, 266 (1939).
[65] W. G. Penney and G. J. Kynch, *Proc. Roy. Soc. London*, A170, 112 (1939).
[66] J. H. Van Vleck and M. H. Hebb, *Phys. Rev.*, 46, 17 (1934).

Confirmation of the above relation has been given by Becquerel [67] and by van den Handel [68] who have made measurements on the ethylsulfates of praseodymium, neodymium, dysprosium, and erbium. For instance, Becquerel gives for dysprosium ethylsulfate the data shown in Table XIV. It seems probable that, in those cases to which it is applicable, Van Vleck and Hebb's method will be found simpler and more accurate than the direct magnetic method.

7. Saturation, Relaxation, and Other Phenomena [69]

For all readily attainable field strengths and temperatures the magnetic susceptibility of most substances is independent of field strength. There are a few substances, such as $FeCl_3$, whose susceptibility varies with field strength at moderately low temperatures, but such substances are unusual. Both classical and modern theories of magnetism suggest that at very low temperatures and high fields saturation effects should appear, corresponding to a maximum orientation of the atomic magnetic moments.

This saturation effect has been observed for gadolinium sulfate octahydrate [70] and for potassium chrome alum.[71] The work of Woltjer and Onnes on the first compound covered temperatures down to 1.31° K. and fields to 22,000 oersteds. The chrome alum work covered the temperature range 4.27 to 1.34° K. These observations constitute a further confirmation of the quantum theory of magnetization.

It is well known that polar liquids show a region of anomalous dispersion and dielectric absorption [72] at high frequencies. This is attributed to a "relaxation" effect, or failure of the polar molecule to follow the alternating field at a certain critical frequency. It might be expected that paramagnetic substances would show a similar effect, but early attempts to detect it were not very successful.[73] The effect was discovered by Gorter [74] who first observed a heating effect due to anomalous absorption of gadolinium sulfate octahydrate at low temperatures and

[67] J. Becquerel, *Compt. rend.*, 201, 1112 (1935); *Physica*, 3, 705 (1936).

[68] J. van den Handel, *Physica*, 8, 513 (1941).

[69] A good, though brief, review of this field is given by E. F. Burton, H. G. Smith, and J. O. Wilhelm, *Phenomena at the Temperature of Liquid Helium.* Reinhold Publishing Corporation, New York 1940.

[70] H. R. Woltjer and H. K. Onnes, *Proc. Acad. Sci. Amsterdam*, 26, 613, 626, 772 (1923).

[71] C. J. Gorter, W. J. de Haas, and J. van den Handel, *Proc. Acad. Sci. Amsterdam*, 36, 158 (1933).

[72] P. Debye, *Polar Molecules.* Chemical Catalog Co., Inc., New York 1929.

[73] G. Breit and H. K. Onnes, *Proc. Acad. Sci. Amsterdam*, 26, 840 (1923).

[74] C. J. Gorter, *Physica*, 3, 503 (1936); *Phys. Rev.*, 51, 778 (1937).

high frequencies. During the course of this work the surprising discovery was made that the high frequency susceptibility is markedly reduced by the presence of a strong constant magnetic field. For iron alum the susceptibility at 2 megacycles and 77° K. is reduced by as much as 75 per cent when the measurements are made in a constant field of 40,000 oersteds. This curious effect is explained by Gorter as follows: The relaxation time, τ, is defined by the expression $\sigma = \sigma_H e^{-t/\tau}$ where σ is the magnetization at time, t, after the removal of a field, H, which produces a magnetization σ_H. In the absence of a constant field this relaxation time is about 10^{-10} seconds and is determined by the interaction energy, ΔE, between the magnetic ions. ΔE is of the order of $(h/2\pi)10^{-10}$. If, however, the Zeeman separations introduced by application of a constant field are larger than ΔE, then changes in the distribution over the Zeeman levels cannot be "paid out" of the relaxation energy. Such changes must then result from the feeble coupling between the magnetic moments and the heat motion of the crystal.

The theory of this effect is discussed by Kronig and Bouwkamp,[75] Fierz,[76] Debye,[77] Kronig,[78] Dänzer,[79] and Van Vleck.[80] Further experimental studies are given by Brons and Gorter;[81] Gorter, Teunissen, and Brons;[82] de Haas and du Pré;[83] Teunissen and Gorter;[84a, 84b] du Pré;[85] and by Starr.[86] For iron alum all but 7 per cent of the susceptibility has been made to disappear. Perhaps the susceptibility would vanish entirely at still lower temperatures. For iron alum diluted with a diamagnetic alum much higher constant fields are required for inhibition of the susceptibility.

Another curious effect which will be mentioned is the anomalous field strength dependence of the susceptibility of bismuth. When magnetic measurements are made on a crystal of bismuth along its axis of maximum susceptibility at or below liquid air temperature, the susceptibility oscillates about an average value as the field strength is increased. This

[75] R. de L. Kronig and C. J. Bouwkamp, *Physica*, **5**, 521 (1938).
[76] M. Fierz, *Physica*, **5**, 433 (1938).
[77] P. Debye, *Physik. Z.*, **39**, 616 (1938).
[78] R. de L. Kronig, *Physica*, **6**, 33 (1939).
[79] H. Dänzer, *Physik. Z.*, **40**, 557 (1939).
[80] J. H. Van Vleck, *Phys. Rev.*, **57**, 426 (1940).
[81] F. Brons and C. J. Gorter, *Physica*, **5**, 60, 999 (1938).
[82] C. J. Gorter, P. Teunissen, and F. Brons, *Physica*, **5**, 657 (1938).
[83] W. J. de Haas and F. K. du Pré, *Physica*, **6**, 705 (1939).
[84a] P. Teunissen and C. J. Gorter, *Physica*, **6**, 1113 (1939).
[84b] C. J. Gorter, L. J. Dijkstra, and H. Groendijk, *Physica*, **7**, 625 (1940).
[85] F. K. du Pré, *Physica*, **7**, 79 (1940).
[86] C. Starr, *Phys. Rev.*, **60**, 241 (1941).

is known as the de Haas-van Alphen effect.[87] Fig. 30 shows the effect at liquid helium temperatures. The effect has been studied by Shoenberg and Uddin,[88, 89] by Blackman,[90] and by Peierls.[91]

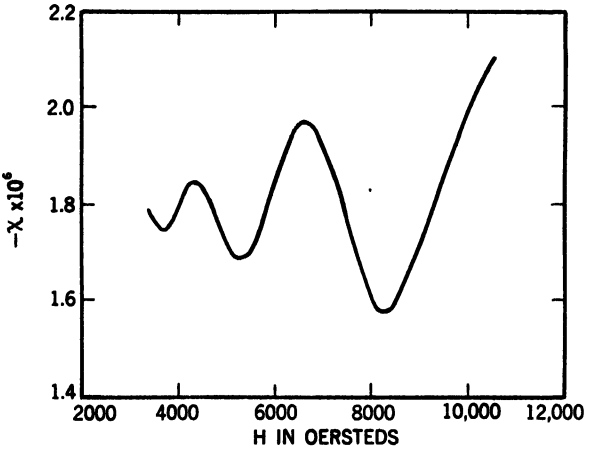


FIG. 30.—The de Haas–van Alphen effect in bismuth at very low temperature.

8. Non-Trivalent Rare Earths

It is well known that certain members of the rare earth family exhibit valences other than three. Cerium is readily oxidized to the ceric (Ce^{+4}) state, praseodymium and terbium form higher oxides, and samarium, europium, and ytterbium may be reduced to the divalent state. Reviews of this field are given by Pearce [92] and by Pearce and Selwood.[93]

The Sommerfeld-Kossel rule states that ions with equal numbers of electrons often have very similar properties. The magnetic susceptibility of the Fe^{+++} ion is, for instance, in fair agreement with that of the Mn^{++} ion. According to this rule the ceric ion, Ce^{+4}, should be diamagnetic like La^{+++}. Ceric oxide, CeO_2, has not been investigated as thoroughly as might be desired, but measurements tend to show that it has a small, temperature-independent paramagnetism.[94] This view has been sup-

[87] W. J. de Haas and P. M. van Alphen, *Proc. Acad. Sci. Amsterdam*, **34**, 1249 (1931); **36**, 158 (1933).

[88] D. Shoenberg, *Proc. Roy. Soc. London*, **A170**, 341 (1939).

[89] D. Shoenberg and M. Z. Uddin, *Proc. Roy. Soc. London*, **A156**, 687, 70 (1936); *Proc. Cambridge Phil. Soc.*, **32**, 499 (1936).

[90] M. Blackman, *Proc. Roy. Soc. London*, **A166**, 1 (1938).

[91] R. Peierls, *Z. Physik*, **81**, 186 (1933).

[92] D. W. Pearce, *Chem. Rev.*, **16**, 121 (1935).

[93] D. W. Pearce and P. W. Selwood, *J. Chem. Education*, **13**, 224 (1936).

[94] S. Meyer, *Ann. Physik*, **68**, 325 (1899).

ported by Foëx [95] who studied carefully purified $Ce(SO_4)_2 \cdot 4H_2O$. The compound is diamagnetic but after correction for the diamagnetism of the sulfate group and the water, the molar susceptibility of the ceric ion is $+ 22 \times 10^{-6}$. The ion, therefore, shows a slight paramagnetism similar to that shown by certain other transition group elements in the oxidation state in which they have the same number of electrons as an inert gas. It is clear at least from the magnetic measurements that ceric oxide is a true dioxide and not a peroxide. On the other hand the corresponding sulfides appear to be of polysulfide structure.[96]

The higher oxides of praseodymium and of terbium, PrO_2 and TbO_2, are rather difficult to characterize exactly, but measurements by Meyer seem to indicate that their susceptibilities are at least in rough agreement with the Sommerfeld-Kossel rule.

The most carefully studied isoelectronic pair [97, 98a] is Eu^{++} and Gd^{+++}. The molar susceptibility of Eu^{++} in the compound $EuSO_4$ at 20° C. is $25{,}800 \times 10^{-6}$. An average value for Gd^{+++} is $25{,}700 \times 10^{-6}$. By comparison, the susceptibility of the Eu^{+++} ion is only 4940×10^{-6}. Furthermore, far from showing an erratic temperature coefficient like Eu^{+++}, Eu^{++} follows the law $\chi = C/(T + \Delta)$. From considerations previously discussed, the value $\Delta = 4$ may be regarded as due to exchange forces because $EuSO_4$ is not a very "dilute" compound, magnetically speaking. It is not common that any ion other than one in an S state has such a low value for Δ. It may therefore be concluded that the electronic configuration of the Eu^{++} ion is identical with that of the Gd^{+++} ion. The outer electron grouping of europium is

$$\cdots 4f^6 5s^2 5p^6 5d^2 6s^1$$

In trivalent europium the 6s and the two 5d electrons are removed. In divalent europium it appears that one of the remaining valence electrons drops back into the 4f shell, leaving a structure identical with that of Gd^{+++}

$$\cdots 4f^7 5s^2 5p^6$$

Klemm [98b] and his co-workers have made a thorough study of divalent europium compounds. Europous chloride, bromide, and iodide all give an effective Bohr magneton number of 7.9 for the Eu^{++} ion, the same as for the Gd^{+++} ion. Europous fluoride gives $\mu_{eff} = 7.4$, but this low value may be due to contamination of the compound with EuF_3 or to

[95] G. Foëx, *Compt. rend.*, **208**, 738 (1939).
[96] W. Klemm, K. Meisel, and H. V. v. Vogel, *Z. anorg. allgem. Chem.*, **190**, 123 (1930).
[97] G. Hughes and D. W. Pearce, *J. Am. Chem. Soc.*, **55**, 3277 (1933).
[98a] P. W. Selwood, *J. Am. Chem. Soc.*, **55**, 4869 (1933).
[98b] W. Klemm and W. Döll, *Z. anorg. allgem. Chem.*, **241**, 233 (1939).

variations in the lattice. Fair agreement is also obtained from europous sulfide, selenide, and telluride.

Similar considerations apply to the ytterbous ion, Yb^{++}, which is isoelectronic with the diamagnetic lutecium ion, Lu^{+++}. The compounds $YbSO_4$ and $YbCl_2$ have been studied by Hughes and Pearce and by Klemm and Schüth [99] respectively. There is still some doubt whether the Yb^{++} ion is diamagnetic or, like Ce^{+4}, has a small temperature independent paramagnetism. Hughes and Pearce report a molar susceptibility of $+ 142 \times 10^{-6}$ for the Yb^{++} ion. The trivalent oxide, Yb_2O_3 has a molar susceptibility of about 7260×10^{-6} and it is rather difficult to be sure that all the ytterbium has been reduced. It would be interesting to have accurate data on the temperature coefficient of susceptibility for say $YbSO_4$. Some unpublished work by the author suggests that the temperature coefficient is zero. Senff and Klemm [100] have studied the selenides and tellurides of bivalent ytterbium. During reduction of Yb_2Te_3 to YbTe the susceptibility drops sharply and may be used to measure the degree of reduction.

Still another isoelectronic pair of rare earths is bivalent samarium, Sm^{++}, and trivalent europium, Eu^{+++}. Measurements on the compound $SmBr_2$ have been reported by Klemm and Rockstroh [101] and by the author.[44]

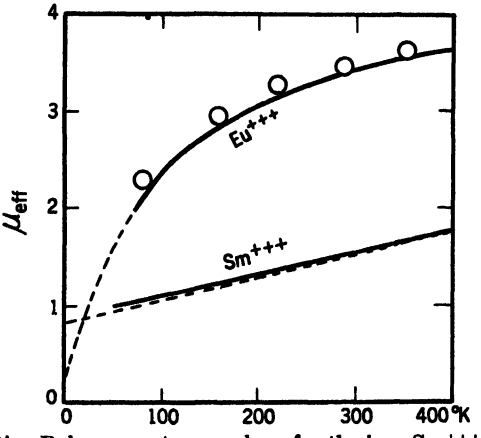


FIG. 31.—Effective Bohr magneton numbers for the ions Sm^{+++}, Sm^{++}, and Eu^{+++} plotted against temperature. The solid lines are for the trivalent ions as shown. The experimental points are for the divalent, Sm^{++}, ion.

Figure 31 shows the effective Bohr magneton numbers for Sm^{+++}, Sm^{++}, and Eu^{+++} plotted against temperature. The solid lines are for

[99] W. Klemm and W. Schüth, *Z. anorg. allgem. Chem.*, 184, 352 (1929).

[100] H. Senff and W. Klemm, *Z. anorg. allgem. Chem.*, 242, 92 (1939); 241, 259 (1939).

[101] W. Klemm and J. Rockstroh, *Z. anorg. allgem. Chem.*, 176, 181 (1928).

the trivalent ions of samarium and europium, and the experimental points are for bivalent samarium. The dotted lines show theoretical extension of the data to absolute zero. It is not possible to estimate the molecular field constant with any degree of accuracy, and it is doubtful if it would have any significance even if obtained. But in view of the correspondence at all temperatures investigated, it is probably safe to say that the electronic configurations of the Sm^{++} and Eu^{+++} ions are also identical.

9. Transition Group Elements and Their Ions

In this section some general remarks will be made concerning the elements of the first transition group. Detailed discussion of each paramagnetic ion will be given later.

Just as for the rare earths, the transition group elements possess an incomplete inner electron shell, the 3d. But for these elements the incomplete shell is by no means so effectively shielded from external influence. Generally this leads to considerable difficulty in estimating the degree of quenching of the orbital contribution to the magnetic moment, but in some cases the results are actually easier to interpret than are those for the rare earths.

The ions of the first transition group starting with the scandium, Sc^{+++}, ion and ending with the zinc, Zn^{++}, ion have progressively 0 to 10 electrons in the 3d shell. The first and last members are diamagnetic but all the others with intermediate numbers of electrons are paramagnetic. It might be supposed that these ions would be alternately paramagnetic and diamagnetic depending on whether they had an odd or an even number of electrons. But, as for the rare earths, the ions are all paramagnetic because the electrons in the incomplete shell tend not to pair off until they are forced to do so. For instance, in the 3d shell there are 10 places available in 5 pairs. If 6 electrons are present they will take 1 paired and 4 unpaired places instead of 3 pairs. The 4 unpaired electrons will contribute to the paramagnetism. It is therefore an easy matter to compute the number of unpaired electron spins in any given ion.

The difficulty that arises is in connection with the orbital contribution. The orbital moments of these ions are not free to move as they are for the rare earths, and yet, on the other hand, they may not be entirely quenched. Various efforts have been made to compute the effective moment of these ions, assuming that the multiplet intervals are infinitely wide compared to kT, or that they are infinitely small compared to kT. Calculations have also been made using the actual multiplet intervals where these are known from spectroscopic data. But the best agreement with experiment is obtained by completely neglecting the orbital mo-

ments. The various types of calculations, together with comparison with experiment are given by Van Vleck (*op. cit.*, p. 285). For ions such as Fe^{+++} or Mn^{++} which are in S states the question of orbital moment does not enter. The result of theoretical calculations for these ions agrees well with experiment. But even for ions which are not in S states the moments calculated on a "spin only" basis are often in excellent agreement with theory. Of course, many of the transition group elements form covalent bonds. When this occurs the magnetism is greatly modified. In fact, as will be shown in Chap. VI, the deviation of the susceptibility from the normal may be used to determine the possible covalency of bonds and the spatial configuration of complex molecules.

The paramagnetic part of the susceptibility of a transition group element is approximately represented by the "spin only" formula

$$\chi_M = \frac{N\beta^2}{3kT}[4S(S+1)]$$

and the effective moment in Bohr magnetons by

$$\mu_{eff} = 2\sqrt{S(S+1)}$$

If the multiplicity, $2S + 1$, is known, S may readily be found, or if the number, n, of unpaired electrons is known,

$$\mu_{eff} = \sqrt{n(n+2)}$$

It is clear, therefore, that the magnetic susceptibility is not directly proportional to the number of unpaired electrons, but rather to $n(n + 2)$ This is a fact which often causes confusion because it is erroneously assumed that two unpaired electrons would produce twice the molar paramagnetism of one.

Comparison of theoretical magneton numbers with experiment is, for transition group elements, further complicated by the possibility of hydrolysis and other chemical changes which do not occur so readily with the rare earths. Table XV gives the various ions in the first transition group with their "spin only" theoretical effective Bohr magneton numbers and the best available experimental data.

The experimental values are those used by Van Vleck except in a few instances where more complete data have become available. A few remarks concerning these data may be in order. It must be realized that owing to crystalline field and exchange effects the simple Curie law is rarely obeyed, so that T in the above expression for χ_M must generally be replaced by $T + \Delta$. But deviations even from the Weiss law are common, especially at low temperatures and it is seldom possible to

TABLE XV

THEORETICAL AND EFFECTIVE BOHR MAGNETON NUMBERS FOR IONS OF THE FIRST TRANSITION GROUP

Ion	3d electrons	Term	$\mu_{eff}=\sqrt{n(n+2)}$	μ_{eff} (expt.)
Sc^{+3}, Ti^{+4}, V^{+5}	0	$^1S_0$	0.00	0.0 0.0 0.0
Ti^{+3}, V^{+4}	1	$^2D_{3/2}$	1.73	1.77–1.79
Ti^{+2}, V^{+3}	2	$^3F_2$	2.83	— 2.76–2.85
V^{+2}, Cr^{+3}, Mn^{+4}	3	$^4F_{3/2}$	3.87	3.81–3.86 3.68–3.86 4.00
Cr^{+2}, Mn^{+3}	4	$^5D_0$	4.90	4.80 5.0
Mn^{+2}, Fe^{+3}	5	$^6S_{5/2}$	5.92	5.2–5.96 5.4–6.0
Fe^{+2}, Co^{+3}	6	$^5D_4$	4.90	5.0–5.5 (2.5)
Co^{+2}	7	$^4F_{9/2}$	3.87	4.4–5.2
Ni^{+2}	8	$^3F_4$	2.83	2.9–3.4
Cu^{+2}	9	$^2D_{5/2}$	1.73	1.8–2.2
Cu^{+1}, Zn^{+2}	10	$^1S_0$	0.00	0.0 0.0

calculate χ_M accurately over a very wide temperature range. Furthermore, small variations of susceptibility with concentration are reported by many experimenters for salts of transition group elements. Oxides are notoriously peculiar in their magnetic properties and little agreement is to be expected from measurements on such compounds. This is especially true of oxides which, like ceric oxide, show temperature independent paramagnetism. It will also be noticed that the magneton numbers of most ions in an isoelectronic sequence are given as nearly the same. Actually they should increase slightly with increasing atomic number because the multiplet intervals are increasing. But of this effect we have no experimental confirmation. Finally, it will be noticed that the agreement of theory with experiment is slightly better in the first half of the

transition series than in the second. This may possibly be due to rather less complete quenching of the orbital component in the second half.

In addition to the rare earths and the first transition series just discussed, there are at least two other transition series of elements in the periodic table. These are the series beginning with yttrium and ending with cadmium, and the series, of which the rare earths form a sub-series, beginning with lanthanum and ending with mercury. For these the incomplete electron shells are respectively the 4d and the 5d. The elements actinium to uranium form the beginning of still another transition series in which the 6d electron shell is incomplete. Not very many experimental data are available for these elements but such as there are show little agreement with theory. Van Vleck (*op. cit.*, p. 312) gives tabulated data on these elements but it is clear that much more remains to be done before even approximate magneton numbers may be calculated. In all cases the observed susceptibilities are much lower than the theoretical, sometimes even being of opposite sign. The field would appear to be a rich one for both theoretical and experimental advance.

In the following sections the ionic paramagnetism of the various transition group elements will be discussed in periodic table order. Extensive references to the earlier literature will be found in the books of Van Vleck and of Stoner. In addition, the references listed below may be useful.[102–106a]

10. Copper, Silver, and Gold

The cupric ion, Cu^{++}, has one unpaired electron and generally shows a magnetic moment of 1.8 Bohr magneton or slightly more, in magnetically dilute compounds and solutions.[106b] But for other compounds the effective Bohr magneton number becomes markedly dependent on temperature and even on field strength. Reekie [107] has measured the susceptibilities of blue vitriol and of several hydrated double sulfates of copper down to 1.6° K. He finds the Weiss law to be obeyed with a remarkably small value for Δ (less than 1°), and with Bohr magneton number averaging about 1.91 with small differences for the different com-

[102] G. Foëx, *Ann. phys.*, 16, 174 (1921).

[103] C. J. Gorter, *Physica*, 11, 171 (1931).

[104] W. J. de Haas and E. C. Wiersma, Rapports et Communications, 6e Congr. Intern. Froid, Buenos Aires, *Commun. Kamerlingh Onnes Lab. Univ. Leiden Suppl.* No. 74, 36 (1932).

[105] B. Cabrera, *Inst. intern. phys. Solvay, 6ième Conseil phys.*, 81 (1932).

[106a] G. Foëx, *J. phys. radium*, 4, 517 (1933).

[106b] J. Amiel, *Compt. rend.*, 213, 240 (1941).

[107] J. Reekie, *Proc. Roy. Soc. London*, A173, 367 (1939).

pounds. Measurements by Bhatnagar, Lessheim, and Khanna [108] are reported on various arsenites, arsenates, and double salts of copper between the temperatures 304° and 368° K. The effective Bohr magneton numbers range from 1.80 to 2.00 in different compounds. The fluctuations are ascribed to uncertainties in the correction to be applied to the negative radical. In any event there seems to be little or no contribution from the orbital component. These authors suggest that compounds such as $[Cu(NH_3)_4](NO_3)_2$ possess covalent bonds and, as a conclusion, that covalence has no influence on the magnetism of the cupric ion. It is doubtful, however, if this conclusion is justified because more concentrated types of compounds show very different effective magneton numbers for copper. Amiel [109] reports that the ionic susceptibility of divalent copper is but little influenced by change of organic substituent in a large number of cupritetrachlorides and cupritrichlorides. On the other hand the paramagnetism of the Cu^{++} ion [110] in cupric salts of long open-chain fatty acids is said to be only about half the normal.

Copper fluoride, CuF_2, has been studied by Henkel and Klemm; [111] and by de Haas, Schultz, and Koolhaus; [112] as well as by Bhatnagar, Lessheim, and Khanna.[108] At higher temperatures the effective Bohr magneton number for the cupric ion in this compound seems to be about 1.8, but for instance at 293° K. it is 1.57, and at 90° K. it is 1.01. At very low temperatures it is much smaller and becomes dependent on field strength. Like some other salts, including $CuSO_4$, it shows the phenomena of remanence and of coercive force.

Crystalline cupric hydroxide has been studied by Chaumeton.[113] The paramagnetism of cupric oxide and its lack of metallic conductivity is discussed by Dressnandt.[114] The phosphides of copper, Cu_3P, and CuP_2, have been measured by Haraldsen.[115] They are both diamagnetic with practically zero temperature coefficient from − 183° to 388° C. Obviously they do not contain any ordinary form of cupric ion.

The paramagnetic anisotropy of copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, has been studied by Krishnan and Mookherji.[116] The

[108] S. S. Bhatnagar, H. Lessheim, and M. L. Khanna, *J. Indian Chem. Soc.*, **14**, 445 (1937).

[109] J. Amiel, *Compt. rend.*, **206**, 1113 (1938).

[110] J. Amiel, *Compt. rend.*, **207**, 1097 (1938).

[111] P. Henkel and W. Klemm, *Z. anorg. allgem. Chem.*, **222**, 73 (1935).

[112] W. J. de Haas, B. H. Schultz, and J. Koolhaus, *Physica*, **7**, 57 (1940).

[113] L. Chaumeton, *Compt. rend.*, **206**, 1104 (1938).

[114] H. Dressnandt, *Z. Physik*, **115**, 369 (1940).

[115] H. Haraldsen, *Z. anorg. allgem. Chem.*, **240**, 337 (1939).

[116] K. S. Krishnan and A. Mookherji, *Nature*, **140**, 896 (1937); *Phys. Rev.*, **50**, 860 (1936); **54**, 533, 841 (1938).

magnetic measurements confirm the view that each Cu^{++} ion is at the center of an approximate octahedron formed by four water molecules and two oxygen atoms. But the results indicate that the crystalline field has a rhombic component in addition to the cubic. The anisotropy is surprisingly large. Parallel and perpendicular to the tetragonal axis of the crystalline field the effective Bohr magneton numbers are respectively 2.13 and 1.80. There is practically no temperature dependence. Other copper compounds whose anisotropy has been measured are the potassium double sulfate,[117] some double chlorides of the general formula $2RCl \cdot CuCl_2 \cdot 2H_2O$,[118] and cupric selenate pentahydrate.[119]

The cuprous ion, Cu^+, has no incomplete electron shell and hence is expected to be diamagnetic. This appears to be the case [120,121] although Perakis and Capatos [122] suggest that it may possess a feeble paramagnetism. If this is true it can only be of the temperature independent type. In measurements on cuprous compounds the necessity of eliminating the paramagnetic cupric ion is obvious. The matter is discussed by Sugden.[123]

The normal silver ion, Ag^+ like Cu^+, is diamagnetic. Silver subfluoride, Ag_2F, has already been mentioned (p. 42) as having a subnormal diamagnetism. The argentic ion, Ag^{++}, has been studied in the compound AgF_2 by Gruner and Klemm [124] who report the small molar susceptibility of 440×10^{-6}. In view of the behavior of CuF_2 the above value for AgF_2 is perhaps not very surprising. Sugden gives a list of argentic compounds such as the tris-$\alpha\alpha'$-dipyridyl chlorate, in all of which the silver ion is paramagnetic. Capatos and Perakis [125] report an approximately normal value of 1.74 Bohr magnetons for the Ag^{++} ion in the compound $AgS_2O_4 \cdot 4C_5H_5N$. These authors have also studied solid solutions of argentic and cupric compounds.[126]

Salts of trivalent copper and silver of the types $M_7^+Cu^{+++}(IO_6)_2 \cdot nH_2O$ and $M_7^+Ag^{+++}(IO_6)_2 \cdot nH_2O$ are diamagnetic.[127] For instance $K_7CuI_2O_{12} \cdot 7H_2O$ has a susceptibility of -40.2×10^{-6} at 18° C. The corresponding tellurates are also diamagnetic.

[117] B. W. Bartlett, *Phys. Rev.*, **41**, 818 (1932); **44**, 687 (1933).

[118] K. S. Krishnan, A. Mookherji, and A. Bose, *Phil. Trans. Roy. Soc. London*, **A238**, 125 (1939).

[119] A. Mookherji and M. T. Tin, *Z. Krist.*, **101**, 412 (1939).

[120] C. Courty, *Compt. rend.*, **202**, 1929 (1936).

[121] F. Hommel, *Ann. Physik.*, **30**, 467 (1937).

[122] N. Perakis and L. Capatos, *J. phys. radium*, **7**, 391 (1936).

[123] S. Sugden, *J. Chem. Soc.*, **1932**, 161.

[124] E. Gruner and W. Klemm, *Naturwissenschaften*, **25**, 59 (1937).

[125] L. Capatos and N. Perakis, *Compt. rend.*, **202**, 1773 (1936).

[126] N. Perakis and L. Capatos, *J. phys. radium*, **10**, 234 (1939).

[127] L. Malatesta, *Gazz. chim. ital.*, **71**, 467 (1941).

If gold formed an ion with a charge of plus two it would doubtless be paramagnetic. No measurements appear to have been made on the unstable oxide AuO. In its normal valences of one and three gold is diamagnetic.

11. Titanium, Zirconium, Hafnium, and Thorium

So far as magnetic measurements are concerned this is a neglected group in the periodic table. Except for the valence of four, these elements should show paramagnetism. Titanium alum has a paramagnetic susceptibility corresponding to the "spin only" formula. This has been examined theoretically by Van Vleck.[128] Certain phase-ratio work on the titanium-oxygen system will be referred to later.

Starr, Bitter and Kaufmann [129] have studied the susceptibilities of solid titanium dichloride and trichloride over a wide range of temperature. These compounds are paramagnetic but they have especially peculiar temperature coefficients, with a strong susceptibility maximum at or near the temperature of specific heat anomaly.

12. Vanadium, Columbium, Tantalum, and Protoactinium

Vanadium is the only element of this group which has received much study. It is a particularly interesting element because of the great range of valence in which it forms stable ionic compounds. Freed [130] has studied di-, tri-, and tetra-valent vanadium and finds the effective Bohr magneton numbers to be respectively 3.805–3.855, 2.760, and 1.745. These are in close agreement with the theoretical, assuming complete orbital quenching.

Vanadium alum, $V_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$, has been measured by van den Handel and Siegert.[131] Over the range 293° to liquid helium temperatures the Weiss law is obeyed with a moment for the V^{+3} ion corresponding to 2.62 Bohr magnetons.

The susceptibilities of several halides, oxides, and sulfides of vanadium have been measured by Klemm and Hoschek.[132] The tri- and tetra-halogenides have susceptibilities in good agreement with theory; the dihalides are a little low. The pentoxide has a small paramagnetism although it might be expected to be diamagnetic. The dioxide, VO_2, has a very low paramagnetism in spite of having an odd number of electrons. This suggests atomic binding between the V^{+4} ions. The compound

[128] J. H. Van Vleck, *J. Chem. Phys.*, **7**, 61 (1939).
[129] C. Starr, F. Bitter, and A. R. Kaufmann, *Phys. Rev.*, **58**, 977 (1940).
[130] S. Freed, *J. Am. Chem. Soc.*, **49**, 2456 (1927).
[131] J. van den Handel and A. Siegert, *Physica*, **4**, 871 (1937).
[132] W. Klemm and E. Hoschek, *Z. anorg. allgem. Chem.*, **226**, 359 (1936).

V_2S_5 probably does not exist. A substance or mixture analyzing for V_2S_5 is strongly paramagnetic. The V^{+5} ion could not have strong paramagnetism. Klemm and some others have done some extensive and interesting work on the vanadium-oxygen and vanadium-sulfur phase-ratios. Discussion of this work will be deferred until later except to mention that V_2O_3 and VO_2 show marked susceptibility—temperature anomalies at $-100°$ and 68° C. respectively. As the temperature rises past these points the susceptibility increases by as much as 14-fold.

As for the elements columbium, tantalum, and protoactinium little or nothing is known. They should all exhibit paramagnetism except in the pentavalent state.

13. Chromium, Molybdenum, Tungsten, and Uranium

The chromous ion, Cr^{++}, has been studied by Lips,[133] in the sulfate hexahydrate, $CrSO_4 \cdot 6H_2O$. Over the temperature range 54° to 400° K. he finds the Weiss law to be obeyed with an effective Bohr magneton number of 4.82, in agreement with the "spin only" formula. For chromous chloride the susceptibility is a complicated function of temperature.

The susceptibilities of anhydrous chromic salts seem nearly always to be lower than those of hydrated salts,[134] and often much more difficult to understand. The compound $Cr_2(SO_4)_2(OH)_2 \cdot 5H_2O$ has been shown by Gorter, de Haas, and van den Handel [135] to follow the Weiss law with $\Delta = 36°$, and $\mu_{eff} = 3.7$ Bohr magnetons. There is a slight deviation at liquid hydrogen temperatures. In $[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$ the crystalline field must be somewhat different, Δ is only 0.4°, but μ_{eff} is 3.8.

Measurements by Jackson [136] and by Krishnan, Mookherji, and Bose [137] show that the potassium and ammonium chromioxalates have unusually low magnetic anisotropies. The influence of crystalline fields on the susceptibilities of chromium and other transition group salts is studied theoretically by Schlapp and Penney.[138]

Chromic halides show peculiar magnetic properties which, however, are common among the more "concentrated" compounds of all transition group elements. The fluoride,[139] CrF_3, and the chloride, $CrCl_3$,[129, 140]

[133] E. Lips, *Helv. Phys. Acta*, 7, 537 (1934).

[134] E. F. Herroun, *Proc. Phys. Soc. London*, 46, 872 (1934).

[135] C. J. Gorter, W. J. de Haas, and J. van den Handel, *Proc. Acad. Sci. Amsterdam*, 36, 168 (1933).

[136] L. C. Jackson, *Proc. Roy. Soc. London*, A140, 695 (1933).

[137] K. S. Krishnan, A. Mookherji, and A. Bose, *Trans. Roy Soc.*, A238, 125 (1939).

[138] R. Schlapp and W. G. Penney, *Phys. Rev.*, 42, 666 (1932).

[139] H. Bizette and B. Tsaï, *Compt. rend.*, 211, 252 (1940).

[140] S. S. Shalyt, *J. Exptl. Theoret. Phys.* (*USSR*), 8, 518 (1938); 9, 1073 (1939); *Compt. rend. acad. sci. URSS*, 24, 680 (1939).

follow the Weiss law reasonably well near room temperature, but near liquid hydrogen temperatures the susceptibility depends markedly on the field strength. As shown by de Haas, Schultz, and Koolhaus,[112] the susceptibility of anhydrous chromic chloride shows a complete hysteresis curve at 14.8° K. (Fig. 32.)

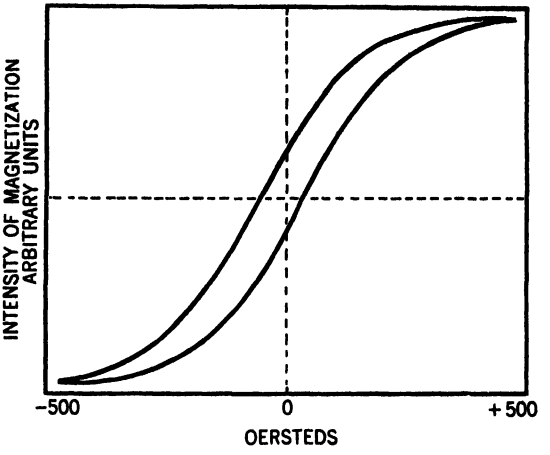


FIG. 32.—Hysteresis curve for $CrCl_3$ at 14.8° K., for a magnetization cycle between +462 and −462 oersteds. To obtain this curve a rather arbitrary subtraction has been made for the reversible part of the susceptibility in this region. Such incipient ferromagnetism is sometimes called "metamagnetism."

The susceptibility of chromic oxide, Cr_2O_3, is reported by several investigators [141, 142] to vary with the mode of preparation. But others [143, 144] claim that the differences are due to traces of adsorbed gases.

The oxide CrO_2 has an effective moment of about 2.95 which is about normal for quadrivalent chromium.[145] The oxide Cr_5O_9 is ferromagnetic.[146] Chromium trioxide, CrO_3, has no unpaired electrons but Tilk and Klemm [147] have shown that all sexivalent chromium, molybdenum, tungsten, and uranium compounds have a small temperature independent paramagnetism. They also discuss the relationship of this effect to position in the periodic table.

[141] W. H. Albrecht and E. Wedekind, *Z. anorg. allgem. Chem.*, 210, 105 (1933).

[142] C. J. Gorter, W. J. de Haas, and J. van den Handel, *Proc. Acad. Sci. Amsterdam*, 36, 168 (1933).

[143] S. S. Bhatnagar, P. L. Kapur, and B. Prakash, *Current Sci.*, 8, 253 (1939).

[144] S. S. Bhatnagar, A. Cameron, E. H. Harbard, P. L. Kapur, A. King, and B. Prakash, *J. Chem. Soc.*, 1939, 1433.

[145] S. S. Bhatnagar, B. Prakash, A. Hamid, *J. Chem. Soc.*, 1938, 1428.

[146] S. S. Bhatnagar, P. L. Kapur, and B. Prakash, *Current Sci.*, 8, 253 (1939).

[147] W. Tilk and W. Klemm, *Z. anorg. allgem. Chem.*, 240, 355 (1939).

Complex compounds of chromium will be discussed in Chap. VI. It may be mentioned that the sulfides, selenides, and tellurides of chromium have been studied by Haraldsen and Kowalski.[148] The compounds CrS and CrSe are paramagnetic but CrTe is ferromagnetic at low temperatures.

There are not many measurements available on compounds of molybdenum. Sucksmith[149] has studied $MoCl_3$ and $MoCl_5$. Klemm and Steinberg[150] report on $MoCl_3$, $MoCl_5$, $MoBr_3$, and $MoBr_5$. The susceptibilities are all temperature dependent and suggest quenching of the orbital component.

The same authors have reported on the halides of uranium. The most extensive work on uranium is that of Lawrence[151] who reports on the susceptibilities of the ions in solution. His results are indicated in Table XVI. These results are in fair agreement with the "spin only"

TABLE XVI

EFFECTIVE MOMENTS OF THE IONS OF URANIUM

Salt	Ion	χ_M	μ_{eff}
UO_2SO_4	UO_2^{++}	56	—
$U(ClO_4)_2$	U^{+4}	3633	2.945
$U(SO_4)_2$	U^{+4}	3643	2.95
UCl_4	U^{+4}	3703	2.97
$UO(ClO_4)_2$	UO^{+2}	3110	2.73
UCl_3	U^{+3}	4335	3.22
$U_2(SO_4)_3$	U^{+3}	4215	3.17

formula. There is a small variation of susceptibility with hydrogen ion concentration. The small temperature independent paramagnetism of the UO_2^{++} ion is confirmed by Nicolau.[152] Some change of susceptibility with concentration was observed. The oxide UO_3 has a small temperature independent paramagnetism.[153a] On the other hand UO_2 and U_3O_8 follow the Weiss law. The susceptibility of U_3O_8 suggests that its structure is $UO_3 \cdot U_2O_5$ rather than $2UO_3 \cdot UO_2$.

Bommer[153b] states that UCl_4 has a moment of 2.7 Bohr magnetons above 20° C., but that at lower temperatures atomic bindings appear and

[148] H. Haraldsen and E. Kowalski, *Z. anorg. allgem. Chem.*, **224**, 329 (1935).
[149] W. Sucksmith, *Phil. Mag.*, **14**, 1115 (1932).
[150] W. Klemm and H. Steinberg, *Z. anorg. allgem. Chem.*, **227**, 193 (1936).
[151] R. W. Lawrence, *J. Am. Chem. Soc.*, **56**, 776 (1934).
[152] A. Nicolau, *Compt. rend.*, **205**, 654 (1937).
[153a] H. Haraldsen and R. Bakken, *Naturwissenschaften*, **28**, 127 (1940).
[153b] H. Bommer, *Z. anorg. allgem. Chem.*, **247**, 249 (1941).

the values of $1/\chi$ lie above the straight line determined by the experimental points above 20°.

14. Manganese and Rhenium

The manganous ion, Mn^{++}, is in an S state, hence one would expect the theoretical magneton numbers to be in somewhat better agreement with experiment. Among the more recent measurements on the more "dilute" manganous compounds the following may be mentioned: Krishnan, Chakravorty, and Banerjee [154] have reported on manganous ammonium sulfate which has an exceedingly small anisotropy and for which $\mu_{eff} = 5.85$ Bohr magnetons compared with 5.95 for five unpaired electrons. The anisotropy and susceptibility of manganous salts have been studied theoretically by Van Vleck and Penney.[155] Jackson [156] has also studied manganous ammonium sulfate and confirms the results of the Indian workers. The molecular field constant, as anticipated, is small, being only 0.7°. The hydrated and anhydrous sulfates have been studied by Jackson and by Herroun, aqueous solutions by Bose,[157] and the anhydrous acetate, formate, lactate, and oxalate by Bhatnagar, Nevgi, and Sharma.[158] In all of these the Curie law is obeyed closely and the "spin only" formula gives a close approximation to experiment.

The manganic ion, Mn^{+3}, has been studied in the compound manganic acetylacetonate by Jackson.[159] This compound obeys the Weiss law with $\Delta = 5.5°$ down to 70° K. below which temperature the susceptibility increases somewhat more rapidly. The effective Bohr magneton number is 4.98, in good agreement with theory for four unpaired spins.

Among somewhat more "concentrated" compounds of manganese the fluoride, chloride, and bromide have been studied respectively by Bizette and Tsaï,[160] by de Haas, Schultz, and Koolhaus, and by Starr, Bitter, and Kaufmann. Even in these compounds the Curie law is obeyed reasonably well at room temperature but at low temperatures striking anomalies, including field strength dependence, make their appearance.

The compounds of divalent manganese with the "chalcogens" oxygen, sulfur, selenium, and tellurium have some unique magnetic properties. They have been studied by Tyler; [161] Haraldsen and Klemm; [162] Mehmed

[154] K. S. Krishnan, N. C. Chakravorty, and S. Banerjee, *Trans. Roy. Soc. London*, A232, 99 (1933).

[155] J. H. Van Vleck and W. G. Penney, *Phil. Mag.*, 17, 961 (1934).

[156] L. C. Jackson, *Proc. Roy. Soc. London*, A140, 695 (1933).

[157] A. Bose, *Nature*, 133, 213 (1934); *Proc. Indian Acad. Sci.*, IA, 605 (1935).

[158] S. S. Bhatnagar, M. B. Nevgi, and R. L. Sharma, *Phil. Mag.*, 22, 409 (1936).

[159] L. C. Jackson, *Proc. Phys. Soc. London*, 47, 1029 (1935).

[160] H. Bizette and B. Tsaï, *Compt. rend.*, 209, 205 (1939).

[161] R. W. Tyler, *Phys. Rev.*, 44, 776 (1933).

[162] H. Haraldsen and W. Klemm, *Z. anorg. allgem. Chem.*, 220, 183 (1934).

and Haraldsen;[163] Bizette, Squire, and Tsaï;[164] Bhatnagar, Cameron, Harbard, Kapur, King, and Prakash; Bhatnagar, Kapur, and Prakash;[165] Bhatnagar, Prakash, and Singh;[166] and Squire.[167a] The specific heat curves of these compounds all show a "hump" at various temperatures from 100° to 300° K. As the temperature is lowered through these transition temperatures the magnetic susceptibility begins to drop and approaches diamagnetism as the absolute zero is approached. This behavior is directly opposite to the normal course of paramagnetism. It is called "antiferromagnetism" and is shown by some other compounds as

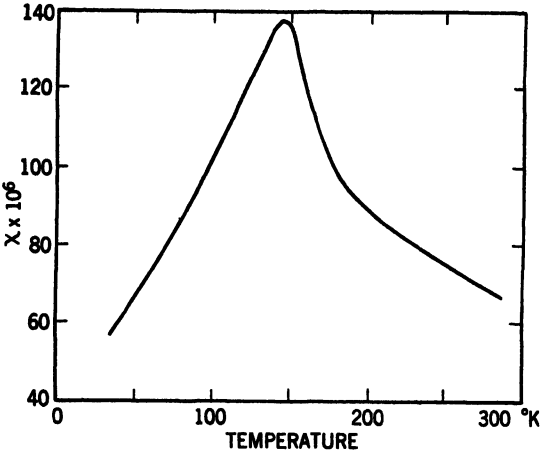


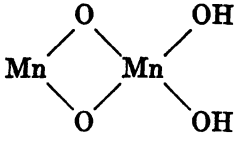
FIG. 33.—An example of "antiferromagnetism" found in manganous selenide.

well.[167b] Manganous selenide shows some hysteresis at the Curie point. Squire attributes this effect to an antiparallel locking of the spins, giving rise to strong exchange forces between the atoms.

A few other manganese compounds which may be mentioned are potassium manganate[168] for which $\mu_{eff} = 1.73$ Bohr magnetons; manganous carbonate,[169] $MnCO_3$, which has a nearly normal effective moment and a slight anisotropy; manganous hydroxide;[170] manganite,[171]

[163] F. Mehmed and H. Haraldsen, *Z. anorg. allgem. Chem.*, 235, 193 (1938).
[164] H. Bizette, C. F. Squire, and B. Tsaï, *Compt. rend.*, 207, 449 (1938).
[165] S. S. Bhatnagar, P. L. Kapur, and B. Prakash, *Current Sci.*, 8, 253 (1939).
[166] S. S. Bhatnagar, B. Prakash, and J. Singh, *J. Indian Chem. Soc.*, 16, 313 (1939).
[167a] C. F. Squire, *Phys. Rev.*, 56, 922 (1939); *J. Chem. Phys.*, 7, 139 (1939).
[167b] G. Foëx and M. Graff, *Compt. rend.*, 209, 160 (1939).
[168] K. A. Jensen and W. Klemm, *Z. anorg. allgem. Chem.*, 237, 47 (1938).
[169] K. S. Krishnan and S. Banerjee, *Z. Krist.*, 99, 499 (1938).
[170] W. H. Albrecht, *Z. anorg. allgem. Chem.*, 232, 382 (1937).
[171] K. S. Krishnan and S. Banerjee, *Nature*, 142, 717 (1938); *Trans. Faraday Soc.*, 35, 385 (1939).

$Mn_2O_3 \cdot H_2O$, which is shown by its feeble anisotropy to have the structure,



that is, with one divalent and one tetravalent manganese atom rather than

with two trivalent atoms. The mineral braunite, a manganese silicate, has been studied by Krishnan and Banerjee,[172] and by Turtsev.[173] The boride and the arsenide of manganese have been studied, respectively, by Hocart and Fallot,[174] and by Bates.[175] Further applications of the magnetic method to structural problems in manganese chemistry are given by Bhatnagar, Prakash, and Maheshwari.[176]

In contrast to manganese there have been few magnetic studies of rhenium. Schüth and Klemm [177] have measured several rhenium compounds in different valence states. For instance Re_2O, $KReO_4$, and ReO_3Cl show a small temperature independent paramagnetism which is, surprisingly, also shown by ReO_3, ReO_2, ReS_2, $ReCl_3$, and $ReBr_3$. The effect is normal for a valence of seven, but may be due to atomic or metallic binding in the other compounds. Compounds in which the valence is five, such as $ReCl_5$ have a susceptibility which at high temperatures approaches that for "spin only." The same is true of the valence of four in such compounds as K_2ReCl_6 and Ag_2ReCl_6. Several of the tetravalent complex halides have also been studied by Perakis, Karantassis, and Capatos [178] with similar results. It is clear that the compounds of rhenium have normal magnetic properties except where the paramagnetic atoms are too highly concentrated.

15. Iron

This element and its compounds have been the subject of almost innumerable magnetic studies. Dilute compounds of ferrous and ferric ions are fairly normal, the latter in particular because the ion is in an S

[172] K. S. Krishnan and S. Banerjee, *Z. Krist.*, 101, 507 (1939).

[173] A. A. Turtsev, *Bull. acad. sci. URSS*, 1938, 508.

[174] R. Hocart and M. Fallot, *Compt. rend.*, 203, 1062 (1936).

[175] L. F. Bates, *Phil. Mag.*, 16, 657 (1933).

[176] S. S. Bhatnagar, B. Prakash, and J. C. Maheshwari, *Proc. Indian Acad. Sci.*, 10A, 150 (1939).

[177] W. Schüth and W. Klemm, *Z. anorg. allgem. Chem.*, 220, 193 (1934).

[178] N. Perakis, T. Karantassis, and L. Capatos, *Compt. rend.*, 206, 1369 (1938).

state. But the more concentrated iron compounds such as the anhydrous halides show anomalies similar to those already reported for chromium, manganese, and other transition group elements. Iron in its oxides and hydroxides often shows varying degrees of ferromagnetism. Consideration of these compounds will therefore be deferred until a later chapter. The earlier literature is reviewed by Stoner (*op. cit.*) who mentions many of the anomalies found but points out that solutions and dilute ferrous and ferric compounds obey the "spin only" formula with considerable accuracy.

Herroun has measured ferrous and ferric salts, both hydrated and anhydrous. There is often a large difference between the ionic susceptibility of iron in different compounds. For instance Herroun finds nearly a 40 per cent difference between anhydrous ferric sulfate and ferric alum. Nicolau [179] has reported on solutions of ferrous ammonium sulfate over a rather narrow temperature range. The solutions obey the Weiss law with $\Delta = 20.6°$, and $\mu_{eff} = 5.15$ Bohr magnetons.

The magnetic anisotropy of mixed Tutton salts has been studied by Jogelkar.[180a] These salts are of the type $MSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, where M is Fe^{++}, Co^{++}, Ni^{++}, or Cu^{++}. It is possible to dilute the paramagnetic ion in these crystals by progressive replacement with the diamagnetic magnesium ion, Mg^{++}, or by Zn^{++}. In this way Jogelkar found that the order of magnitude of the anisotropy of any given paramagnetic ion is the same at all dilutions.

Bizette and Tsaï [180b] report that the susceptibility of ferrous fluoride passes through a maximum of $\chi_M = 19500 \times 10^{-6}$ at 79° K. Above 90° K. the Weiss law holds with $\mu_{eff} = 5.59$.

Considerable work has been done on anhydrous ferrous chloride at low temperatures. This substance has a specific heat anomaly in the neighborhood of 14° K. and another at slightly higher temperature. The magnetic susceptibility shows remanence and hysteresis near these temperatures. One of the most extensive studies of these effects is that of Starr, Bitter, and Kaufmann, but they have also received careful examination by Shalyt.[181, 182]

The susceptibility of ferric ammonium alum at very low temperatures has been studied by Kürti, Lainé, and Simon,[183] and by Casimir, de Haas,

[179] A. Nicolau, *Compt. rend.*, **205**, 557 (1937).

[180a] M. S. Jogelkar, *Z. Krist.*, **98**, 411 (1938).

[180b] H. Bizette and B. Tsaï, *Compt. rend.*, **212**, 119 (1941).

[181] S. S. Shalyt, *Compt. rend. acad. sci. URSS*, **20**, 657 (1938); *J. Exptl. Theoret. Phys. (USSR)*, **8**, 518 (1938); *Nature*, **143**, 799 (1939).

[182] G. A. Milyutin and S. S. Shalyt, *Compt. rend. acad. sci. URSS*, **24**, 680 (1939).

[183] N. Kürti, P. Lainé, and F. Simon, *Compt. rend.*, **204**, 675 (1937).

and de Klerk.[184] This compound, although it is magnetically dilute, shows remanence and hysteresis very near the absolute zero. The phenomena are also shown by cesium-titanium and potassium-chromium alums, and by ammonium-manganese, and potassium-manganese hydrated double sulfates.

The magnetic anisotropy of the ferric alums has been studied by Jackson;[185] Forrest;[186] Krishnan and Banerjee;[187] Krishnan and Mookherji;[188] and from a theoretical standpoint by Van Vleck and Penney;[189] and by Siegert.[190] Although the ferric ion is in an S state, like compounds of divalent manganese, its salts show a definite, though feeble, anisotropy. This seems to be due in part to the diamagnetic anisotropy of the crystal, and in part to the mutual influence of the magnetic moments and their non-cubic arrangement in the crystal lattice. After allowing for the above, the remaining anisotropy is due to Stark splitting under the influence of the crystalline field. Jackson includes data for ferric acetylacetonate for which the average susceptibility follows the Weiss law with $\mu_{eff} = 5.97$ Bohr magnetons and $\Delta = 4°$.

Studies on aqueous solutions of ferric salts yield rather complicated results. Bose[191a] has reported on solutions of the chloride, nitrate, and sulfate. Hydrolysis and other effects render the results rather difficult to interpret. Use has even been made of the deviations from additivity to calculate the degree of hydrolysis of ferric chloride solutions.[191b] In some cases, however, the paramagnetism is approximated by the "spin only" formula even at great dilution.[192]

Ferric fluoride has been studied by Bizette and Tsaï.[160] As might be expected it shows field strength dependence and other characteristics of incipient ferromagnetism.

Ferric chloride in the anhydrous state has been studied by Lallemand.[193] Rather surprisingly the susceptibility follows the Weiss law with $\mu_{eff} = 5.8$ Bohr magnetons and $\Delta = 12°$ over the temperature range 150° to 293° K. Below 150° K. anomalies would doubtless begin to intrude. The most interesting feature of Lallemand's work is on ferric

[184] H. B. G. Casimir, W. J. de Haas, and D. de Klerk, *Physica*, 6, 241 (1939).
[185] L. C. Jackson, *Proc. Roy. Soc. London*, A140, 695 (1933).
[186] J. Forrest, *Phil. Mag.*, 15, 1153 (1933).
[187] K. S. Krishnan and S. Banerjee, *Trans. Roy. Soc. London*, A235, 343 (1936).
[188] K. S. Krishnan and A. Mookherji, *Trans. Roy. Soc. London*, A237, 135 (1938).
[189] J. H. Van Vleck and W. G. Penney, *Phil. Mag.*, 17, 961 (1934).
[190] A. Siegert, *Physica*, 4, 138 (1937).
[191a] A. Bose, *Proc. Indian Acad. Sci.*, 1A, 754 (1935).
[191b] M. Auméras and M. Mounic, *Bull. soc. chim. mém.*, 4, 536 (1937).
[192] R. Mercier, *Ann. phys.* [11] 3, 201 (1935).
[193] A. Lallemand, *Ann. phys.*, 3, 97 (1935).

chloride in the vapor state. Consideration of this, however, must be deferred for Chap. VI.

16. Cobalt and Nickel

Many studies have been made on cobalt and nickel compounds. Only the more recent will be mentioned here. In general, the moments derived from solutions are the same as those from magnetically dilute compounds. Auer [194] questions the validity of extrapolations to infinite dilution to find the moment of the free ion. It is probable, of course, that in solution the paramagnetic ions are no less subject to the fields of oriented solvent molecules than they are in hydrated crystals. Foëx [195] in particular claims that several distinct magnetic states of the ions of cobalt and nickel exist in aqueous solution. On the other hand Mercier [196,192] finds that even at great dilution the effective moment of the cobalt ion, Co^{++}, is independent of concentration but diminishes somewhat with falling temperature.

One of the most careful studies of nickel seems to be that of Nicolau who measured the susceptibility of nickel sulfate solution over the temperature range 23° to 76° C. The effective moment for the Ni^{++} ion is 3.37 Bohr magnetons.

Other studies on solutions of cobalt and nickel salts have been made by Datta.[197]

Magnetically dilute compounds of nickel and cobalt have been studied by Serres,[198] by Herroun, and by Janes.[199] The sulfate, chloride, bromide, and most simple and double salts are normal. The cyanide, $Ni(CN)_2$ is reported by Serres to have a much lower susceptibility, a result which is confirmed by Fereday.[200] This may possibly be due to covalent binding, which, in a sense would place nickel cyanide in the class of complex compounds.

The magnetic anisotropies of dilute compounds of cobalt and of nickel have been studied by Bartlett; by Krishnan and Mookherji; and by Krishnan, Mookherji, and Bose.[201] The last named point out that the observed anisotropies of nickel salts permit calculation of the strength of

[194] H. Auer, *Physik. Z.*, **33**, 869 (1932).
[195] G. Foëx, *J. phys. radium*, **3**, 337 (1932).
[196] R. Mercier, *Helv. Phys. Acta*, **6**, 240 (1933); *Compt. rend.*, **196**, 164 (1933).
[197] S. Datta, *Phil. Mag.*, **17**, 585, 1160 (1934).
[198] A. Serres, *Ann. phys.*, **20**, 441 (1933).
[199] R. B. Janes, *Phys. Rev.*, **48**, 78 (1935).
[200] R. A. Fereday, *Proc. Phys. Soc. London*, **46**, 214 (1934).
[201] K. S. Krishnan, A. Mookherji, and A. Bose, *Trans. Roy. Soc. London*, **A238**, 125 (1939).

coupling between orbital and spin angular moments of the nickel ion, Ni^{++}, giving results in agreement with the spectroscopic values.

Before leaving magnetically dilute solutions, we should mention the work of Bhatnagar and Kapur [202] who studied the well-known color changes of cobalt chloride from the magnetic standpoint. In all aqueous solutions they found the Co^{++} ion to have the same effective moment, but slightly lower results were obtained with solutions of $CoCl_2 \cdot 6H_2O$ in methyl, ethyl, and amyl alcohols. They suggest that the color change from red to blue is due to complex ion formation rather than to the formation of different hydrates.

More concentrated compounds of nickel and cobalt begin to show the anomalies already mentioned for the other transition group elements. For instance the anhydrous fluorides which have been studied by Henkel and Klemm show variations as shown in Table XVII. Cobalt fluoride

TABLE XVII

EFFECTIVE BOHR MAGNETON NUMBERS FOR SOME FLUORIDES

Temp. ° K.	CoF_2 μ_{eff}	NiF_2 μ_{eff}	CoF_3 μ_{eff}
90	4.00	2.13	1.60
195	4.36	2.62	2.00
293	4.60	2.85	2.46

is one of the few compounds of trivalent cobalt which have been subjected to magnetic investigation.

Some further studies of trivalent cobalt compounds will be referred to in Chap. VI.

Klemm and Schüth [203] have studied the chlorides, bromides, and iodides of cobalt and nickel, as well as the oxides and sulfides. The last two are of especial interest. Nickel oxide, NiO, is intermediate in properties between para- and ferromagnetism and may have a Curie point near 350° C. The sulfides are slightly paramagnetic and have some metallic properties. Klemm's interesting use of magnetic measurements to establish the nickel-oxygen and nickel-sulfur phase ratios will be deferred to Chap. IX. Foëx and Fehrenbach [204] report that the cobaltous, Co^{++}, ion shows a rather sharp change in effective moment at 409° K. The change amounts to almost exactly 1 Weiss magneton and the authors claim this is evidence for the fundamental nature of the Weiss magneton. It

[202] S. S. Bhatnagar and P. L. Kapur, *J. Indian Chem. Soc.*, 9, 341 (1932).
[203] W. Klemm and W. Schüth, *Z. anorg. allgem. Chem.*, 210, 33 (1933).
[204] G. Foëx and C. Fehrenbach, *Compt. rend.*, 203, 307 (1936).

should be pointed out that changes of 0.2 Bohr magnetons and more are extremely common in compounds such as $CoCl_2$, but, of course, they do not generally occur so sharply as in this case. A somewhat similar effect was observed for nickel chloride by Laurent [205] who found a change of effective moment at 540.5° K. The change amounted to only 0.77 Weiss magnetons. Other studies on cobalt and nickel compounds have been made by Shalyt; Bhatnagar, Khanna, and Nevgi; [206] de Haas and Schultz; [207a] Milyutin and Shalyt; de Haas, Schultz, and Koolhaus; Starr, Bitter, and Kaufmann; and by Schultz. [207b]

17. The Palladium and Platinum Groups

The elements of these groups show peculiar magnetic properties in all their compounds. The situation has been summarized by Van Vleck (*op. cit.*, p. 311), and not very much has been added to our knowledge during the past twelve years. In brief the compounds do not obey the Weiss law although Cabrera [208,209] points out that the susceptibilities may be represented by $(\chi + K)(T + \Delta) = C$. The effective Bohr magneton numbers probably have little significance and are all small compared with the theoretical "spin only" predictions. Values given by Cabrera and Duperier are shown in Table XVIII. It will be noticed that the Pt^{++} ion

TABLE XVIII

EFFECTIVE BOHR MAGNETON NUMBERS OF THE PALLADIUM AND PLATINUM GROUPS

Ion	μ_{eff}
Ru^{+++}	2.09
Rh^{+++}	0.06
Pd^{++}	0.07–0.13
Os^{++}	0.27–0.50
Ir^{+++}	0.11
Pt^{++}	0

is diamagnetic in spite of having an incomplete electron shell. The divalent palladium ion is stated by Janes [210] to be diamagnetic also. In

[205] P. Laurent, *J. phys. radium*, 9, 331 (1938).

[206] S. S. Bhatnagar, M. L. Khanna, and M. B. Nevgi, *Phil. Mag.*, 25, 234 (1938).

[207a] W. J. de Haas and B. H. Schultz, *J. phys. radium*, 7 (1939); *Physica*, 6, 481 (1939).

[207b] B. H. Schultz, *Physica*, 7, 413 (1940).

[208] B. Cabrera and H. Fahlenbrach, *Ann. Physik*, 21, 832 (1935).

[209] B. Cabrera and A. Duperier, *Proc. Phys. Soc. London*, 51, 845 (1939).

[210] R. B. Janes, *J. Am. Chem. Soc.*, 57, 471 (1935).

any event its paramagnetism is very small. Reasons for these peculiarities are obscure. Probably the elements of these groups do not form salts in the normal sense and the simple theory of ionic paramagnetism must be abandoned in favor of the "complex" theory described in Chap. VI. In some cases there is actually an odd number of electrons in the diamagnetic compounds, as for instance in $Pd(NH_3)_2Cl_2$. The diamagnetism here is probably to be explained by dimerization to $[Pd(NH_3)Cl_2]_2$, a view which is supported by freezing point data. In any event there remains much to be learned about these elements.

18. Nuclear Magnetism

The atomic nucleus possesses a magnetic moment as is shown by the hyperfine structure of series spectra. Methods have been developed for the accurate determination of nuclear moments and they are of considerable interest to workers in the field of nuclear physics. But because of their small magnitude, amounting to only about 10^{-3} Bohr magnetons, nuclear moments have not as yet assumed much importance in chemistry. Reviews of the subject are given by Tuve, Hafsted, and Heydenburg,[211] and elsewhere.[212] Some applications have been made of the *ortho-para*hydrogen method to the determination of nuclear moments.

[211] M. A. Tuve, L. R. Hafsted, and N. P. Heydenburg, *Carnegie Inst. Wash. Pub.*, No. 501, 161 (1938).

[212] *Inst. intern. phys. Solvay, 7th Conseil phys. Brussels*, 1933.

CHAPTER FIVE

MOLECULAR PARAMAGNETISM

1. "Odd" Molecules

In 1934 Stoner [1] was able to cover the field of molecular paramagnetism in six pages, most of which were devoted to oxygen. Now we shall find it difficult to do justice to the most important investigations in this field in a chapter. Molecular paramagnetism and the field of complex compounds have become the two most active branches of magnetochemistry.

The very great majority of chemical substances is made up of molecules possessing an even number of electrons. It was first pointed out by Lewis [2] that those comparatively few molecules with an odd number of electrons should have a permanent magnetic moment and hence be paramagnetic. This view was supported by the experiments of Soné [3] who showed that paramagnetism is a property of nitric oxide, NO, and of nitrogen dioxide, NO_2, but that other oxides of nitrogen, having an even number of electrons, are diamagnetic. Proof of Lewis's theory was established by the experiments of Taylor [4] who studied chlorine dioxide, ClO_2, and the organic free radical α-naphthyldiphenylmethyl, both of which are paramagnetic. Thallium amalgam and sodium dissolved in liquid ammonia also showed definite, though slight, paramagnetism.

In such substances there seems to be little or no contribution from the orbital moment so that the susceptibilities are accurately represented by

$$\chi_M = \frac{N\beta^2 4s(s+1)}{3kT}$$

or for a single unpaired electron, for which $s = \frac{1}{2}$, the molar susceptibility at 20° C. is about

$$\chi_M = 1270 \times 10^{-6}$$

Except for rather minor deviations the susceptibilities follow the Curie law, although, as for nitric oxide, there are some notable exceptions.

[1] E. C. Stoner, *Magnetism and Matter*. Methuen and Co., Ltd., London 1934, p. 340.

[2] G. N. Lewis, *Valence and the Structure of Atoms and Molecules*. The Chemical Catalog Co., New York 1923, p. 148; *Chem. Rev.* 1, 231 (1924).

[3] T. Soné, *Science Repts. Tôhoku Imp. Univ., First Ser.*, 11, 139 (1922).

[4] N. W. Taylor, *J. Am. Chem. Soc.*, 48, 854 (1926).

2. Oxygen and Ozone

It may seem peculiar, after the foregoing, that our detailed discussion of molecular paramagnetism should start with a molecule having an even number of electrons. But oxygen is almost unique in that its normal state is $^3\Sigma$ so that although it has an even number of electrons, two of these remain unpaired and the oxygen molecule is as a consequence strongly paramagnetic. The number of molecules which are similar to oxygen in this respect is extremely small, being limited to a very few recently discovered organic "biradicals" and possibly to some forms of sulfur vapor.

As for paramagnetic atoms, Van Vleck [5] considers limiting cases for diatomic paramagnetic molecules. These may have multiplet intervals small compared to kT, or large compared to kT. For molecular Σ states the multiplet intervals are negligibly small and the Σ state of molecular oxygen is established both from the magnetic measurements and from spectroscopic studies. The molar susceptibility is given by

$$\chi_M = \frac{8N\beta^2}{3kT} = \frac{0.993}{T}$$

At 20° C. the theoretical molar susceptibility is 3390×10^{-6}.

The paramagnetism of molecular oxygen has been the subject of much experimental work. Magnetic deflection of a molecular beam of oxygen gives a moment equal to two Bohr magnetons.[6] Susceptibility measurements are reviewed by Van Vleck [7] and by Stoner.[8] Various results on the gas measured near room temperature give $\chi_M T$ ranging from 0.970 to 1.021 with an average 0.991 very close to the theoretical value 0.993. Results of some of the more important individual determinations are given in Table XIX.

The Curie law is obeyed very closely by oxygen as has been determined by several of the above workers, and by Stössel.[9] Woltjer, Coppoolse, and Wiersma, however, believe that there is a small deviation, amounting to about 2 per cent, from the Curie law even after their data are extrapolated to zero density to avoid interference from molecular interactions. At higher pressures the deviations may become appreciable. Goldstein and Rocard [10] find that the susceptibility of oxygen, gaseous,

[5] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*. Oxford University Press, Oxford 1932, p. 264.

[6] R. Schnurmann, *Z. Physik*, **85**, 212 (1933).

[7] J. H. Van Vleck, *op. cit.*, p. 266.

[8] E. C. Stoner, *op. cit.*, p. 342.

[9] R. Stössel, *Ann. Physik*, **10**, 393 (1931).

[10] L. Goldstein and Y. Rocard, *Compt. rend.*, **196**, 1722 (1933).

TABLE XIX

CURIE CONSTANTS OF OXYGEN GAS AS DETERMINED BY VARIOUS INVESTIGATORS

Experimenter	$\chi_M T$
Curie [11]	0.983[a]
Onnes and Oosterhuis [12]	.970
Soné [13]	.975
Bauer and Piccard [14]	1.001
Wills and Hector [15]	1.021
Lehrer [16]	.979
Woltjer, Coppoolse, and Wiersma [17]	1.002

[a] Corrected for calibration.

liquid, or dissolved in nitrogen, follows the Weiss law $\chi(T + \Delta) = C$ where Δ is 40 times the density. This is probably only a rough approximation, but the belief that the susceptibility of oxygen is affected by the density is supported by Kanzler [18] who finds strict observance of the Curie law between 290° and 625° K. for all densities below 0.12 g. per cc. (corr. to 20° C.). But at $d_{20} = 0.2$ g. per cc. the Weiss law is followed with $\Delta = 5.6°$, and for $d_{20} > 0.4$ g. per cc., $\Delta = 25.8°$.

Liquid oxygen follows the Weiss law. Perrier and Onnes [19] discovered that for solutions of oxygen in liquid nitrogen the term Δ varies with the concentration of oxygen, from 2.2° for 8.1 per cent O_2, to 29.5° for 74.6% O_2. Analysis of such data led Lewis [20] to postulate the presence of O_4 molecules. This view is supported by the discovery of O_4 in the atmosphere.[21] In any event the stability of O_4 must be very low. Its properties are discussed by Pauling.[22]

Solidification of oxygen gives a sudden decrease of susceptibility and a large increase in Δ. There is an anomaly at 33° K. below which the

[11] P. Curie, *Ann. chim. phys.*, **5**, 289 (1895).

[12] H. K. Onnes and E. Oosterhuis, *Leiden Communications*, **134d**.

[13] T. Soné, *Phil. Mag.*, **39**, 305 (1920).

[14] E. Bauer and A. Piccard, *J. phys. radium*, **1**, 97 (1920).

[15] A. P. Wills and L. G. Hector, *Phys. Rev.*, **23**, 209 (1924).

[16] E. Lehrer, *Ann. Physik*, **81**, 229 (1926).

[17] H. R. Woltjer, C. W. Coppoolse, and E. C. Wiersma, *Proc. Acad. Sci. Amsterdam*, **32**, 1329 (1929).

[18] M. Kanzler, *Ann. Physik*, **36**, 38 (1939).

[19] A. Perrier and H. K. Onnes, *Leiden Communications*, **139d**, 48.

[20] G. N. Lewis, *J. Am. Chem. Soc.*, **46**, 2027 (1924).

[21] O. R. Wulf, *Proc. Nat. Acad. Sci.*, **14**, 609 (1938).

[22] L. Pauling, *The Nature of the Chemical Bond*. Cornell University Press, Ithaca 1939, p. 253.

paramagnetism decreases down to 13° K. This effect may be due to dimerization to O_4 molecules or to even higher non-magnetic polymers.

The susceptibility of adsorbed oxygen has been studied by Juza and Langheim.[23] On charcoal surfaces the paramagnetism depends on the density of the layer of adsorbed oxygen and on the time. This work is of particular interest in connection with catalysis. Further reference to it will be made in Chap. IX.

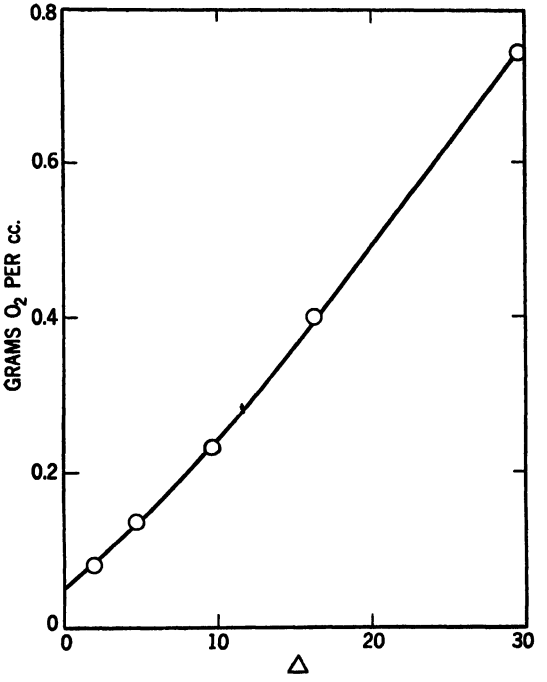


FIG. 34.—Variations of the molecular field constant, in the Weiss law $\chi(T' + \Delta) = C$, for solutions of oxygen in liquid nitrogen.

Ozone, O_3, has been the subject of some very conflicting reports in the literature. The molecule has an even number of electrons and there is no particular reason for expecting it to be like O_2. Furthermore, experimental work on ozone, especially the pure gas and liquid, becomes very difficult, if not hazardous. The most impressive work on this substance has been done by Lainé.[24] He finds the susceptibility of pure liquid O_3 to be $0.14(\pm 0.02) \times 10^{-6}$. This small paramagnetism seems to be independent of temperature. Lainé's last paper (1935) includes a thorough survey of the literature on the magnetic properties of ozone.

[23] R. Juza and R. Langheim, *Z. Elektrochem.*, **45**, 689 (1939).

[24] P. Lainé, *Compt. rend.*, **196**, 910 (1933); **198**, 918 (1934); *Ann. phys.*, **3**, 461 (1935).

3. Sulfur

Because of its similarity to oxygen, the molecule S_2 might be expected to be paramagnetic. Spectroscopic studies by Naudé and Christy [25] show that the ground state of the molecule is $^3\Sigma$, the same as that of oxygen. That sulfur vapor is paramagnetic has been shown by the molecular beam experiments of Shaw and Phipps.[26] The moment is approximately 2 Bohr magnetons. Direct measurement of the susceptibility of sulfur vapor is difficult. It has been attempted by Néel.[27] The vapor is definitely paramagnetic but the results are rather difficult of interpretation because of the presence of S_6 and S_8 molecules as well as S_2. In terms of Bohr magnetons the effective moment of the S_2 molecule is about 2.4 at 600° C. and 2.1 at 800° C. Two unpaired spins would give 2.83 Bohr magnetons. Within the rather large experimental error the results are therefore satisfactory. There is no trace of paramagnetism in the susceptibility of liquid or solid sulfur.

4. Oxides of Nitrogen and Their Derivatives

Nitric oxide, NO, is paramagnetic but the effective moment is dependent on the temperature. Accurate theoretical prediction of this temperature dependence is one of the outstanding accomplishments of the modern theory of magnetism.[28] The doublet width in NO is comparable to kT. The situation is then like those of samarium and europium which show marked deviations from the Curie law. Theoretical effective magneton numbers plotted against temperature are shown in Fig. 35. The theoretical temperature coefficient is in good agreement with the experimental results.[29–32] At 20° C. the theoretical effective Bohr magneton number is 1.836. Bauer and Piccard, and Soné, found 1.86. Although the normal boiling point of nitric oxide is 123° K. the data of Wiersma, de Haas, and Capel extend down to 112.8° K. Below that temperature it is scarcely to be expected that the theory for the gas phase would hold. Furthermore, NO dimerizes [33] at low temperatures to N_2O_2 which is doubtless diamagnetic. Bizette and Tsaï [34] find the susceptibility at 100° K. to be 3.53×10^{-6}. They claim that this indicates 97

[25] S. M. Naudé and A. Christy, *Phys. Rev.*, **37**, 490 (1931).
[26] E. J. Shaw and T. E. Phipps, *Phys. Rev.*, **38**, 174 (1931).
[27] L. Néel, *Compt. rend.*, **194**, 2035 (1932).
[28] J. H. Van Vleck, *op. cit.*, p. 269.
[29] F. Bitter, *Proc. Nat. Acad. Sci. U. S.*, **15**, 632 (1929).
[30] J. Aharoni and P. Scherrer, *Z. Physik*, **58**, 749 (1929).
[31] R. Stössel, *Ann. Physik*, **10**, 393 (1931).
[32] E. C. Wiersma, W. J. de Haas, and W. H. Capel, *Leiden Communications*, **212b**.
[33] O. K. Rice, *J. Chem. Phys.*, **4**, 367 (1936).
[34] H. Bizette and B. Tsaï, *Compt. rend.*, **206**, 1288 (1936).

per cent association to N_2O_2. The variable effective magneton number for NO, however, makes the calculation a little uncertain. Lips [35] finds solid NO to have a very feeble paramagnetism. Like NO, NO_2 has an odd number of electrons. The susceptibility has been measured by Havens.[36] After allowance has been made for association to N_2O_4, the moment for nitrogen dioxide corresponds to one unpaired electron spin. The Curie law seems to be followed. Other oxides of nitrogen have an even number of electrons.

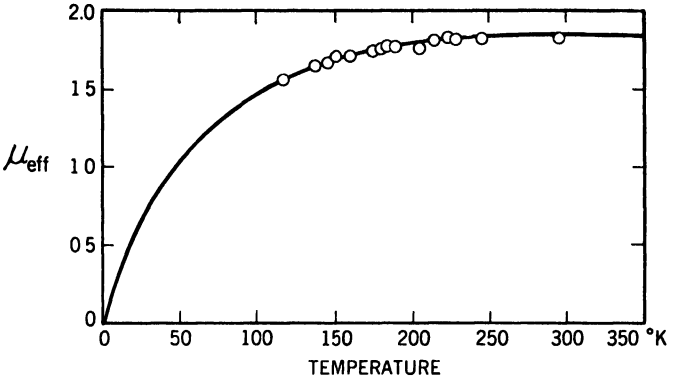


FIG. 35.—Theoretical and experimental effective Bohr magneton numbers for nitric oxide. The experimental data are all relative, hence the agreement may be less accurate than is shown.

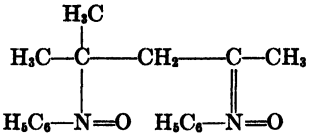
There are a rather large number of complex compounds containing nitric oxide. These will be discussed in the following chapter. Other compounds of this nature more properly belong here. Fremy's salt, $(KSO_3)_2NO$, is an example. This compound is formed by the oxidation of potassium hydroxylamine sulfonate. It forms yellow diamagnetic crystals which dissolve in water to form a rather reactive, violet-blue paramagnetic solution. Asmussen[37,38] points out that the process of solution must be a chemical change represented by the following equation.

$$\underset{\text{yellow, diamagnetic}}{[(KSO_3)_2NO]_2} \rightleftarrows \underset{\text{violet, paramagnetic}}{2(KSO_3)_2NO}$$

The diaryl nitric oxides form another class of paramagnetic compounds. The simplest of these is diphenyl nitric oxide, $(C_6H_5)_2NO$, studied by Cambi.[39] At 18° C. this compound has an effective moment

[35] E. Lips, *Helv. Phys. Acta*, **7**, 663 (1934); **8**, 247 (1935).
[36] G. G. Havens, *Phys. Rev.*, **41**, 337 (1932).
[37] R. W. Asmussen, *Z. anorg. allgem. Chem.*, **212**, 317 (1933).
[38] H. Katz, *Z. Physik*, **87**, 238 (1933).
[39] L. Cambi, *Gazz. chim. ital.*, **63**, 579 (1933).

of 1.71 Bohr magnetons, corresponding closely to one unpaired spin. Several other similar compounds have been studied. Di-*p*-anisyl nitric oxide, $(p\text{-}CH_3OC_6H_4)_2NO$, is reported by Cambi;[39] Galavics;[40] Katz;[38] and by Müller, Müller-Rodloff, and Bunge[41] to have a moment corresponding to one unpaired electron spin. Katz states that it follows the Weiss law $\chi(T + 13) = C$. Müller gives $\Delta = 3°$. Cambi has measured di-*p*-nitrophenylene nitric oxide, $(p\text{-}O_2NC_6H_4)_2NO$, over the range 84° to 343° K. This compound also follows the Curie law with $\mu_{eff} = 1.74$ Bohr magnetons. A somewhat more complicated compound



has been studied by Kenyon and Sugden,[42] and by Müller.[41] This also follows the Curie law with a normal molar susceptibility at 20° of about 1300×10^{-6}. According to Müller $\Delta = 2°$ which is scarcely distinguishable from zero. In all these compounds there seems to be no tendency toward association, at least over the temperature ranges investigated. There is also no sign of the peculiar temperature coefficient shown by nitric oxide itself. The question might be raised as to whether or not these nitric oxide derivatives should be called "free radicals." Their magnetic behavior is analogous to that of the triarylmethyls to be discussed below. Most workers in the field feel inclined to call a "free radical" any molecule possessing an odd number of electrons. Oxygen is, strictly speaking, a "biradical."

At one time it was thought that nitrosyl chloride, NOCl, and other nitroso compounds might be in Σ states like molecular oxygen. Wilson,[43] however, reports that liquid nitrosyl chloride, solid and dissolved nitrosobenzene, and dissolved *p*-nitrosodimethylaniline are all diamagnetic. Beeson and Coryell[44] find gaseous nitrosyl chloride to be diamagnetic. The compound is clearly not in a triplet state.

If nitrosyl chloride is diamagnetic there is no particular reason why its addition compounds with salts should be paramagnetic. Asmussen[45] finds such compounds as $ZnCl_2 \cdot NOCl$ to be diamagnetic unless the salt itself contains a paramagnetic ion, as in $MnCl_2 \cdot NOCl$. An exception is

[40] F. Galavics, *Helv. Phys. Acta*, **6**, 555 (1933).
[41] E. Müller, I. Müller-Rodloff, and W. Bunge, *Ann.*, **520**, 235 (1935).
[42] J. Kenyon and S. Sugden, *J. Chem. Soc.*, **1932**, 170.
[43] E. B. Wilson, Jr., *J. Am. Chem. Soc.*, **56**, 747 (1934).
[44] C. M. Beeson and C. D. Coryell, *J. Chem. Phys.*, **6**, 656 (1938).
[45] R. W. Asmussen, *Z. anorg. allgem. Chem.*, **243**, 127 (1939).

$CuCl \cdot NOCl$ which is paramagnetic although it presumably contains the diamagnetic cuprous ion. It may be that the compound rearranges to give $(CuNO)Cl_2$.

5. Oxides of Chlorine

The paramagnetism of chlorine dioxide has already been mentioned. Another oxide of chlorine of interest is the hexoxide, Cl_2O_6. This has been studied in the solid and liquid phases by Farquharson, Goodeve, and Richardson.[46] Between $-40°$ and 10° C. the susceptibility varies with temperature in a manner which may be explained by the existence of the equilibrium

$$Cl_2O_6 \rightleftarrows 2ClO_3$$

The monomolecular form has an odd number of electrons and would of course be paramagnetic. In the gas phase the compound is known to exist as ClO_3. Analysis of the magnetic data permits calculation of the equilibrium constant which varies from 2.54×10^{-3} at $-40°$ C. to 4.91×10^{-3} at 10° C. The logarithm of the equilibrium constant plotted against the reciprocal of temperature gives a straight line from which the heat of dissociation is found to be 1730 ± 500 calories per mole. Such calculations are based on the assumption that the paramagnetism of ClO_3 is due to one unpaired electron spin and that the Curie law is obeyed. Such assumptions are probably justified because compounds such as nitric oxide in which they are not obeyed are quite unusual.

6. Alkali Metal Polyoxides and Related Compounds

Oxidation of alkali metals yields compounds to which the formula R_2O_4 and the name alkali "tetroxides" were formerly assigned. But magnetic measurements by Neuman [47] and by Klemm and Sodomann [48] have shown potassium "tetroxide" to be paramagnetic with a moment corresponding to only slightly more than one unpaired electron spin. At one time Klemm pointed out that another interpretation of the paramagnetism was formation of an addition complex with molecular oxygen, $O_2 \cdot O_2^{-2}$. This, however, has been disproved by x-ray investigations.[49] Helms and Klemm [50] have shown that rubidium and cesium "tetroxides" are also paramagnetic. Effective moments are shown in Table XX. There seems no reason for retaining the name "tetroxide" for these com-

[46] J. Farquharson, C. F. Goodeve, and F. D. Richardson, *Trans. Faraday Soc.*, **32**, 790 (1936).

[47] E. W. Neuman, *J. Chem. Phys.*, **2**, 31 (1934).

[48] W. Klemm and H. Sodomann, *Z. anorg. allgem. Chem.*, **225**, 273 (1935).

[49] W. Kassatochkin and W. Kotow, *J. Chem. Phys.*, **4**, 458 (1936).

[50] A. Helms and W. Klemm, *Z. anorg. allgem. Chem.*, **241**, 97 (1939).

TABLE XX

EFFECTIVE BOHR MAGNETON NUMBERS FOR ALKALI METAL "TETROXIDES"

Temp.	KO_2	RbO_2	CsO_2
90° K.	1.97	1.89	1.91
293	1.84	1.89	1.89

pounds. They may properly be called "dioxides" although the name "superoxide" has also been suggested. Electronic configurations of these compounds are discussed by Pauling.[51]

It might be thought that alkali metal chalcogenides such as the compound K_2S_4 would also be paramagnetic. But Klemm, Sodomann, and Langmesser [52] have found that such is not the case. A large number of alkali metal sulfides, selenides, and tellurides were studied. In all cases they were diamagnetic.

Quite recently Hubard [53] has shown that cesium tetraiodide is diamagnetic and should therefore be written Cs_2I_8 rather than CsI_4.

7. Hexaarylethanes

Application of magnetic methods has, during the past few years, revolutionized the study of organic free radicals. Several standard procedures such as the colorimetry and ebulliometry of these compounds have been shown to be subject to the grossest errors. Susceptibility measurements have also been of the greatest service in testing the various theories of free radical stability.

The method of calculating the degree of dissociation for the reaction

$$Ar_3C—CAr_3 \rightleftarrows 2Ar_3C$$

has been given by Müller,[54,55] and by Roy and Marvel.[56] This method will be explained with the aid of an example taken from the paper of Roy and Marvel.

The degree of dissociation of hexaphenylethane in benzene solution at 20° C. may be calculated from the magnetic susceptibility of the solution as follows:

[51] L. Pauling, *op. cit.*, p. 251.

[52] W. Klemm, H. Sodomann, and P. Langmesser, *Z. anorg. allgem. Chem.*, **241**, 281 (1939).

[53] S. S. Hubard, *J. Phys. Chem.*, **46**, 227 (1942).

[54] E. Müller, I. Müller-Rodloff, and W. Bunge, *Ann.*, **520**, 235 (1935).

[55] E. Müller and I. Müller-Rodloff, *Ann.*, **521**, 89 (1935).

[56] M. F. Roy and C. S. Marvel, *J. Am. Chem. Soc.*, **59**, 2622 (1937).

(*1*) The percentage of ethane in solution (5.49%) may be calculated from the weights of benzene and chloromethane used to make the chloromethane solution. It is assumed that conversion of chloromethane to ethane is complete with no loss of solvent.

(*2*) The susceptibility of the ethane may be calculated from the observed susceptibility of the solution ($\chi = -0.700 \times 10^{-6}$) by an application of the Wiedemann additivity law. The susceptibility of benzene is taken as -0.708×10^{-6}. This gives the susceptibility of the ethane as -0.56×10^{-6}.

(*3*) The molar susceptibility of the partly dissociated ethane is obtained by multiplying its susceptibility by its molecular weight. $\chi_M = -272 \times 10^{-6}$.

(*4*) From this must be subtracted the diamagnetism of the ethane. This may be calculated from Pascal's empirical constants and is equal to -325×10^{-6}.

(*5*) The molar paramagnetism of that part of the ethane which is existing as free radicals is then $[-272 - (-325)] \times 10^{-6} = 53 \times 10^{-6}$.

(*6*) The degree of dissociation (α) is obtained from the fraction $53/2540 = 2.1\%$. The quantity 2540×10^{-6} is the molar paramagnetism produced at 20° C. by one mole of ethane completely dissociated into two moles of free radicals.

There are several assumptions in the above calculation. It is, for instance, never quite certain that the concentration of ethane is accurately obtained from the analytical data. There may be small deviations from the additivity law. It is unfortunate that there is no direct method of obtaining the diamagnetic correction. The molar paramagnetism produced by one unpaired electron spin at 20° C. is about 1270×10^{-6} only if the Curie law is obeyed. Experiments by Müller and others seem to indicate molecular field constants for free radicals may not always be zero. In spite, however, of these possible sources of error, the magnetic method is, on the whole, satisfactory and is certainly much more accurate than other methods.

One of the principal problems in this field has been to determine the effect of substituents on the degree of dissociation. This is important because it may ultimately throw some light on the puzzling question of why trivalent carbon exists at all. A very large number of hexaarylethanes has been studied by Marvel and by Müller and their respective co-workers during the past few years. It is beyond the scope of this book even to summarize the results obtained by these workers. The writer understands that a review of the field is in preparation.[57] In general, it

[57] Private communication from Dr. C. M. Himel.

may be said that magnetic measurements have placed discussion of degrees of dissociation on a quantitative basis and have made it possible to draw certain conclusions regarding the "resonance" theory and other theories of free radical stability.

Amongst the many papers already published on hexaarylethanes a very few will be mentioned as being representative. Müller and Kruck [58] have studied the effect of introducing groups such as phenanthryl and anthracyl which strongly favor an increase of resonance energy. Marvel and his co-workers [56,59–61c] have shown that in general *ortho* substituents are more effective in promoting dissociation than *meta* substituents, and that *para* substituents are least effective. Their work on substituents has also shown that the effect of resonance energy is minor as compared with the effect of steric factors. Quite recently Marvel and Himel [62] have shown that unsymmetrical ethanes may be much less dissociated than the corresponding symmetrical ethanes. By an unsymmetrical ethane is meant one such as may be prepared by treating with molecular silver equimolecular portions of tri-*p*-*t*-butylphenylmethylchloride and *p*-*t*-butylphenyldiphenylmethylchloride. The two symmetrical ethanes are respectively 20 and 7.5% dissociated. The mixture containing the unsymmetrical ethane appears to be only about 3.5% dissociated.

A review of magnetic methods as applied to hexaarylethanes is given by Müller.[63]

Marvel and his co-workers [64] have in several publications drawn attention to the fact that hexaarylethanes disproportionate to form substituted methanes and olefinic compounds with the consequent disappearance of the free radical. The reaction is evidenced as a gradual decrease of magnetic susceptibility with time when a solution containing a free radical is warmed, or, in some cases, simply held at room temperature or even lower. For many ethanes, when the temperature is held near 100° C. for several hours the concentration of free radical as measured by its susceptibility may fall to near zero. Different ethanes disproportionate

[58] E. Müller and W. Kruck, *Ber.*, **71B**, 1778 (1938).

[59] C. S. Marvel, E. Ginsberg, and M. B. Mueller, *J. Am. Chem. Soc.*, **61**, 77 (1939).

[60] C. S. Marvel and C. M. Himel, *J. Am. Chem. Soc.*, **62**, 1550 (1940).

[61a] C. S. Marvel, J. F. Kaplan, and C. M. Himel, *J. Am. Chem. Soc.*, **63**, 1892 (1941).

[61b] C. S. Marvel, J. W. Schackleton, C. M. Himel, and J. Whitson, *J. Am. Chem. Soc.*, **64**, 1824 (1942).

[61c] C. S. Marvel, F. C. Dietz, and C. M. Himel, *J. Org. Chem.*, **7**, 392 (1942).

[62] C. S. Marvel and C. M. Himel, *J. Am. Chem. Soc.*, **64**, 2227 (1942).

[63] E. Müller, *Z. Elektrochem.*, **45**, 593 (1939).

[64] C. S. Marvel, W. H. Rieger, and M. B. Mueller, *J. Am. Chem. Soc.*, **61**, 2769 (1939), *et seq.*

at different rates. Marvel, Mueller, Himel, and Kaplan [65] have determined that *ortho* and *para* substituted phenylethanes disproportionate far more rapidly than those with *meta* substituents, but that unless the α carbon atom of the substituent has a hydrogen attached to it, disproportionation is extremely slow. The order of this reaction and its activation energy have also been determined.[66] The importance of this disproportionation reaction is that it raises doubts about the use of ebulliometric determinations of free radical concentration. In all cases disproportionation takes place at the boiling point of benzene, and rapid disproportionation takes place at the boiling point of toluene.

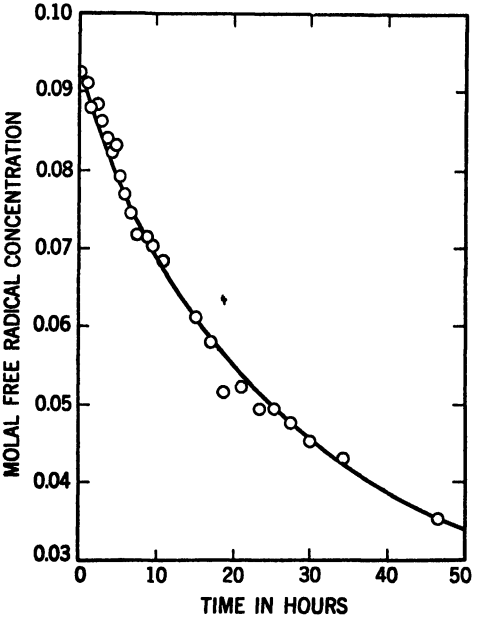


FIG. 36.—The disproportionation, with time, of a 0.0517 *M* solution of di-*o*-tolyltetraphenylethane in benzene at 80° C.

One of the most interesting observations made during magnetic studies of free radicals has to do with the color of the solutions before and after disproportionation. For a long time colorimetric measurements have been used in the study of free radicals and it has been assumed that color in a solution is evidence for the presence of free radicals. But Marvel has shown that colorimetric measurements cannot be relied upon

[65] C. S. Marvel, M. B. Mueller, C. M. Himel, and J. F. Kaplan, *J. Am. Chem. Soc.*, 61, 2771 (1939).

[66] P. W. Selwood and R. Preckel, *J. Am. Chem. Soc.*, 65, 895 (1943).

for accurate determination of free radical concentration. The solution often remains richly colored after disproportionation has completely destroyed all trace of free radicals.

If degrees of dissociation may be calculated from magnetic measurements then it is obvious that measurements over a range of concentration and of temperature will give means of calculating equilibrium constants, and the heats, entropies, and free energies of dissociation. This has been done for the following ethanes:[67] hexaphenylethane, di-*o*-tolyltetraphenylethane, di-α-naphthyltetraphenylethane, and tetra-*o*-tolyldiphenylethane. The results show that the heats of dissociation (about 11 kilocalories per mole) are all about the same.

Because free radicals are paramagnetic they may be expected to catalyze the *ortho-para*hydrogen conversion. The possibility of using this conversion as a measure of free radical concentration has been examined by Schwab and Agallidis.[68]

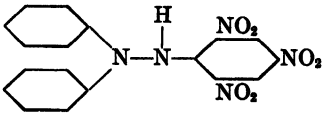
8. Organo-Metallic Free Radicals

In Group IV of the periodic table there are several elements which form compounds analogous to ethanes. Compounds such as hexaphenylditin are well known. On the basis of boiling point elevation and freezing point depression several such compounds are apparently dissociated to free radicals in a manner comparable to hexaphenylethane. Certain reactions undergone by these compounds also suggest dissociation, but on the other hand, the solutions are colorless whereas all triarylmethyls are colored. In an effort to settle this question magnetic measurements have been made on various organo-metallic compounds such as hexaphenyldigermanium,[69] hexaphenyldilead,[70] hexamethylditin,[71] hexacyclohexyldilead,[71] and hexa-*o*-tolylditin.[72] In every case the compound is shown to be entirely diamagnetic and hence not dissociated. In certain cases the measurements were extended over a considerable range of temperature and of concentration. It is not entirely clear why the magnetic measurements should be so directly contradictory to the ebullioscopic and cryoscopic results. This work makes it probable that no stable organo-metallic free radical has yet been prepared, although the literature contains many references to such compounds.

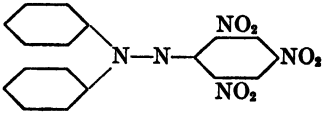
[67] R. Preckel and P. W. Selwood, *J. Am. Chem. Soc.*, **63**, 3397 (1941).
[68] G. M. Schwab and E. Agallidis, *Z. physik. Chem.*, **B41**, 59 (1938).
[69] P. W. Selwood, *J. Am. Chem. Soc.*, **61**, 3168 (1939).
[70] R. Preckel and P. W. Selwood, *J. Am. Chem. Soc.*, **62**, 2765 (1940).
[71] H. Morris and P. W. Selwood, *J. Am. Chem. Soc.*, **63**, 2509 (1941).
[72] H. Morris, W. Byerly, and P. W. Selwood, *J. Am. Chem. Soc.*, **64**, 1727 (1942).

9. Hydrazyls

Substituted hydrazines of the type



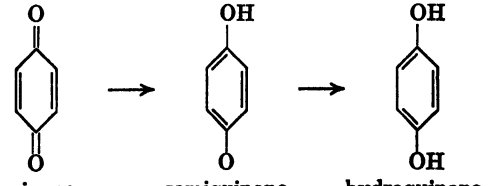
may readily be oxidized to yield hydrazyls such as α,α-diphenyl-β-picrylhydrazyl.



Such compounds, containing divalent nitrogen are highly dissociated even in the solid state. The magnetic properties of the above compound have been studied by Katz;[38] by Müller, Müller-Rodloff, and Bunge;[41] and by Turkevich and Selwood.[73] Katz reports an effective Bohr magneton number of about 0.9, but this is probably a mistake because the other sets of workers report $\mu_{eff} = 1.73$ and 1.66. The molecular field constant is positive but of uncertain magnitude, being reported as 10°, 20°, and 37°. Such compounds as this lend themselves to accurate determination of the diamagnetic correction because the corresponding hydrazine differs from the hydrazyl only by one hydrogen atom whose diamagnetism is extremely small. The molar diamagnetism of the hydrazine is found by experiment to be -200×10^{-6}. This method for making the diamagnetic correction is somewhat more satisfactory than the method of Pascal's constants. It could readily be applied to the hexaarylethanes if trouble were taken to prepare the methanes corresponding to the free radicals.

10. Semiquinones and Related Compounds

During the past few years some very interesting types of free radicals have been discovered, chiefly by Michaelis and his co-workers. Reduction of a quinone to the corresponding hydroquinone goes through an intermediate unstable stage of reduction called a semiquinone. The semiquinone has an odd number of electrons,



[73] J. Turkevich and P. W. Selwood, *J. Am. Chem. Soc.*, **63**, 1077 (1941).

and it may be stabilized in alkaline solution, forming the semiquinone ion which should be paramagnetic. The study

semiquinone ion

of such substances, which are discussed by Pauling,[74] is quite difficult. Michaelis, Boeker, and Reber,[75] however, have proved the existence of a paramagnetic intermediate during alkaline reduction of phenanthrenequinone-3-sulfonate. They used the manometric balance of Wills and Boeker, as modified by Woodbridge. Three different solutions all showed

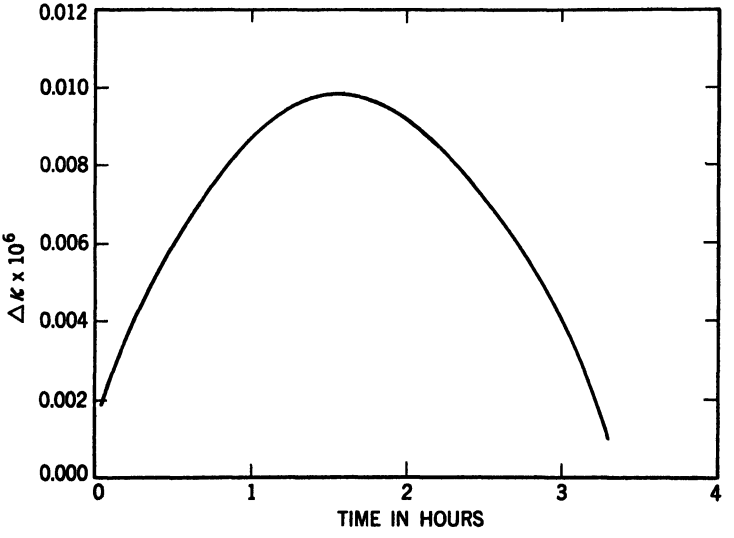


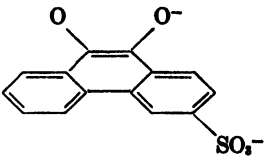
FIG. 37.—Production of the semiquinone of phenanthrenequinone-3-sulfonate. The maximum fraction of the dye present as free radical is 44 per cent. $\Delta\kappa$ is obtained by subtracting the volume susceptibility of the solution when the reaction is complete from that at time t.

a fall of diamagnetism followed by a rise (Fig. 37) as the semiquinone ion was formed and then destroyed. The free radical ion is believed to have the formula

[74] L. Pauling, *op. cit.*, p. 256.

[75] L. Michaelis, G. F. Boeker, and R. K. Reber, *J. Am. Chem. Soc.*, 60, 202 (1938).

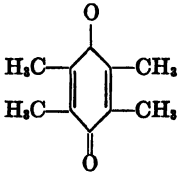
semiquinone ion



which is in equilibrium with the reduced form and with the oxidized form, as well as possibly with a dimerized form. The method used to observe the susceptibilities while the reaction is taking place is particularly ingenious because it eliminates the difficult problem of changing diamagnetic corrections. Measurements made on an acid solution of potassium phenanthrenequinonesulfonate during reduction showed changes in the diamagnetism of the same order of magnitude as the experimental error.[76] Hence, as expected, during acid reduction any appearance of the free radical ion is negligible. This is the first case to be described of a free radical which is also an ion, but both positive and negative radical ions are becoming known.

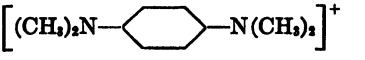
Quinhydrone, normally the first product of reduction of quinone is diamagnetic.[77]

Duroquinone [78]



in a strongly alkaline solution forms a paramagnetic semiquinone free radical of brown color as an intermediate step of the reduction. This free radical has no dimeric form.

Similar types of compounds are formed by many compounds containing nitrogen. For instance radicals derived from aromatic *p*-diamines, of the type of Wurster's salts, have been studied by Michaelis, Schubert, and Granick [79] by the potentiometric method. Magnetic evidence for the free radical form of the tetramethyl-*p*-phenylenediaminium ion



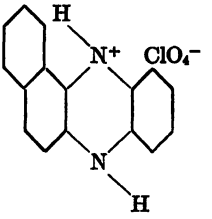
[76] L. Michaelis, R. K. Reber, and J. A. Kuck, *J. Am. Chem. Soc.*, **60**, 214 (1938).

[77] Measurements by Dr. C. D. Coryell referred to by L. Pauling, *op. cit.*, p. 258.

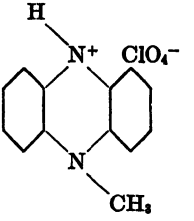
[78] L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck, and S. Granick, *J. Am. Chem. Soc.*, **60**, 1678 (1938).

[79] L. Michaelis, M. P. Schubert, and S. Granick, *J. Am. Chem. Soc.*, **61**, 1981 (1939).

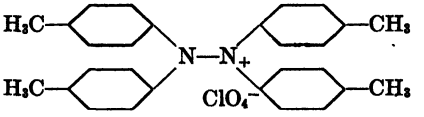
as the perchlorate has been given by Katz.[38] Wurster's red has also been studied by Rumpf and Trombe.[80] Still more paramagnetic compounds containing semiquinone ions as reported by Katz are hydro-*p*-naphthophenazinium perchlorate



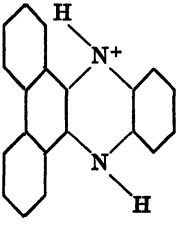
dihydropyocyaninium perchlorate

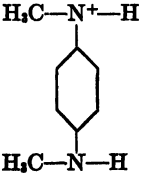


and tetra-*p*-tolylhydrazinium perchlorate



Some of these have rather lower susceptibilities than might be expected. It is not clear whether this is due to faulty experimentation or to dimerization or possibly decomposition. The paramagnetism of the semiquinone ion of pyocyanine has also been demonstrated by Kuhn and Schön.[81] Experiments by Pauling and Sturdivant [82] have shown the two following ions to be paramagnetic:

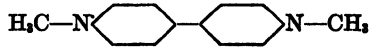




[80] P. Rumpf and F. Trombe, *J. chim. phys.*, **35**, 110 (1938).
[81] R. Kuhn and K. Schön, *Ber.*, **68B**, 1537 (1935).
[82] L. Pauling and J. H. Sturdivant, Pauling *op. cit.*, p. 259.

Tri-*p*-tolylaminium perchlorate $[(C_6H_4CH_3)_3N]^+ClO_4^-$ has been shown by Katz and by Rumpf and Trombe [83] to have a molar paramagnetism corresponding closely to one unpaired electron spin.

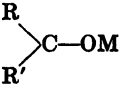
Still more complicated paramagnetic substances are formed by certain dyestuffs such as the semiquinone ions prepared by reduction of dipyridyl bases. An example of one of these is N,N′-dimethyl γ,γ′-dipyridinium chloride, (methyl viologen), reported by Michaelis.[84]



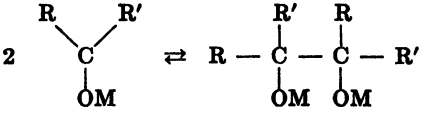
Michaelis has also prepared semiquinone ions from thiazine dyestuffs, thionine, aminothiazine, and oxonine.

11. Metal Ketyls

Certain aromatic ketones on treatment with alkali metals give metal ketyls of the general formula



and which have, for a long time, been suspected of being free radicals. The paramagnetism of such compounds was first demonstrated by Sugden [85] who studied *p*-biphenylphenyl ketone potassium and benzophenone potassium. Doescher and Wheland,[86] almost simultaneously, showed that the corresponding sodium ketyls are paramagnetic. The results of the two investigations are in qualitative but not quantitative agreement. This is, perhaps, not surprising in view of later observations that the degree of dissociation is dependent on the particular metal used. Doescher and Wheland measured the dissociation of the *p*-biphenylphenyl metal ketyl in different solvents. They found the degree of dissociation in benzene to be 1.7 per cent and in dioxane 41 per cent. This is a very large difference which does not seem to be paralleled in the dissociation of hexaarylethanes in different solvents. The effect of solvent on the stability of free radicals, however, is a field which deserves further investigation. Presumably the association of metyl ketyls proceeds according to the reaction



[83] P. Rumpf and F. Trombe, *Compt. rend.*, **206**, 671 (1938).
[84] L. Michaelis, *J. Am. Chem. Soc.*, **63**, 2446 (1941).
[85] S. Sugden, *Trans. Faraday Soc.*, **30**, 18 (1934).
[86] R. N. Doescher and G. W. Wheland, *J. Am. Chem. Soc.*, **56**, 2011 (1934).

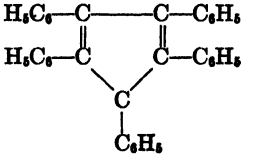
One wonders if the presence of two different metals in the pinacolate would affect the degree of dissociation like disymmetry affects the dissociation of hexaarylethanes.

Magnetic properties of the metal ketyls have been investigated with great thoroughness by Müller and his co-workers.[87, 88] The work is reviewed and chemical and magnetic data on a large number of metal ketyls and related compounds are summarized and compared by Müller and Janke.[89] The free radical concentration is very different for different compounds, ranging from negligibly small for 2,3,6,7-dibenzoxanthone potassium to about 96 per cent for Michler's ketone potassium, $[(CH_3)_2NC_6H_4]_2COK$. The degree of dissociation is shown by Müller to be dependent on the nature of the aryl groups, on the presence of oxygen or sulfur attached to the metal, and also on the alkali metal. It is rather surprising that the molecular field constant shows very wide variations of from $-2°$ for Michler's ketone potassium to $-125°$ for fluorenone potassium. This variation cannot be due to the usual crystalline field or exchange effects but must certainly be due to some reversible chemical change taking place with changing temperature.

12. Highly Conjugated Systems, Biradicals

The existence of organic molecules possessing an unpaired electron at once suggests the possibility of two such unpaired electrons being present simultaneously in the same molecule. This situation is found in oxygen, as already described, and, of course, many of the transition group ions have more than one unpaired electron. But only recently have organic biradicals been prepared. Most progress in this field is due to Müller who has pursued the elusive biradicals with great persistence and success.

The best chance of finding such compounds would appear to be in highly conjugated systems. For instance, pentaphenylcyclopentadienyl [90] is completely dissociated, even in the solid state, although it is



not a biradical. On the other hand, substances such as 9-(1-naphthyl)

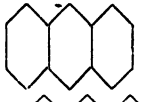
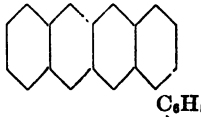
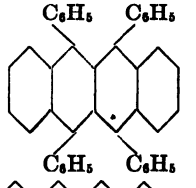
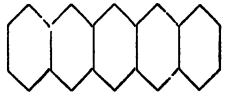
[87] E. Müller and F. Teschner, *Ann.*, **525**, 1 (1936).
[88] E. Müller and W. Wiesemann, *Ann.*, **532**, 116 (1938); **537**, 86 (1939).
[89] E. Müller and W. Janke, *Z. Elektrochem.*, **45**, 380 (1939).
[90] E. Müller and I. Müller-Rodloff, *Ber.*, **69B**, 665 (1936).

xanthyl,[91] tetraphenylrubrene,[92] diphenyldiazomethane,[93] 2,3,6,7-dibenzanthracene, tetra- and triaryl α-naphthyl derivatives of quinodimethane,[94] p,p'-tetramethyldiaminothiobenzophenone, and numerous ω,ω'-phenylpolyenes [95] are all diamagnetic and quite free from free radical form within the limits of experimental error.

It should, however, be pointed out that, with increasing complexity, aromatic molecules show an increasing deviation from Pascal's additivity rules. Enderlin [96] has collected the data on several such compounds as

TABLE XXI

DEVIATIONS FROM PASCAL'S RULES WITH INCREASING MOLECULAR COMPLEXITY

Hydrocarbon	$[\chi_M(\text{Pascal}) - \chi_M(\text{obs.})] \times 10^{-6}$
Benzene	0
Naphthalene	+48
Anthracene 	+106
Naphthacene 	+142
Tetraphenylnaphthacene 	+140 (Müller) +125 (Enderlin)
Dibenzoanthracene 	+289

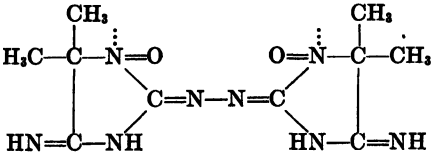
shown in Table XXI. These deviations may be due to faults of the Pascal rules, or possibly to temperature-independent paramagnetism.

[91] S. Allard, *Compt. rend.*, **199**, 1125 (1934).
[92] L. Enderlin, *Compt. rend.*, **200**, 912 (1935).
[93] E. Müller, *Z. Elektrochem.*, **40**, 542 (1934).
[94] E. Müller and I. Müller-Rodloff, *Ber.*, **68B**, 1276 (1935).
[95] E. Müller and I. Dammerau, *Ber.*, **70B**, 2561 (1937).
[96] L. Enderlin, *Ann. chim.*, **10**, 5 (1938).

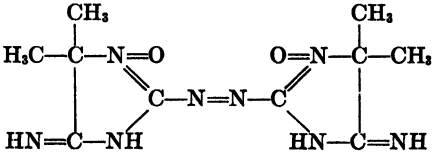
Müller shows that the magnitude of the deviations is independent of temperature. The deviations, therefore, are probably not due to partial free radical formation.

Many nitrogen compounds have been studied for possible biradical form, but, as pointed out by Müller and Wiesemann,[97] whenever valency tautomerism with formation of the quinoid structure is possible, the magnetic behavior is in accord only with such quinoid structure, even though the chemical behavior of the substance may point to the existence of free radicals.

The first true organic biradical discovered was porphyrindine [98] which has been shown by Kuhn, Katz, and Franke,[99] and by Müller and Müller-Rodloff [100] to exist in biradical form with a susceptibility corresponding to two unpaired electron spins. The effective Bohr magneton number is dependent on temperature, and apparently would approach zero at very low temperatures. A possible explanation for this phenomenon is the existence of an equilibrium of the paramagnetic form with a diamagnetic form



paramagnetic high temperature porphyrindine



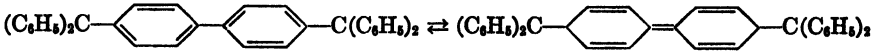
diamagnetic low temperature porphyrindine

Müller gives the heat of reaction as about 0.56 kilocalories per mole. Proof of the biradical form of this compound suggested the definition (Kuhn, Katz, and Franke) of a free radical as a compound containing an uncompensated electron, but not necessarily an odd number of electrons.

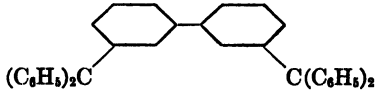
A rather obvious approach to the biradical problem is to be found in the Chichibabin hydrocarbon, bis(1,4-phenylenediphenylmethyl), but this compound is diamagnetic,[101] presumably owing to its equilibrium

[97] E. Müller and W. Wiesemann, *Ber.*, **69B**, 2157 (1936).
[98] O. Piloty and W. Vogel, *Ber.*, **36**, 1283 (1903).
[99] R. Kuhn, H. Katz, and W. Franke, *Naturwissenschaften*, **22**, 808 (1934).
[100] E. Müller and I. Müller-Rodloff, *Ann.*, **521**, 81 (1935).
[101] E. Müller and I. Müller-Rodloff, *Ann.*, **517**, 134 (1935).

with the quinoid form in which the

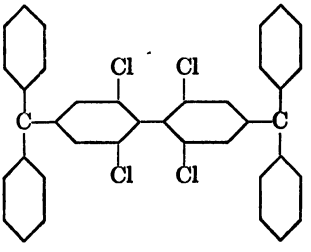


two unpaired electrons become paired off. If the diphenylmethyl groups are attached at the meta rather than the ortho positions, then the quinoid form cannot be assumed, and Müller has shown that bis(1,3-phenylenediphenylmethyl) exists about



6 per cent as free radical at 74° C. in 8 per cent benzene solution. It is clear, therefore, that although the Chichibabin hydrocarbons are highly colored and show high reactivity, they exist principally as the quinoid tautomer. Only when valency tautomerism is impossible do they exist in appreciable proportion as the biradical. The theory of such compounds has been discussed by Hückel.[102] Some measurements by Schwab suggest that the Chichibabin hydrocarbon may be a free radical with antiparallel but nevertheless unpaired electron spins. This work is referred to in Chap. IX, page 252.

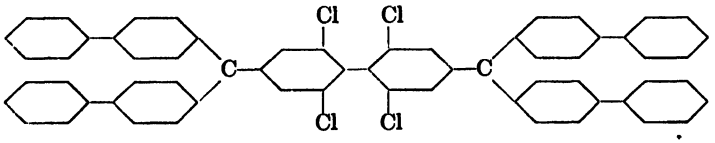
As soon as it was realized that valency tautomerism to form the quinoid structure must be prevented if biradicals are to be formed, Müller proceeded to restrict rotation about the biphenyl group by the introduction of chlorine atoms to form, for instance, bis((3,5-dichloro-1,4-phenylene) diphenylmethyl).[103]



This compound in 4 per cent benzene solution at 291° K. is 10 per cent dissociated, and at 353° K., 19 per cent. If two of the phenyl groups are substituted by xenyl, or other groups, the dissociation [104,105] rises to 14

[102] E. Hückel, *Z. physik. Chem.*, **B34**, 339 (1936).
[103] E. Müller and H. Neuhoff, *Ber.*, **72B**, 2063 (1939).
[104] E. Müller and E. Tietz, *Naturwissenschaften*, **28**, 189 (1940).
[105] E. Müller, *Angew. Chem.*, **54**, 192 (1941).

per cent at room temperature and 37 per cent at 80° C. The heat of dissociation is 7 ± 2 kcal. per mole. Final solution to the "biradical" problem came by substituting xenyl groups for all four phenyl groups, as in bis((3,5-dichloro-1,4-phenylene) dixenylmethyl). This compound [106] is at least 80 per cent in the

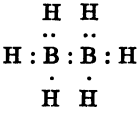


free radical form at 80° C. in a 2 per cent benzene solution. Still more biradicals are being reported by Müller.[107]

It will be observed that such compounds as those above raise some interesting questions as to possible modes of association, whether linear or possibly cyclic. They also suggest the question of whether two unpaired electrons at considerable distance from one another produce the same resultant moment as two such electrons in a transition group ion.

13. Miscellaneous Structural Problems

The structure of boron hydride, B_2H_6, has been the subject of much discussion, because there are insufficient electrons in the compound to give a full quota of electron pair bonds. It has been argued that perhaps two of the hydrogen atoms are held to the borons by single-electron bonds as shown.



This suggestion implies that the compound be paramagnetic. Farkas and Sachsse [108] have studied the parahydrogen conversion in the presence of boron hydride. They reach the conclusion that this compound is diamagnetic. The structure is probably a resonance hybrid wherein each bond partakes both of electron pair and single electron character.

A somewhat related problem is the structure of the salt-like compounds, diborane potassium, $K_2(B_2H_6)$, and dioxydiborane potassium, $K_2(B_2H_4)(OH)_2$. The ions BH_3^- and BOH_3^- both have an odd number of electrons, and should therefore be paramagnetic. But Klemm [109] has shown that the potassium salts of these ions are diamagnetic. The ions

[106] E. Müller and E. Tietz, *Ber.*, **74B**, 807 (1941).
[107] E. Müller and H. Pfanz, *Ber.*, **74B**, 1051, 1075 (1941).
[108] L. Farkas and H. Sachsse, *Trans. Faraday Soc.*, **30**, 331 (1934).
[109] L. Klemm and W. Klemm, *Z. anorg. allgem. Chem.*, **225**, 258 (1935).

are, therefore, probably $(B_2H_6)^-$ and $(B_2O_2H_6)^-$. For the diborane potassium there is a slight temperature coefficient of susceptibility, with the higher diamagnetism at the lower temperatures. This effect cannot be due to impurities or to temperature independent paramagnetism. It may result from slight dissociation $(B_2H_6)^- \rightleftarrows 2(BH_3)^-$ with about 1 per cent of the compound existing as an ionic free radical at 350° K.

Ammonium hexabromohypoantimonate, with the stoichiometrical formula $(NH_4)_2SbBr_6$, suggests antimony with the unusual valence of four which should be paramagnetic. Measurements by Elliott, however, show that the compound is diamagnetic. Elliott [110] suggests that the compound may be $(NH_4)_4Sb^{+3}Sb^{+5}Br_{12}$, or that possibly there is a covalent link between two quadrivalent antimony ions. The crystal structure of $(NH_4)_2SbBr_6$, Rb_2SbBr_6, and Rb_2SbCl_6 has been investigated by Jensen,[111] who finds the lattice to be face-centered cubic with all antimony atoms equivalent. Elliott's first suggestion would, therefore, appear to be ruled out, while the second is doubtful because, as he points out, the formula suggests that each antimony is surrounded by six bromines. It may be noticed that Elliott's value for the susceptibility of $(NH_4)_2SbBr_6$ is only -0.036×10^{-6}. This value is so low that paramagnetic impurities may have been present. An investigation of the susceptibility over a temperature range would be interesting. Asmussen [112] reports that the systems $SbCl_3$–$SbCl_5$ and $SbCl_3$–Rb_2SbCl_6 give no paramagnetic component.

The quadrivalence of bismuth in the dioxide, BiO_2, is confirmed by the paramagnetism of the compound.[113]

Hyposulfurous acid, $H_2S_2O_4$, is commonly assumed to exist in the dimeric form as written. If the acid and its salts contained the ion SO_2^- they would be paramagnetic. Li Klemm [114] shows that the salts are diamagnetic. The magnetic evidence, therefore, confirms the view that the doubled formula is correct. The same is true of the hypophosphates which have been studied by Bell and Sugden.[115] They find that sodium hypophosphate, $Na_2H_2P_2O_6$; its hydrate, $Na_2H_2P_2O_6 \cdot 6H_2O$; silver hypophosphate, $Ag_4P_2O_6$; and guanidine hypophosphate, $(CN_3H_5)_4H_4P_2O_6$, are all diamagnetic and hence correctly written as shown. The same is true of solutions containing the methyl and ethyl esters of hypophosphoric acid.

[110] N. Elliott, *J. Chem. Phys.*, 2, 298 (1934).

[111] K. A. Jensen, *Z. anorg. allgem. Chem.*, 232, 193 (1939).

[112] R. W. Asmussen, *Z. Elektrochem.*, 45, 698 (1939).

[113] S. S. Bhatnagar and K. N. Mathur, *Physical Principles and Applications of Magnetochemistry*. MacMillan and Co., Ltd., London 1935, p. 214.

[114] L. Klemm, *Z. anorg. allgem. Chem.*, 231, 136 (1937).

[115] F. Bell and S. Sugden, *J. Chem. Soc.*, 1933, 48.

Another problem which has been solved by magnetic measurements is the structure of calomel, and the old question of whether the formula should be written HgCl or Hg_2Cl_2. Magnetic measurements on the solid [116] and on the liquid [117] have shown it to be diamagnetic. The formula HgCl, which implies an odd number of electrons, is therefore excluded. The vapor phase of calomel has been shown by Gucker and Munch [118] to exist, in the neighborhood of 400° C., either as HgCl or as a mixture of Hg + $HgCl_2$.

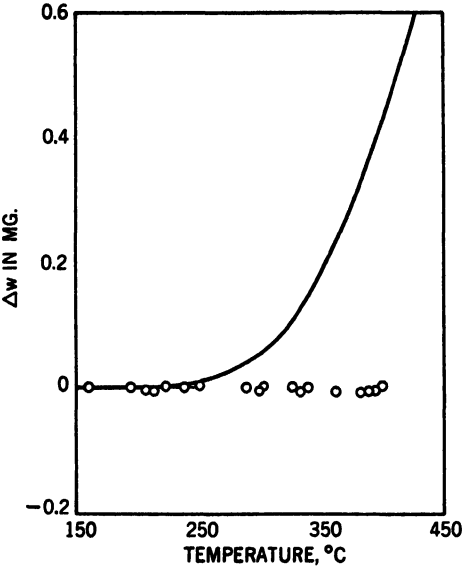


FIG. 38.—The upper curve shows the theoretical Δw (on a Gouy balance) expected for the formula HgCl. The experimental points show observed Δw's.

Magnetic studies by Selwood and Preckel [119] show, as in Fig. 38 that the vapor is also diamagnetic. The monomeric formula HgCl is, therefore, excluded in all three phases.

Farquharson and Heymann have also shown that solutions of metallic cadmium in molten cadmium chloride are diamagnetic. This rules out the possibility of CdCl molecules or of univalent, Cd^+, ions existing as such in these solutions.[120]

[116] *International Critical Tables*, Vol. 6, p. 357.
[117] J. Farquharson and E. Heymann, *Trans. Faraday Soc.*, 31, 1004 (1935).
[118] F. T. Gucker and R. H. Munch, *J. Am. Chem. Soc.*, 59, 1275 (1937).
[119] P. W. Selwood and R. Preckel, *J. Am. Chem. Soc.*, 62, 3055 (1940).
[120] W. R. A. Hollens and J. F. Spencer, *J. Chem. Soc.*, 1935, 495.

Similar studies [121] have been made on the supposed dichlorides of gallium and of indium. These are diamagnetic and probably exist in the dimeric form.

In this discussion no mention has been made of magnetic measurements being applied to short-lived free radicals such as CH_3. The ordinary forms of magnetic balances are not applicable to such substances. The *ortho-para*hydrogen method has, however, been applied to them with some success.

[121] W. Klemm and W. Tilk, *Z. anorg. allgem. Chem.*, 207, 175 (1932).

CHAPTER SIX

COMPLEX COMPOUNDS

1. Introduction to Complex Compound Formation

There are many chemical compounds which consist of a central atom or positive ion surrounded by neutral or negative atoms or groups of atoms. Recognition of such a type of compounds is due to Werner. For instance platinum forms the following series of compounds $[PtCl_6]H_2$, $[PtCl_5OH]H_2$, $[PtCl_4(OH)_2]H_2$, $[PtCl_3(OH)_3]H_2$, $[PtCl_2(OH)_4]H_2$, $[PtCl(OH)_5]H_2$, $[Pt(OH)_6]H_2$. All these are known except the fourth. Similar types of compounds are formed by many elements and many groups. Often these are of great complexity. The number of complex compounds and ions known is very large. Complex formation is a general property and is the rule rather than the exception with most elements.

Early attempts to interpret magnetic susceptibilities in terms of chemical structure were made by Jackson;[1] Bose;[2] Baudisch and Welo;[3,4] and others. Welo and Baudisch[5] and later Sidgwick and Bose expressed essentially the following rule: "The magnetic moment of a complex is the same as that of the atom with the same number of electrons as the central atom of the complex, counting two for each electron pair."

Thus Fe^{++} has 24 electrons, add 12 for six bonds gives 36, the atomic number of krypton, so that the diamagnetism of ferrocyanide is explained. This number of electrons about the center atom of the complex is often called the "effective atomic number" or E. A. N. But there are many exceptions to this rule. For instance $Ni(CN)_4^{=}$ is diamagnetic, but the rule would make it paramagnetic as for $Ni(NH_3)_4^{++}$. Diamagnetic complexes such as $Ni(CN)_4^{=}$ are sometimes referred to as "penetration" complexes as opposed to normal complexes such as $Ni(NH_3)_4^{++}$. This terminology is not much used now.

The binding forces within the complex may be due to electrostatic attraction for the surrounding ions or oriented dipoles, or to covalent

[1] L. C. Jackson, *Phil. Mag.*, **2**, 86 (1926).
[2] D. M. Bose, *Z. Physik*, **43**, 864 (1927).
[3] O. Baudisch and L. A. Welo, *Chem. Rev.*, **15**, 1 (1934).
[4] O. Baudisch, *Ber.*, **68**, 769 (1935).
[5] L. A. Welo and O. Baudisch, *Nature*, **116**, 606 (1925).

binding, or to some combination of the types. Application of magnetic measurements to the study of complex compounds is due largely to Pauling,[6,7] and nearly all of the recent literature on the subject is expressed in terms of atomic-orbitals and other characteristics of Pauling's nomenclature. This nomenclature will therefore be adhered to here, although it will be pointed out that alternative methods of regarding these structural problems have been suggested. It will be assumed that the reader is in general familiar with the relative stability and the directional properties of atomic bond orbitals, but the subject will be reviewed very briefly.[8,9]

The order of decreasing stability for atomic bond orbitals is approximately as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p. The number of orbitals for the s, p, d, f groups is respectively 1, 3, 5, and 7. Each orbital may be occupied either by one electron or by two electrons provided these have opposed spins. It should be noticed that electrons first tend to occupy stable orbitals by pairing, but that when several orbitals of the same energy are available the electrons tend to keep their spins parallel and to occupy different orbitals. One must, of course, distinguish between the orbitals and the electrons which occupy them. The orbitals are strictly speaking the wave functions associated with the orbital motion of the electrons. An electron pair bond may be formed for each stable orbital of the atoms held together. It is clear then that for bond formation it is necessary to have two electrons with opposed spins and for each of the bonded atoms to have a stable orbital.

Such bonds, commonly called covalent bonds, are characterized by having definite directions in space. The bond angles may be found experimentally by electron diffraction and other methods, or they may be found theoretically. When only s electrons are available for bond formation, as in molecular hydrogen, the bond is spherically symmetrical about the nucleus. If p electrons are involved in the bond formation the bonds are at right angles to one another. In most cases the situation is complicated by what Pauling calls "hybridization" which is a combination of s and p and other orbitals. Various types of bonds are summarized by Rice (*op. cit.*, p. 267). If the structure involves all s and p orbitals the result will be a tetrahedron. The fact that one s and three p orbitals are involved is indicated by calling them sp^3 bonds.

[6] L. Pauling, *J. Am. Chem. Soc.*, **53**, 1391 (1931); **54**, 988 (1932).

[7] L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 214 (1934).

[8] L. Pauling, *Nature of the Chemical Bond.* Cornell University Press, Ithaca 1939, 2nd ed., 1940.

[9] O. K. Rice, *Electronic Structure and Chemical Binding.* McGraw-Hill Book Co., Inc., New York 1940.

The structure is a square if it involves all s, and all p orbitals of a given level, and one d orbital. This is designated as sp^2d bonding. It might be thought that the proper designation should be sp^3d, but one of the p orbitals is used for a non-bonding combination.

For all s, all p orbitals of a given level, and three or more d orbitals (sp^3d^3) the structure is a tetrahedron.

For all s, all p, and two or more d orbitals (sp^3d^2) the six bonds may form an octahedron.

The use of magnetic susceptibility measurements in the study of complexes arises from the fact that electrons used in covalent bond formation are of necessity paired and so contribute nothing to the permanent magnetic moment of the molecule. It is possible therefore to compute the number of paired and unpaired electrons in any complex because the effective moment is given approximately by $2\sqrt{S(S+1)}$ or by $\mu_{eff} = \sqrt{n(n+2)}$ where n is the number of unpaired electrons. The effective moment is, of

TABLE XXII

EFFECTIVE SPIN MOMENTS IN BOHR MAGNETONS

Number of unpaired electrons	1	2	3	4	5
μ_{eff}	1.73	2.83	3.87	4.90	5.92

course, also equal to $2.84\sqrt{\chi_M T}$ or to $2.84\sqrt{\chi_M(T+\Delta)}$ if the Weiss rather than the Curie law is obeyed. From a knowledge of the number of electrons used in covalent bond formation it is possible to deduce the nature of the orbitals involved and hence the spatial configuration of the complex. For instance, the compound $(NH_4)_3FeF_6$ has an effective moment of 5.9 Bohr magnetons, while $K_3Fe(CN)_6$ has an effective moment of about 2.3 Bohr magnetons. The ferric ion, Fe^{+++}, has five unpaired d electrons with a theoretical effective moment of $\sqrt{5(5+2)} = 5.92$. It is assumed that the spins only are involved. As pointed out in Chap. IV, the orbital moments are appreciable for the rare earth elements but are probably not very large for other transition group elements. The moment for the FeF_6^{-3} corresponds therefore to a structure primarily ionic. If, on the other hand, covalent sp^3d^2 bonds are formed, two of the five d orbitals are used up, and only three d orbitals remain for five electrons. These must then pair off so far as possible leaving only one electron unpaired. If such is the case the complex should have a moment of about 1.7 Bohr magnetons. It would appear, therefore, that while the FeF_6^{-3} complex is dominantly ionic, the $Fe(CN)_6^{-3}$ complex is essentially covalent. Magnetic measurements do not contribute much to our knowl-

edge of the spatial configuration of complexes such as the above because the sp^3d^2 bonds are octahedral, and it may be assumed that ionic bonds would lie at the largest possible angle from one another so that they would also be octahedral. But where the covalent structure leads to a square, or to a tetrahedron involving only three bonds, then the information so obtained may be very valuable.

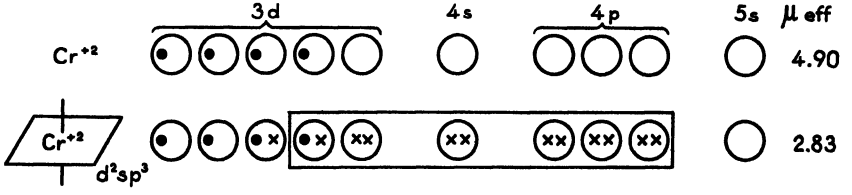
Van Vleck [10] has pointed out that Pauling's interpretation in terms of directed wave functions is not the only possible explanation of the magnetic properties of complex compounds. Alternatives are the crystalline potential model of Penney and Schlapp or the molecular orbital method of Mulliken. The three theories give results so similar that no preference can be established between them. The current literature is nearly all given in terms of Pauling's interpretation.

The experimental evidence on the stereochemistry of multivalent atoms has recently been collected by Sidgwick and Powell.[11] This review is very impressive, with over 300 references. It does not contain specific references to magnetic measurements. The usefulness of magnetic data in determining bond types in distorted complexes is reviewed by Mellor.[12]

In the following sections various complexes will be described under the central element of the group.

2. Complexes of Chromium and Related Elements

The chromous, Cr^{++}, ion has four 3d electrons, all unpaired, leading to a theoretical effective moment of 4.90 Bohr magnetons for the ion and for ionically bound complexes. In chromous chloride the observed moment is actually 5.0. Octahedral covalent bond formation (d^2sp^3) results in pairing of two electrons leaving $\mu_{eff} = 2.83$.



Various complexes of divalent chromium have been studied by Hume and Stone.[13] The observed effective moments are shown in Table XXIII. It will be seen that with one exception the complexes are all ionic. The exception is the cyanide which, in common with many other cyanides,

[10] J. H. Van Vleck, *J. Chem. Phys.*, **3**, 807 (1935).
[11] N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc. London*, **A176**, 153 (1940).
[12] D. P. Mellor, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 129 (1940).
[13] D. N. Hume and H. W. Stone, *J. Am. Chem. Soc.*, **63**, 1200 (1941).

TABLE XXIII

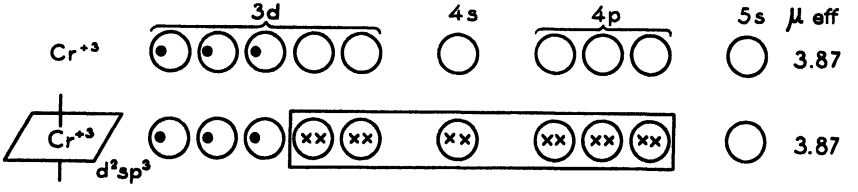
EFFECTIVE BOHR MAGNETON NUMBERS FOR SOME CHROMOUS COMPLEXES

Complex	μ_{eff}
Ammonia (uncertain composition)	4.90
Ethylenediamine	4.4–4.5
Thiocyanate	4.90
Chromocyanide	3.15

gives an octahedral complex with essentially covalent bonds. The low moment for the chromocyanide ion has also been indicated by Bose.[14]

The only other complex derived from divalent chromium which has received attention is the dinitrosyl diethyldithiocarbamate,[15] $(ON)_2CrSCSN(C_2H_5)_2$. Such compounds are called chromonitrosyl salts but it is not certain what oxidation state is reached by the chromium. The substance is diamagnetic which is unique among derivatives of chromium having a valence less than six. The distribution of electrons in this complex is uncertain.

Trivalent chromium complexes have been the object of much investigation. Unfortunately not much can be learned from magnetic measurements on such compounds because the structures of the extreme types of electrovalence and covalence have the same number of unpaired electrons.



A very large group of trivalent chromium complexes has been studied by Rosenbohm,[16] Bose,[17] Berkman and Zocher,[18] Jackson,[19] Welo,[20] Biltz,[21]

[14] D. M. Bose, *Z. Physik*, **65**, 677 (1930).

[15] L. Malatesta, *Gazz. chim. ital.*, **70**, 729 (1940). This paper was not available to the author.

[16] E. Rosenbohm, *Z. physik. Chem.*, **93**, 693 (1919). The old value for water, $\chi = -0.75 \times 10^{-6}$, was used by Rosenbohm for calibration purposes. Consequently his very extensive and useful data should all be corrected by the factor 72/75.

[17] D. M. Bose, *Z. Physik*, **35**, 219 (1926).

[18] S. Berkman and H. Zocher, *Z. physik. Chem.*, **124**, 318 (1926).

[19] L. C. Jackson, *Phil. Mag.*, **4**, 1070 (1927).

[20] L. A. Welo, *Phil. Mag.*, **6**, 481 (1928).

[21] W. Biltz, *Z. anorg. allgem. Chem.*, **170**, 161 (1928).

Leiterer,[22] and others.[23–27] These consist of polyammines, cyanides, organo-acid derivatives, polynuclear compounds, and many others. Without exception they all have an effective moment of very close to 3.8 Bohr magnetons. It is true that Bhatnagar [24] finds the green modification of $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ to have a susceptibility only half that of the red and gray modifications, but this lone case probably does not constitute an exception to the rule. Chemical analogy and stereochemical evidence suggest that these compounds range from essentially covalent as in the cyanides, to essentially electrovalent as in the ammonia complexes. For relatively simple complexes the Weiss law is obeyed with values of Δ equivalent to only a few Centigrade degrees, positive or negative. (Leiterer suggests a possible relationship between Δ and the absorption spectra.) The polynuclear compounds are a marked exception. Welo has shown that in compounds of the type $[Cr_3(CH_3COO)_6(OH)_2]Cl \cdot 8H_2O$ and in mixed polynuclear complexes such as $[Cr_2Fe(CH_3COO)_6(OH)_2]Cl \cdot 6H_2O$ the temperature coefficient is very peculiar with Δ often being as large as 500° or even larger. The polynuclear complexes of iron are similar in this respect. Such behavior raises doubts as to the meaning of the effective magnetic moment, which nevertheless seems to be about normal for the several transition group atoms involved in these compounds. A possible explanation [28] along classical lines is that the orientation of the magnetic dipoles in the metallic atoms is controlled by the oriented electric dipoles of the coordinated groups. There are few similar magnetic measurements on polynuclear complexes in which all the coordinated groups are neutral molecules rather than ions. It would be expected that the value of Δ would be considerably diminished under such circumstances and some of Rosenbohm's data [16] suggest this for binuclear complexes in which half the coordinated groups are ammonia or a diamine. On the other hand the same situation in $Fe_2(CO)_9$ leads to diamagnetism. Of course, it should be pointed out in connection with this explanation that all direct efforts to detect a magnetoelectric directive effect have failed.

Chromium is supposed to have an oxidation state of four in the dioxide, CrO_2, prepared by the action of chromic acid on chromium hydroxide. This valence is supported by Bhatnagar, Prakash, and Hamid,[24] who

[22] L. Leiterer, *Z. physik. Chem.*, **B36**, 325 (1937).
[23] D. M. Bose, *Phil. Mag.*, **5**, 1048 (1928); *Z. Physik*, **65**, 677 (1930).
[24] S. S. Bhatnagar, B. Prakash, and A. Hamid, *J. Chem. Soc.*, **1938**, 1428.
[25] D. S. Datar and S. K. K. Jatkar, *J. Indian Inst. Sci.*, **22A**, 225 (1939).
[26] P. C. R. Chaudhury, *J. Indian Chem. Soc.*, **16**, 652 (1939).
[27] L. Malatesta, *Gazz. chim. ital.*, **69**, 752 (1939).
[28] L. A. Welo, *Phys. Rev.*, **32**, 320 (1928).

show that the chromium atom has an atomic susceptibility of 2955×10^{-6}, corresponding reasonably well with 3332×10^{-6} for two unpaired electrons. Triamminochromium tetroxide, $(NH_3)_3CrO_4$, also has a susceptibility corresponding to two unpaired electrons.

The familiar red and blue perchromates are sometimes supposed to contain chromium with a valence of seven. The red potassium perchromate, K_3CrO_8, has an effective moment of 1.80 Bohr magnetons at room temperature.[29–31a] This clearly indicates a single unpaired electron. The valence of seven is not excluded by these measurements but the electronic configuration renders such a valence improbable. The oxidation state of five is compatible with the magnetic results. On the other hand the blue perchromate has a very small positive susceptibility probably not greatly dependent on temperature. This strongly suggests an oxidation state of six as is found in the chromates. The pyridine salt of perchromic acid is shown by Bhatnagar, Prakash and Hamid [24] to have a small positive susceptibility, probably because the chromium here also has an oxidation state of six.

Chromic acid anhydride, CrO_3, and many chromates have a small temperature independent paramagnetism.[31b] There are no unpaired electrons in such compounds. Thus sodium chromate has a susceptibility of about 0.04×10^{-6}, and the polychromates show corresponding values. Silver chromate in both green and red modifications is diamagnetic with a susceptibility of about -0.12×10^{-6}. Pyridinium tetrachlorohydroxychromate is slightly paramagnetic, and the corresponding quinolinium compound is diamagnetic.

The substances called chromium chromates prepared by thermal decomposition of chromates, or by action of $AgCrO_4$ on $CrCl_3$ have been studied by Datar and Jatkar,[31c] and by Chaudhury.[31d] The magnetic susceptibility corresponds to about 2.2 Bohr magnetons per atom of chromium. This is a little difficult to reconcile with the chemical evidence that the ratio $Cr^{+3}/CrO_4^{=}$ in chromium chromate is 2/3. The magnetic data would support a ratio of 3/2.

Chromium carbonyl, $Cr(CO)_6$, is diamagnetic,[23,32] as appears to be the case for all transition group metal carbonyls.

[29] B. T. Tjabbes, *Proc. Acad. Sci. Amsterdam*, **35**, 693 (1932).
[30] B. T. Tjabbes, *Z. anorg. allgem. Chem.*, **210**, 385 (1933).
[31a] W. Klemm and H. Werth, *Z. anorg. allgem. Chem.*, **216**, 127 (1933).
[31b] F. W. Gray and J. Dakers, *Phil. Mag.*, **11**, 297 (1931).
[31c] D. S. Datar and S. K. K. Jatkar, *J. Indian Inst. Sci.*, **22A**, 309 (1939).
[31d] P. C. R. Chaudhury, *J. Indian Chem. Soc.*, **16**, 652 (1939).
[32] W. Klemm, H. Jacobi, and W. Tilk, *Z. anorg. allgem. Chem.*, **201**, 1 (1931).

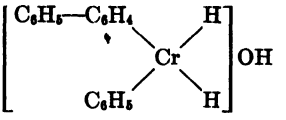
Magnetic properties of the peculiar polyphenylchromium compounds [33] have been studied by Klemm and Neuber.[34] All these substances whether containing three, four, or five phenyl groups on one chromium atom have an effective moment of about 1.7 Bohr magnetons. For instance tetraphenylchromium iodide has the magnetic properties shown in Table XXIV. This apparently means that there is one unpaired electron,

TABLE XXIV

MAGNETIC PROPERTIES OF $(C_6H_5)_4CrI$

Temperature °K.	$\chi \times 10^6$	μ_{eff}
293	1.87	1.68
195	3.01	1.66
90	7.27	1.66

contrary to Hein's original proposal that the pentaphenyl series contains chromium with a valence of six. It may be that the tri- and tetra-phenyl chromiums contain phenylene groups, such as, for instance



which would account for the magnetic data. This problem must be regarded as unsettled. It is further discussed by Emeléus and Anderson.[35]

The electronic configuration of molybdenum, $4s^2$, $4p^6$, $4d^5$, 5s, parallels that of chromium, and the magnetic properties of molybdenum atoms in compounds are similar to those of chromium with a significant exception. The molybdenum atom is larger and as a consequence often has a coordination number of eight rather than six. For essentially covalent complexes this often results in diamagnetism, where the corresponding chromium compound may be paramagnetic.

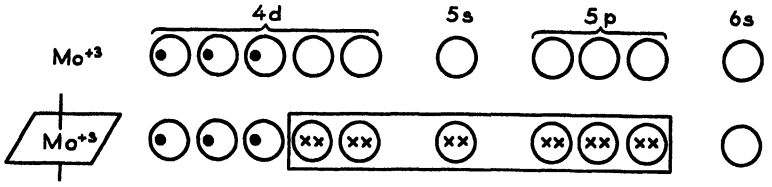
Compounds in which molybdenum has a valence of three have been studied by Bose,[23] by Tjabbes,[29,30] and by Klemm and Steinberg.[36] $K_3(MoCl_6)$, $K_3(MoCl_6)\cdot 2H_2O$, and $(NH_4)_3[Mo(SCN)_6]\cdot 4H_2O$, all have effective moments of about 3.7 Bohr magnetons corresponding to three unpaired electrons.

[33] F. Hein, *Ber.*, 54, 2708 (1921) *et seq.*; *J. prakt. Chem.*, 132, 59 (1931).

[34] W. Klemm and A. Neuber, *Z. anorg. allgem. Chem.*, 227, 261 (1936).

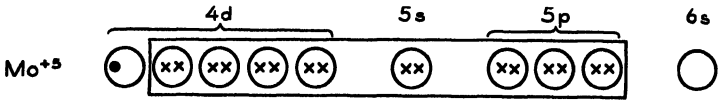
[35] H. J. Emeléus and J. S. Anderson, *Modern Aspects of Inorganic Chemistry*. D. Van Nostrand Company, Inc., 1939, p. 419.

[36] W. Klemm and H. Steinberg, *Z. anorg. allgem. Chem.*, 227, 193 (1936).

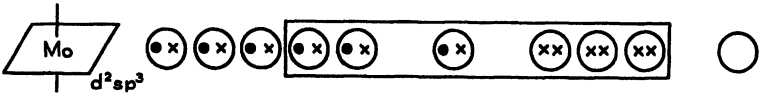


Two complexes containing tetravalent molybdenum have been reported by Klemm and Steinberg as having moments corresponding to one unpaired electron. These are $(C_5H_6N)_2[MoOBr_4]$ and $(C_9H_8N)_2[MoOBr_4]$. The structures are not clear because exactly the same moment is given for the compounds $Rb_2[MoOCl_5]$, $(C_5H_6N)_2[MoOCl_5]$, $(C_5H_6N)_2[MoOBr_5]$, $(C_9H_8N)_2[MoOBr_5]$, and $(C_5H_6N)_2[MoO(SCN)_5]$ in which the molybdenum would appear to have an oxidation state of five. The complex cyanides of tetravalent molybdenum $K_4Mo(CN)_8$ and $K_4Mo(CN)_8 \cdot 2H_2O$, are all diamagnetic. These have been studied by Klemm and Steinberg, Rawlinson,[37] Biltz,[21] and Bose.[23]

Rawlinson has also studied potassium molybdicyanide, $K_3Mo(CN)_8$, in which the molybdenum clearly has a valence of five. The effective moment of this compound is 1.66 Bohr magnetons.



Molybdenum carbonyl, $Mo(CO)_6$, has been shown by Klemm, Jacobi, and Tilk [32] to be diamagnetic.



Molybdic acid anhydride, MoO_3, and the normal molybdates seem to have been neglected by the magnetochemists. They are doubtless diamagnetic, or perhaps have a small temperature independent paramagnetism. Tjabbes [29,30] shows that zinc ammonia peroxymolybdate, $Zn(NH_3)_4MoO_8$, is diamagnetic. A group of polymolybdates including the xanthates, thiocarbamates, $(C_5H_5N)_2[Mo_2O_4Cl_4Cl_4]$ aq., $(C_5H_6N)_2[Mo_2O_4(SCN)_6]$, and $Ba[Mo_2O_4(C_2O_4)_2] \cdot 5H_2O$, are either diamagnetic or have very small positive susceptibilities.[36,38]

Not very many tungsten complexes have been studied. $K_3W_2Cl_9$ in which tungsten has a valence of three is stated by Bose to be diamagnetic

[37] W. A. Rawlinson, *Australian Chem. Inst. J. & Proc.*, **8**, 42 (1941).

[38] L. Malatesta, *Gazz. chim. ital.*, **69**, 408, 752 (1939).

although Klemm and Steinberg[36] give it fractional moment of 0.47. The complex cyanide of tetravalent tungsten $K_4[W(CN)_8]$[36] and its hydrate $K_4[W(CN)_8]\cdot 2H_2O$[20] have zero moment, but $K_2[WCl_5(OH)]$[36] has a moment corresponding to one unpaired electron. The only pentavalent tungsten complex on which magnetic measurements have been given is $Rb_2[WOCl_5]$. This has a moment of 1.5 Bohr magnetons. $(C_5H_6N)_2[WOCl_4]$ has exactly the same moment, a situation which is paralleled for the corresponding molybdenum compounds. It is not certain, however, that the tungsten necessarily has a valence of five in this pyridinium salt.

It would be interesting, and perhaps instructive, to have magnetic measurements on the tungsten bronzes.

3. Manganese and Rhenium

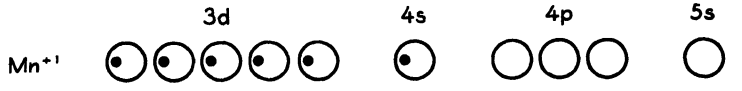
The complex compounds of manganese can scarcely be better described than by reference to a review by Goldenberg.[39] It is greatly to be desired that all the transition group elements receive as thorough treatment. Before presenting detailed discussion of the magnetic properties of manganese complexes it is necessary to repeat two often neglected observations. First, many of the compounds for which data are available were investigated at one temperature only, and the Curie law $\chi C = T$ then used to calculate the magnetic moment. This procedure is equivalent to assuming that the molecular field constant Δ is zero, or at least very small. There is abundant evidence that Δ may be far from small. Manganic phosphate offers a good example. The susceptibility suggests a moment of only 4.49 provided the Curie law is followed. This is much lower than the theoretical $\mu = 4.90$ for the Mn^{+++} ion. It has, however, been shown that manganic phosphate follows the Weiss law $\chi(T + 53) = C$. On recalculation of μ on this basis, an effective moment of 4.89 is obtained, in excellent agreement with theory.

A second observation worth making is that few magnetic measurements on complex compounds have been accompanied by accurate analyses proving the identity of the compound. Failure to establish purity may readily explain deviations in susceptibilities reported by various authors.

The experimental data on manganese compounds show almost without exception effective moments equivalent to ionic binding. Exceptions are the cyanides which give good evidence of covalent bonding.

[39] N. Goldenberg, *Trans. Faraday Soc.*, **36**, 847 (1940).

Univalent manganese is not common. It occurs in the cyanide, $K_5Mn(CN)_6$, which is reported by Goldenberg to have a moment of 1.04, and by Bhatnagar, Prakash and Maheshwari [40] to have $\mu = 1.76$. The difference is not critical because the Mn^+ ion should have an effective moment of 6.93 Bohr magnetons corresponding to six unpaired electrons.

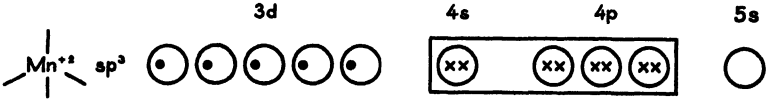


The magnetic data suggest that not more than one electron is left unpaired in this cyanide, but it is not clear why the compound should not be diamagnetic. The slight paramagnetism may be due to partial oxidation, or perhaps to temperature independent paramagnetism.

Divalent ions of manganese are common, they have an effective moment of about 5.92. This is approximately the case for Mn (*o*-phenanthroline)Cl_2,[41] $Mn(NH_3)_6Br_2$,[42] $NH_4MnPO_4 \cdot H_2O$, $K_2Mn(C_2O_4)_2 \cdot 2H_2O$,[39] and $(C_5H_6N)_2MnCl_2$.[43] The pyridinium salts $(C_5H_6N)MnCl_3 \cdot H_2O$ and $(C_5H_6N)_2MnCl_4$ are also reported as having moments of 5.86 and 5.95 respectively.[40] $K_2MnFe(CN)_6$ apparently contains normal divalent Mn^{++} ions.[44] Presumably such is the case also with $MnCl_2 \cdot ClNO$ [45] although a precise value for its susceptibility is not given.

Manganese phthalocyanine has been studied by Senff and Klemm.[46] It may contain partly covalent bonds. The phthalocyanines will be discussed in a later section.

Some further remarks should be made concerning manganous dipyridine dichloride. The tetrahedral sp^3 bonded atom would also have a moment of 5.92 but a tetrahedral configuration is not compatible with



the small dimensions of the C-axis, 3.73 Å. Mellor and Coryell suggest that each metal ion shares four coplanar chloride ions in pairs and holds two pyridine molecules at right angles to the plane of the chloride ions. This contains an ionic octahedral complex with two shared edges.

[40] S. S. Bhatnagar, B. Prakash, and J. C. Maheshwari, *Proc. Indian Acad. Sci.*, **10A**, 150 (1939).

[41] L. Cambi and A. Cagnasso, *Atti accad. Lincei*, **19**, 458 (1934).

[42] B. Cabrera, *Inst. int. chim. Solvay, Conseil chim.*, 1929.

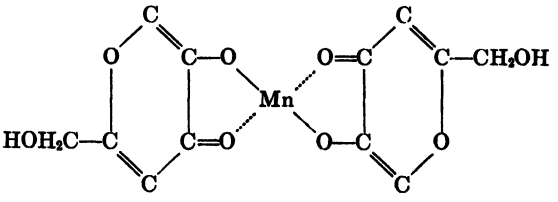
[43] D. P. Mellor and C. D. Coryell, *J. Am. Chem. Soc.*, **60**, 1786 (1938).

[44] J. Richardson and N. Elliott, *J. Am. Chem. Soc.*, **62**, 3182 (1940).

[45] R. W. Asmussen, *Z. anorg. allgem. Chem.*, **243**, 127 (1939).

[46] H. Senff and W. Klemm, *J. prakt. Chem.*, **154**, 73 (1939).

Some complex kojates of the transition group elements have been studied by Wiley, Tyson, and Steller.[47] The manganese kojate complex has an effective moment of 6.2, corresponding to a tetrahedral structure, as shown:



Two cyanide complexes of divalent manganese[48–50] have been studied. The first is $K_4Mn(CN)_6 \cdot 3H_2O$, the effective moment for which is given as 2.04 to 2.78. Goldenberg[39] gives 2.18. It can scarcely be decided, therefore, whether the manganese contains one or two unpaired electrons in this compound. The other cyanide $KMn(CN)_3$ is reported by Goldenberg to have a moment of 4.22, roughly corresponding to three unpaired electrons. Emeléus and Anderson (*op. cit.*)[35] suggest that it contains the ion $Mn(CN)_6^{-4}$ and should perhaps be written $K_2MnMn(CN)_6$. On this basis the $Mn(CN)_6^{-4}$ group would have one unpaired electron and the entire compound would have six unpaired electrons per double molecule, in reasonably good agreement with the experimental result.

Trivalent manganese[39,51] has a normal moment of about 4.90 in the complexes $NH_4[Mn(C_6H_4OCO_2)_2(H_2O)_2] \cdot 2H_2O$, $K_3[Mn(C_2O_4)] \cdot 3H_2O$, $Mn(CH_3COO)_3 \cdot 2H_2O$,[52] $Mn(CH_3COCH_2COCH_3)_3$,[53] $Mn(C_5H_7O_2)_3$, $Mn(C_{14}H_{14}NCS_2)_3$, $Mn(C_8H_{18}NCS_2)_3$, and $Mn(C_5H_1 \cdot NCS_2)_3$.[54] In double salts such as cesium manganese sulfate, the moment of the manganese is also 4.90 as is to be expected.[55]

Moments of from 2.95 to 3.61 have been reported for the cyanide $K_3Mn(CN)_6$ suggesting a d^2sp^3 octahedral configuration.[48,49,56] Goldenberg[39] gives an almost negligible moment of 0.62 for the compound $K_3Mn_2(CN)_9 \cdot 4KOH$ which he obtained by adding concentrated potassium permanganate solution to potassium cyanide solution.

[47] J. W. Wiley, G. N. Tyson, Jr., and J. S. Steller, *J. Am. Chem. Soc.*, **64**, 963 (1942).
[48] L. Szegö and P. Ostinelli, *Gazz. chim. ital.*, **60**, 946 (1930).
[49] P. Rây and H. Bhar, *J. Indian Chem. Soc.*, **5**, 497 (1928).
[50] S. Freed and C. Kasper, *J. Am. Chem. Soc.*, **52**, 1012 (1930).
[51] C. H. Johnson, *Trans. Faraday Soc.*, **28**, 845 (1932).
[52] W. J. de Haas and B. H. Schultz, *Physica*, **6**, 481 (1939).
[53] L. C. Jackson, *Proc. Phys. Soc. London*, **47**, 1029 (1935).
[54] L. Cambi and L. Szegö, *Ber.*, **B64**, 2591 (1931).
[55] H. Bommer, *Z. anorg. allgem. Chem.*, **246**, 275 (1941).
[56] W. Biltz, *Z. anorg. allgem. Chem.*, **170**, 161 (1928).

Complexes in which manganese has a valence of four are represented by $K_2Mn(IO_3)_6$,[39] $K_2MnF_6 \cdot H_2O$,[39] and $(KCl)_2MnCl_4$.[40] The moment in every case is close to 3.87.

The manganates exhibit a normal paramagnetism for one unpaired electron. For $BaMnO_4$ Goldenberg finds a moment of 1.80 which is probably more accurate than the earlier value 2.47 given by Wedekind and Horst.[57] Potassium manganate, K_2MnO_4, has a moment of 1.73 at 295° K. and 1.69 at 90° K.[58]

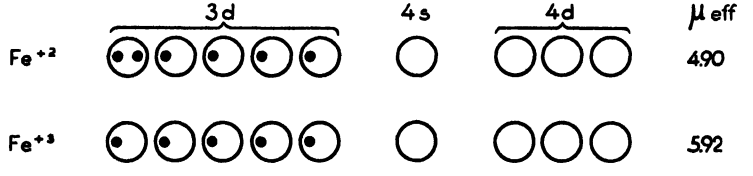
Potassium permanganate appears to have a small temperature independent paramagnetism which is exhibited both in the solid and in solution.[57,59,60]

Silver permanganate, on the other hand, is reported by Bhatnagar, Prakash, and Maheshwari as being diamagnetic.[40]

Rhenium complexes have not been very thoroughly studied and they give rather anomalous results.[61,62] For instance the supposedly trivalent rhenium in $[Re(NH_3)_6]Cl_3$, $[Re(NH_3)_6]Br_3$, and $Rb[ReCl_4]$ yields diamagnetic compounds. $Na_2[ReO_3]$ is also diamagnetic or perhaps very slightly paramagnetic, even though the compound apparently has an odd number of electrons. Perhaps this is due to Re—Re bonds or to a Re^{+3}—Re^{+5} combination. Other compounds of tetravalent rhenium such as $K_2[ReCl_6]$, $Ag_2[ReCl_6]$, and $K_2[ReBr_6]$ are paramagnetic and have moments of about 3.2, but the moments are dependent on the temperature. Pentavalent rhenium may exist in the compounds K_2ReOCl_5, $Re(NH_3)_6Cl_5$, $K_3[ReO_2(CN)_4]$, and $Tl[ReO_2(CN)_4]$ but with the possible exception of the first these are all diamagnetic.

4. Iron

It will be recalled that ferrous ions have a theoretical spin moment of 4.90 Bohr magnetons and that ferric ions, with one more unpaired electron, have a moment of 5.92. For magnetically dilute compounds



[57] E. Wedekind and C. Horst, *Ber.*, **48**, 105 (1915).
[58] K. A. Jensen and W. Klemm, *Z. anorg. allgem. Chem.*, **237**, 47 (1938).
[59] P. Collet, *Compt. rend.*, **183**, 1031 (1926).
[60] D. P. Raychaudhuri and P. N. Sengupta, *Indian J. Phys.*, **10**, 245 (1936).
[61] W. Klemm and H. Steinberg, *Z. anorg. allgem. Chem.*, **227**, 193 (1936).
[62] W. Klemm and G. Frischmuth, *Z. anorg. allgem. Chem.*, **230**, 220 (1937).

these values are closely approximated experimentally. Complex compounds of iron in which the bonds are essentially ionic in nature have about the same respective moments. A few representative values are given in Table XXV. Other ionic complexes of iron will be discussed later.

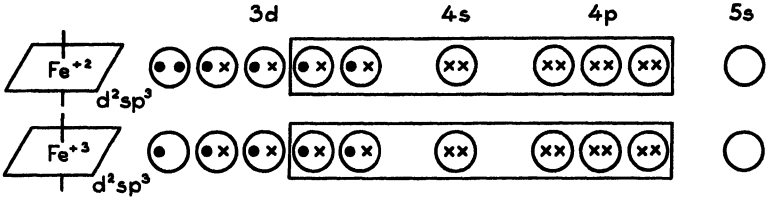
TABLE XXV

ESSENTIALLY ELECTROVALENT COMPLEXES OF IRON [16,22,32,56]

Compound	μ_{eff}
$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	5.25
$Fe(N_2H_4)_2Cl_2$	4.87
$Fe(N_2H_4)_2(C_2O_4)$	5.3
$[Fe(OH_2)_4]Cl_2$	5.2
$[Fe(OH_2)_6]SO_4 \cdot H_2O$	5.2
$Fe(NH_3)Cl_2$	5.3
$Fe(NH_3)_2Br_2$	5.3
$Fe(NH_3)_6Cl_2$	5.3
$Fe(NH_3)_6Br_2$	5.3
$NH_4Fe(SO_4)_2$	5.86
NH_4FeF_6	5.88
$(NH_4)_2FeF_5 \cdot H_2O$	5.91
$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	5.75
$Fe(NH_3)_6Cl_3$	4.5
Na_3FeF_6	5.2

It has already been mentioned that certain polynuclear complexes show normal moments but extremely large values of the molecular field constants. Thus Welo [20] has shown that iron complexes of the type $[Fe_3(CH_3COO)_6(OH)_2]NO_3 \cdot 6H_2O$ may follow the Weiss law with Δ often in excess of 500°. This behavior is also shown by chromium polynuclear complexes as stated in a previous section, and by mixed polynuclear salts such as $[Cr_2Fe(CH_3COO)_6(OH)_2]Cl \cdot 6H_2O$, $[Cr_2Fe(CH_3COO)_6(OH)_2]NO_3 \cdot 6H_2O$, and $[Fe_2Cr(CH_3COO)_2(OH)_2]NO_3 \cdot H_2O$, which have $\Delta = 380$, 458, and 342 respectively. The relationship of the metal atoms to one another in these compounds is not known but a clue may be found in the diamagnetic enneacarbonyl, $Fe_2(CO)_9$, which will be discussed later.

In sharp contrast to the compounds already mentioned, the cyanides of iron have low or diamagnetic susceptibilities. $K_4Fe(CN)_6$ is diamagnetic, and $K_3Fe(CN)_6$ has a moment corresponding to one unpaired electron. The complexes are octahedral and the reason for the magnetic moments being as they are should be clear from a consideration of the electron distribution.



Potassium ferricyanide has an astonishingly large magnetic anisotropy at low temperatures.[63] At 14° K. the anisotropy amounts to 400 per cent and apparently becomes still greater as the temperature is lowered. Howard [64] has obtained reasonably good theoretical agreement with experiment for this effect by use of the crystalline potential method.

Solutions of iron cyanides in dilute perchloric acid and in water have been studied by Simon and Knauer.[65] Some changes in susceptibility are probably to be expected owing to hydrolysis and other effects. The susceptibility of the paramagnetic ferricyanide is less in solution than in the solid state. The diamagnetism of the ferrocyanides appears to increase.

When potassium ferrocyanide is added to ferric ion a soluble blue compound is first formed. This is called soluble Prussian Blue or potassium berlinate and it has the formula $KFe_2(CN)_6$. The familiar insoluble Prussian Blue is next formed, with the formula generally written $Fe_4[Fe(CN)_6]_3$. X-ray data show that both these substances contain octahedral complexes and the magnetic evidence of Davidson and Welo [66] explains the distribution of iron atoms. The soluble compound gives a susceptibility corresponding to one normal ferric ion for every six cyanide radicals. The insoluble compound gives a moment (Fig. 39) corresponding to 4/3 of one normal ferric ion for every six cyanide ions. The magnetic data therefore strongly support the formulas $KFe[Fe(CN)_6]$ and $Fe_4[Fe(CN)_6]_3$ for the soluble and insoluble compounds respectively. Alternative interpretations involving trivalent iron in the complex might be possible but they do not seem very consistent with the chemical evidence. There does not appear to be any significant difference in the susceptibilities of Prussian Blue and the so-called Turnbull's Blue.[67]

[63] L. C. Jackson, *Proc. Roy. Soc. London*, **A140**, 695 (1933); *Proc. Phys. Soc. London*, **50**, 707 (1938).

[64] J. B. Howard, *J. Chem. Phys.*, **3**, 813 (1935).

[65] A. Simon and H. Knauer, *Z. Elektrochem.*, **46**, 13 (1940).

[66] D. Davidson and L. A. Welo, *J. Phys. Chem.*, **32**, 1191 (1928).

[67] A. K. Bhattacharya, *J. Indian Chem. Soc.*, **18**, 71 (1941).

Ferrocyanides of other transition group elements such as $K_2MnFe(CN)_6$, $K_2CoFe(CN)_6$, $K_2CuFe(CN)_6$, and $Cu_2Fe(CN)_6$ have been studied by Rollier and Arreghini,[68] and by Richardson and Elliott.[69]

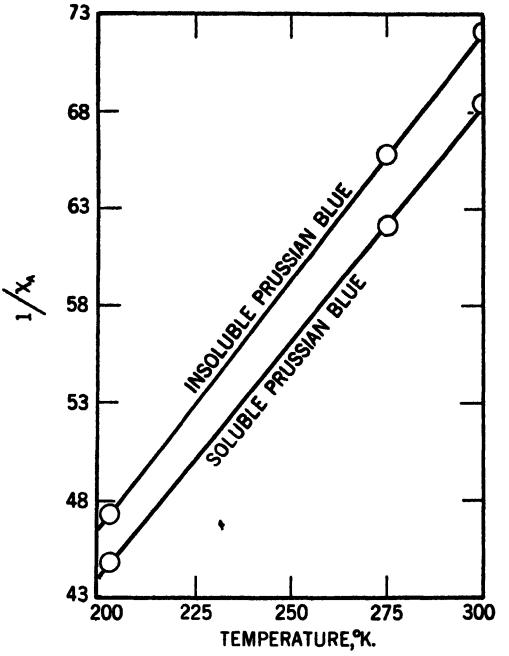


FIG. 39.—Reciprocal of the atomic susceptibility of iron in the Prussian Blues plotted against temperature.

In each case (Table XXVI) the observed moments agree with those calculated on the assumption that the substance contains an octahedral covalent complex with d^2sp^3 bonds from the iron to the cyanides. The

TABLE XXVI

EFFECTIVE MAGNETIC MOMENTS OF SOME FERROCYANIDES

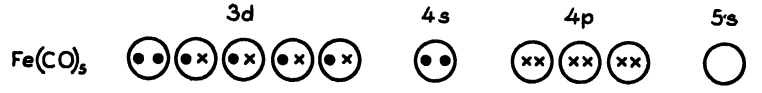
Compound	μ_{eff}
$K_2MnFe(CN)_6$	6.05
$K_2CoFe(CN)_6$	4.90
$K_2CuFe(CN)_6$	1.81–1.85
$Cu_2Fe(CN)_6$ hydrate	1.86

[68] M. A. Rollier and E. Arreghini, *Gazz. chim. ital.*, 69, 499 (1939).
[69] J. Richardson and N. Elliott, *J. Am. Chem. Soc.*, 62, 3182 (1940).

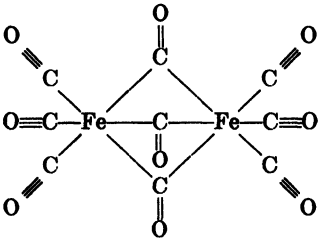
other heavy metals exist as simple ions. The moment for cobalt ferrocyanide is rather high, suggesting that for cobalt the orbital moment may be appreciable.

In addition to those already mentioned, a number of other cyanides of iron have been studied. The following are diamagnetic, $Na_3Fe(CN)_5NH_3$, $Na_3Fe(CN)_5SO_3$, $Na_4Fe(CN)_5NO_2$, $Na_3Fe(CN)_5OH_2$, $Na_2Fe(CN)_5NO$, and $K_3Fe(CN)_5CO$ and many others.[70] Most of these have water of hydration not shown in the formula. It is easy to see why these compounds should be diamagnetic, but Klemm, Jacobi, and Tilk [32] state that $Na_3[Fe(CN)_5NO_2]$ has a moment of about 2.2 Bohr magnetons. This probably means that the iron is ferric. It is not clear whether or not the NO_2 should be put outside the square brackets. Another peculiarity is the diamagnetism quoted by Bose for $K[Fe(NO)_2S_2O_3]$. A rather large group of nitroso complexes of ferrous iron, most of which are paramagnetic, has been investigated chiefly by Cambi.[71–75]

The three carbonyls of iron, $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ are all diamagnetic.[32, 18, 23] The diamagnetism of the liquid pentacarbonyl is easy to understand, but the other two carbonyls are very peculiar compounds. Powell and Ewens [76] have demonstrated the structure of



the enneacarbonyl to be as shown



with the Fe—Fe distance only 2.46 Å. We have therefore a situation in

[70] A. Simon, G. Morgenstern, and W. H. Albrecht, *Z. anorg. allgem. Chem.*, **230**, 225 (1937).

[71] L. Cambi and A. Cagnasso, *Gazz. chim. ital.*, **63**, 767 (1933).

[72] L. Cambi, *IX Congr. intern. quim. pura aplicada, Madrid*, **2**, 199 (1934).

[73] L. Cambi, *Z. anorg. allgem. Chem.*, **247**, 22, 33 (1941).

[74] W. Hieber and R. Nast, *Z. anorg. allgem. Chem.*, **247**, 31 (1941).

[75] G. Jacini, *Gazz. chim. ital.*, **69**, 714 (1939).

[76] H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, **1939**, 286.

which two atoms, each with an odd number of electrons, coexist in the same molecule, and yet the molecule is diamagnetic. This will at once recall the Chichibabin hydrocarbons which are also diamagnetic. There are two possible explanations. Either the electron spins are antiparallel but uncoupled, or else there is some kind of electron pairing taking place. This last might be because of the close proximity of the iron atoms to one another or because of the ring structure present in the molecule. Polynuclear structures involving metal atoms are extremely rare. Fe_2Cl_6 to be discussed below, is of this type, and the non-volatile iron complexes described by Welo are another example, but these involve a much smaller degree of interaction than in $Fe_2(CO)_9$. At one time it was thought that the brown ferric complex with *o*-phenanthroline [77] was of the same type, but Michaelis and Granick [78] have very recently shown this to be not so.

Iron tetracarbonyl, which has a molecular weight roughly corresponding to the formula $Fe_3(CO)_{12}$, is also diamagnetic. Berkman and Zocher [23] give a susceptibility of -0.01×10^{-6}, but the earlier value of Freundlich and Cuy [79] is -1.3×10^{-6}. The first value is very small and suggests contamination with iron oxide or even a trace of metallic iron. The Freundlich and Cuy value is very large for diamagnetic substances. It would probably be worth repeating these measurements, because a susceptibility of -1.3×10^{-6} suggests some kind of resonating layer structure as in graphite. It might also be instructive to have magnetic anisotropy measurements on the tetracarbonyl.

Compounds related to the iron carbonyls are also, like all carbonyls whose susceptibilities have been measured, diamagnetic. Some of these are $Fe(CO)_3$(*o*-phenanthroline), $Fe(CO)_4I_2$, $Fe(CO)_4Br_2$, and $Fe(CO)_2(NO_2)$.[80, 81]

This seems a good place to discuss iron trichloride vapor, Fe_2Cl_6, although it is not closely related to the substances just mentioned, in fact some might deny that that it is a complex compound. The only magnetic study on this substance is that of Lallemand.[82] From room temperature to 400° K. the susceptibility of the solid follows the Curie law. Above this temperature χ decreases rapidly owing to sublimation of the salt. From 600° to 703° K. $\chi = 4.59 \times 10^{-6}$ and is independent of temperature.

[77] A. Gaines, Jr., L. P. Hammett, and G. H. Walden, Jr., *J. Am. Chem. Soc.*, **58**, 1668 (1936).

[78] L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **65**, 481 (1943).

[79] H. Freundlich and E. J. Cuy, *Ber.*, **B56**, 2264 (1923).

[80] W. Klemm, H. Jacobi, and W. Tilk, *Z. anorg. allgem. Chem.*, **201**, 1 (1931).

[81] L. Pauling, *op. cit.*,[8] p. 115.

[82] A. Lallemand, *Ann. phys.*, **3**, 97 (1935).

At still higher temperatures the susceptibility decreases once more. The relationship between temperature and molar susceptibility is shown in Fig. 40. These results are scarcely as accurate as might be desired but they raise some very interesting questions. Lallemand suggests that the constant paramagnetism is due to Fe_2Cl_6 molecules and that dissociation to $FeCl_3$ above about 700° K. causes the reappearance of temperature dependent paramagnetism. Of course, some decomposition to $FeCl_2$ and Cl_2 occurs but this is not appreciable below 973° K.

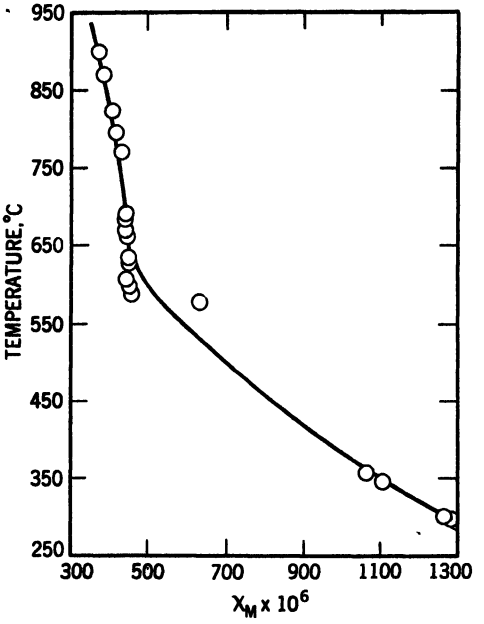


FIG. 40.—Molar susceptibility of ferric chloride in the vapor state.

These results would appear to rule out the Werner formula $[FeCl_6]Fe$, but the alternative is a structure involving an Fe — Fe bond, as in $Cl_3Fe - FeCl_3$. Quite apart from the correctness of this formula, Lallemand's results emphasize the mutual effect of adjacent iron atoms in a molecule, whether these atoms are united in a formal bond or not. Somewhat similar results have been obtained by a magnetic study of ferric chloride in non-aqueous solutions.[82a]

We turn now to a large group of complex iron compounds whose stereochemical configuration has been the principal object of study. Of these the most important is hemin and its derivatives. First, however, we shall mention some less complicated structures.

[82a] A. Quartaroli, *Gazz. chim. ital.*, **46**, 371 (1916).

The complex kojate of ferrous iron has been studied by Wiley, Tyson, and Steller.[47] It has a moment of 5.4, corresponding reasonably well with that expected for four unpaired electrons. The structure is ionic tetrahedral, similar to the kojate of manganese shown on page 153.

Ferric dithiocarbamates, of the type $Fe(S_2CNRR')_3$, have been studied by Cambi and Szegö,[83] and by Cambi and Malatesta.[84] These compounds have irregular temperature coefficients, perhaps owing to some kind of isomerism. Other complexes studied by Cambi [85] include the ferrous salts of α-pyridine, α-quinolinecarboxylic acid, the glyoximes, phenanthroline, and dipyridyl.

The α-(yellow), and β-(black) forms of ferrous tetrapyridinediothiocyanates, $[Fe(C_5H_6N)_4(SCN)_2]$, have been shown by Asmussen [86] to have substantially the same susceptibility, with moments of 5.47 and 5.40 Bohr magnetons respectively. They must both, of course, be essentially ionic complexes.

Ferrous and ferric complexes of dipyridyl and of phenanthroline are quite different from those in which the coordinated molecule has only one functional group. $[Fe^{+2}(dipyridyl)_3]Br_2$,[32] $[Fe^{+2}(dipyridyl)_3]SO_4$,[32] and $[Fe^{+2}(o\text{-phenanthroline})_2]I_2$ [56] are diamagnetic. The corresponding ferric salts such as $[Fe^{+3}(dipyridyl)]Cl_3$ and $[Fe^{+3}(o\text{-phenthroline})]Cl_3$ are paramagnetic, both with moments of 5.91 Bohr magnetons, corresponding to ionic binding. $[Fe(dipyridyl)_3]_2[PtCl_6]_3$ and $[Fe(o\text{-phenthroline})_3]_2[PtCl_6]$ have moments corresponding to one unpaired electron, which is normal for covalent ferric iron.[87, 88]

There are two forms of the ferric complex containing two molecules of phenanthroline, $[Fe(o\text{-phenthroline})_2]^{+3}$. The blue form is obtained by oxidation of the ferrous complex, and the brown form by direct reaction of phenanthroline with a ferric salt.[89–91] The iron in the blue form has a moment of about 2.6. The brown form in solution has $\mu = 2.14$, and in the solid 2.41. The structure is probably an octahedral d^2sp^3 complex in which two octahedra share an edge of which the two corners are occu-

[83] L. Cambi and L. Szegö, *Ber.*, **66B**, 656 (1933).

[84] L. Cambi and L. Malatesta, *Ber.*, **70B**, 2067 (1937).

[85] L. Cambi and A. Cagnasso, *Gazz. chim. ital.*, **64**, 772 (1934).

[86] R. W. Asmussen, *Z. anorg. allgem. Chem.*, **218**, 425 (1934).

[87] A. Simon, G. Morgenstern, and W. H. Albrecht, *Z. anorg. allgem. Chem.*, **230**, 225 (1937).

[88] A. Simon and H. Knauer, *Z. Elektrochem.*, **45**, 678 (1939).

[89] G. H. Walden, Jr., L. P. Hammett, and A. Gaines, Jr., *J. Chem. Phys.*, **3**, 364 (1935).

[90] A. Gaines, Jr., L. P. Hammett, and G. H. Walden, Jr., *J. Am. Chem. Soc.*, **58**, 1668 (1936).

[91] L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **65**, 481 (1943).

pied by oxygen atoms. The iron atoms are thus considerably farther apart than in iron enneacarbonyl and the mutual interaction leading to depression of the magnetic moment is absent.

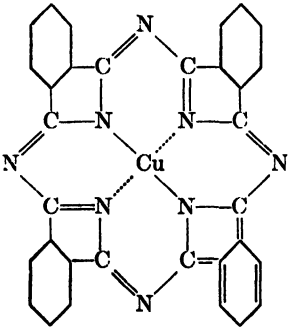
The metal phthalocyanines have been studied by Klemm.[92, 93] The effective moments, which are nearly independent of temperature, are given in Table XXVII. For the sake of convenience these compounds

TABLE XXVII

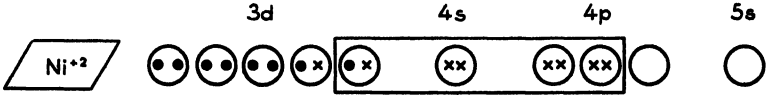
MAGNETIC MOMENTS FOR THE PHTHALOCYANINE COMPLEXES

Complex	μ_{eff}
Cu^{+2}	1.73
Ni^{+2}	0
Co^{+2}	2.16
Fe^{+2}	3.96
Mn^{+2}	4.55
VO^{+2}	1.70

will all be discussed here. The structure, of which that for copper is shown, suggests either a square planar structure or a tetrahedron. The



magnetic evidence is most striking for the nickel complex which is shown by its diamagnetism to have the square dsp^2 structure, which is confirmed



by x-ray evidence.[94] The magnetic evidence is consistent also with square structures for the copper and cobalt complexes if we recall that the

[92] L. Klemm and W. Klemm, *J. prakt. Chem.*, **143**, 82 (1935).
[93] H. Senff and W. Klemm, *J. prakt. Chem.*, **154**, 73 (1939).
[94] I. Woodward, *J. Chem. Soc.*, **1940**, 601.

orbital contribution to the magnetic moment is appreciable for the latter. For the iron and manganese complexes the moments are definitely too high for the dsp^2 configuration. These might be accounted for by tetrahedral structures, but this is improbable, if for no other reason than that of analogy. They probably mark a transition to ionic binding which is not inconsistent with what has already been said respecting the tendencies of iron and especially of manganese to enter complexes. For the vanadyl ion the magnetic data are less useful because both ionic and covalent bonding give the same magnetic moment corresponding to one unpaired electron, which is the moment actually found. No single crystal studies of the phthalocyanines seem to have been made, but Miss Woodward mentions that the related tetrabenzmonazaporphin is strongly anisotropic as is to be expected. Senff and Klemm have also studied the complexes formed when iron phthalocyanine is dissolved in pyridine or quinoline. The structures are probably octahedral. In both the magnetic moment falls to zero.

On November 8, 1845 Michael Faraday investigated the magnetic properties of dried blood and noted that he "must try recent fluid blood." Had he done so he would have discovered the difference between arterial and venous blood. The difference between completely oxygenated and deoxygenated blood amounts to twenty per cent. There have been several magnetic studies of blood, and even of hemoglobin and related compounds,[95–98a] since that time, but we are indebted chiefly to Pauling and Coryell and their co-workers for a brilliant series of magnetic studies which have led to a great extension of our knowledge of blood components.

With this better understanding of the structure of hemoglobin and related compounds there has arisen a need for a simpler, more logical nomenclature than the one in use. The system adopted by Pauling and Coryell will, therefore, be explained first and its relation to the older names shown because these are still met with, especially in the biochemical and medical literature.[98b]

Hemoglobin is a conjugated protein containing native globin and a complex of iron with a porphyrin. From the magnetic standpoint it is the complex with which we are most concerned. The structure of the porphyrin complex is shown below:

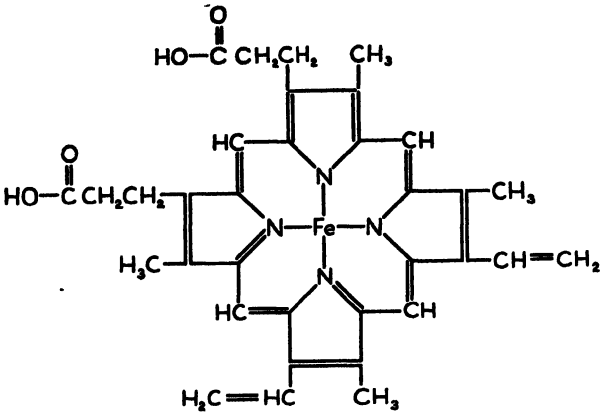
[95] A. Gamgee, *Proc. Roy. Soc. London*, **68**, 503 (1901).

[96] H. Kudo, *Acta Med. Scand.*, **81**, 511 (1934).

[97] F. Haurowitz and H. Kittel, *Ber.*, **66B**, 1046 (1933).

[98a] P. Berthier, *Compt. rend.*, **207**, 1254 (1938); **208**, 943, 1435 (1939); **209**, 774 (1939).

[98b] The nomenclature of porphyrin derivatives is discussed by D. L. Drabkin, *Ann. Rev. Biochem.*, **11** (1942), Stanford University Press, p. 531. This article also contains a valuable review of the magnetochemical method as applied to substances of biochemical interest.



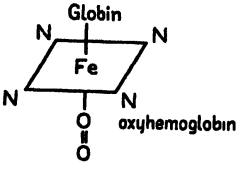
The iron may be removed from this complex and the resulting iron-free pigment is called protoporphyrin. Protoporphyrin is diamagnetic. The important features of the new nomenclature are tabulated below:

heme: the iron-porphyrin complex, the iron may be ferrous or ferric;
ferroheme: the ferrous-porphyrin complex, sometimes called reduced hemin;
ferriheme: the ferric-porphyrin complex ion;
ferriheme chloride, or *hemin:* ferriheme plus chloride;
ferriheme hydroxide, or *hematin:* ferriheme plus hydroxide;
hemochromogen: a substance with a distinctive absorption spectrum, formed from ferroheme and denatured globin;
ferrihemochromogen: hemochromogen containing ferric iron, sometimes called parahematin;
ferrohemoglobin: ferroheme plus globin; there are four hemes per globin molecule;
ferrihemoglobin: ferriheme plus globin; there are four hemes per globin molecule. Ferrihemoglobin is sometimes called acid methemoglobin.
oxyhemoglobin: ferrohemoglobin plus oxygen;
carbonmonoxyhemoglobin: ferrohemoglobin plus carbon monoxide;
ferrihemoglobin hydroxide: alkaline methemoglobin.

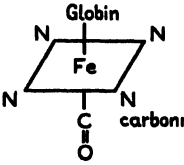
The iron in hemin, or ferriheme chloride, has a magnetic moment of about 5.8 Bohr magnetons,[99] although as we shall see the precise magnitude depends upon several conditions. The moment obtained from ferrihemoglobin is substantially the same. This corresponds quite closely to five unpaired electrons which is normal for Fe^{+++}. We must therefore regard the iron as being ionically bound. What, precisely, this may mean will be discussed later.

[99] L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci.*, **22**, 159 (1936).

The iron in ferrohemoglobin, and in ferroheme, has a moment of about 4.91, or perhaps a little higher, corresponding to ionic binding in this compound too. On the other hand, oxyhemoglobin and carbonmonoxyhemoglobin have zero moments.[100] These results are particularly interesting. They show that the complexes probably have d^2sp^3 octahedral covalent bonds. The oxygen in the oxy-complex cannot be molecularly adsorbed or held without dislocation of the two unpaired electrons which give oxygen its paramagnetism. Rather it must be attached in some such fashion as shown, perhaps in resonance with other electron distribu-



oxyhemoglobin



carbonmonoxyhemoglobin

tions. The structure for carbonmonoxyhemoglobin is probably very much the same, at any rate the great similarity of properties of the two compounds supports this idea. A quantitative study of the reaction between ferrohemoglobin and oxygen has been made by Coryell, Pauling, and Dodson.[101] This involves the interesting technique of magnetic titration, that is, of determining the susceptibility and course of a reaction mixture during addition of a reagent. Data obtained from the reaction of oxyhemoglobin with sodium dithionite are shown in Fig. 41. This, and similar studies with the carbon monoxide and nitric oxide complexes demonstrate that the susceptibilities of intermediate compounds formed in hemoglobin reactions are linearly related to the number of hemes which have undergone reaction.

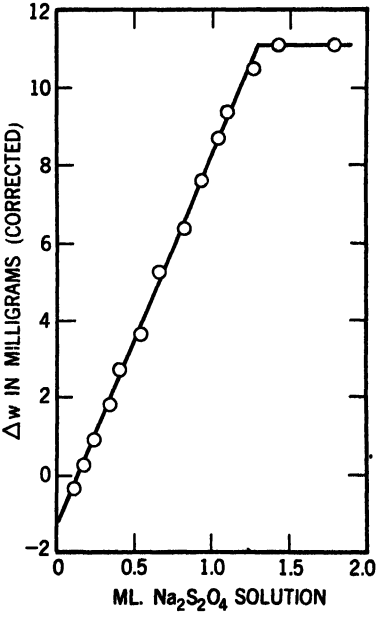


FIG. 41.—Magnetic titration of oxyhemoglobin with sodium dithionite.

Hematin, or ferriheme hydroxide gives a moment of 4.47 according to Coryell, Stitt, and Pauling,[102] or about 3.5 according to Rawlin-

[100] L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci.*, 22, 210 (1936).
[101] C. D. Coryell, L. Pauling, and R. W. Dodson, *J. Phys. Chem.*, 43, 825 (1939).
[102] C. D. Coryell, F. Stitt, and L. Pauling, *J. Am. Chem. Soc.*, 59, 633 (1937).

son.[103] Magnetic titration by the American authors yields results of the type shown in Fig. 42 where the molar susceptibility is plotted against *p*H. The reaction is first order in hydroxide ions, and it is of course possible to obtain equilibrium constants from these data. The figure shows only those data obtainable at low ionic concentration. For higher concentra-

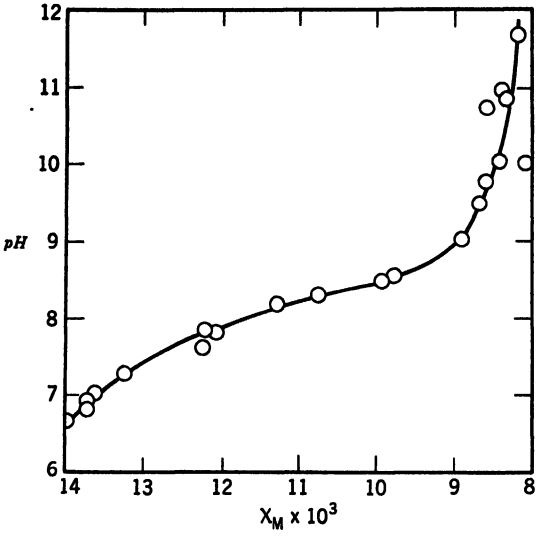
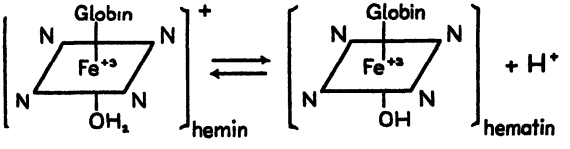


FIG. 42.—Magnetic titration of hemin to hematin.

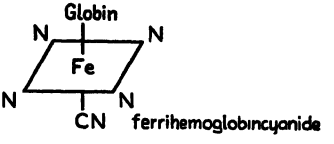
tions the point of inflection is shifted somewhat to higher *p*H values. The magnetic moment suggests three unpaired electrons, a type which is rare for iron. The complexes of $Fe(CNS)_2$ with a *o*-phenanthroline and with dipyridyl may be of this type.[104] Granick and Michaelis [105] find that the iron in ferritin has a moment of 3.8 Bohr magnetons which may make the compound another member of this small group. Ferritin is an iron containing protein extracted from horse spleen. The existence of an octahedral covalent complex for hematin suggests that in ferrihemoglobin the coordination may still be six, the sixth place being taken by a water molecule. Perhaps the ion should be written as shown, the transition to



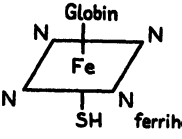
[103] W. A. Rawlinson, *Australian J. Expil. Biol. Med. Sci.*, **18**, 185 (1940).
[104] L. Cambi and A. Cagnasso, *Rend. ist. lombardo sci.*, **67**, 741 (1934).
[105] S. Granick and L. Michaelis, *Science*, **95**, 439 (1942).

the hydroxide involving loss of a proton, with change of bond type, rather than gain of an OH^- ion.

Ferrihemoglobin cyanide and ferrihemoglobin hydrosulfide [102] have moments of 2.50 and 2.26, respectively, indicating one unpaired electron and six octahedral, essentially covalent bonds. The structures are therefore similar to that of the ferricyanide ion. It is necessary, however, to



ferrihemoglobincyanide



ferrihemoglobinhydrosulfide

postulate a rather large orbital contribution in order to explain the relatively high moments. The possible existence of an orbital moment is an almost too convenient explanation for what may actually be faulty interpretation or experimental technique. The magnetic titration of cyanide with hemoglobin is shown in Fig. 43. Ferrihemoglobin fluoride has, as

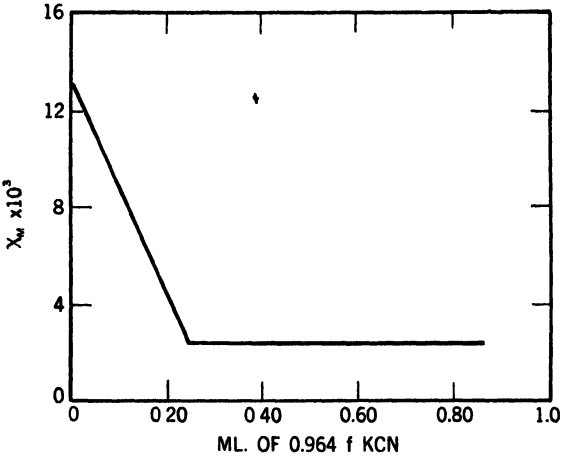


FIG. 43.—Magnetic titration of hemin with potassium cyanide.

might be expected, a moment of 5.92 and is therefore an essentially ionic complex.

Other ferrihemoglobin derivatives which have been studied are the compounds with azide ion, ammonia, ethanol and other alcohols; [106] pyridine; [108] and imidazole.[107] The iron in these complexes has moments as shown in Table XXVIII. Analysis of magnetic and electrode poten-

[106] C. D. Coryell and F. Stitt, *J. Am. Chem. Soc.*, **62**, 2942 (1940).

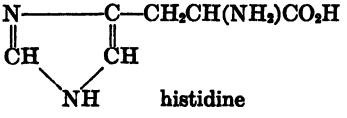
[107] C. D. Russell and L. Pauling, *Proc. Natl. Acad. Sci.*, **25**, 517 (1939).

TABLE XXVIII

MAGNETIC MOMENTS OF IRON IN SOME DERIVATIVES OF FERRIHEMOGLOBIN

Compound	μ_{eff}
ethanol ferrihemoglobin	5.89
ferrihemoglobin azide	2.84
ammonia ferrihemoglobin hydroxide	2.98
ethanol ferrihemoglobin hydroxide	5.39–5.48
imidazole ferrihemoglobin	about 2

tial data indicate that ferrihemoglobin may exist in three acid forms, two of which have slightly different susceptibilities than the third.[108] It is postulated that one acid group is a histadine imidazolium ion in poor position for electrostatic coordination of the basic form with the iron atom. The second acid group is the imino group of a histidine residue whose 3-N atom is strongly coordinated by either an essentially ionic or an essentially covalent bond with the iron atom. The third acid group of ferrihemo-



histidine

globin is the iron atom itself which may add a hydroxide ion or, more probably, coordinate a water molecule which may lose a proton.

Imidazole ferrihemoglobin is of considerable interest because it may be that the bond between the heme and the globin involves the imidazole group of the side-chain of a histidine residue. The moment of the iron in imidazole ferrihemoglobin can only be approximated; it corresponds roughly to one unpaired electron or a little higher. The structure is probably of the octahedral covalent type.

Except for the hemochromogens, complexes derived from ferrohemoglobin have been much less thoroughly studied. The equilibrium between ferrohemoglobin, cyanide ion, and cyanide ferrohemoglobin has been investigated by Stitt and Coryell.[109] The stability of the compound is much less than that of the corresponding ferriheme complex. Cyanide ferrohemoglobin is diamagnetic with octahedral covalent bonds.

The hemochromogens,[99,103] compounds of ferroheme and denatured globin, have been studied by Pauling and Coryell, and by Rawlinson. Other organic bases, such as pyridine, form hemochromogen-like substances. In fact metals other than iron may also be introduced into the

[108] C. D. Coryell and L. Pauling, *J. Biol. Chem.*, **132**, 769 (1940).

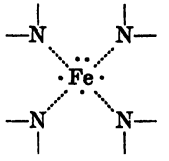
[109] F. Stitt and C. D. Coryell, *J. Am. Chem. Soc.*, **61**, 1263 (1939).

porphyrin complex. The name hemochromogen is generally used to cover those characteristically colored compounds derived from ferroheme and an organic base. These substances are all diamagnetic with octahedral covalent d^2sp^3 bonds. The hemochromogens investigated are those of globin, pyridine, nicotine, and the dicyanide.

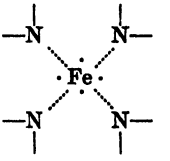
The interrelationships between the various derivatives of iron protoporphyrin may be clarified by the following table from Rawlinson's paper:

TABLE XXIX

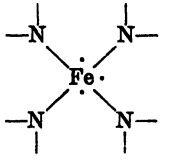
DERIVATIVES OF IRON PROTOPORPHYRIN



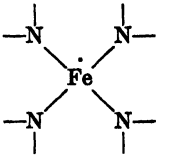
hemin, five ionic bonds, $\mu = 5.91$



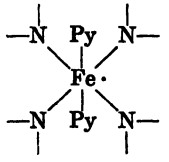
ferroheme, four ionic bonds, $\mu = 4.90$



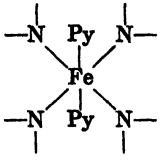
hematin (ferriheme hydroxide), four dsp^2 covalent bonds, $\mu = 3.88$



(unknown)



pyridine ferrihemochromogen (parahematin), six octahedral d^2sp^3 covalent bonds, $\mu = 1.73$



pyridine ferrohemochromogen, six octahedral d^2sp^3 covalent bonds, $\mu = 0$

The magnetic state of iron derived from the hemoglobin of different animals has been studied by Taylor and Coryell.[110] The magnetic moments of iron from cow, horse, sheep, and human blood are respectively 5.43, 5.43, 5.46, and 5.35. The only one significantly different is the value for human blood, and as it was determined on a single sample from a single individual (C. D. C.) perhaps the difference is not important. An extensive study of bovine hemoglobin indicates that the susceptibility is constant from individual to individual within a species. Hemoglobin content is often measured by the capacity of the blood for oxygen absorption. Taylor and Coryell show, however, that this is not a reliable

[110] D. S. Taylor and C. D. Coryell, *J. Am. Chem. Soc.*, **60**, 1177 (1938).

measure for either the hemoglobin or the total iron. Magnetic measurements reveal a certain fraction of the total iron which is inactive in the absorption of oxygen. For cow blood this amounts to 5.7 per cent of the iron. The results suggest that the "inactive" iron may be a different percentage in human blood. The state of this "inactive" iron is not known with certainty but it may be in the form of ferrihemoglobin which has no oxygen absorbing power.[111]

In this work Taylor and Coryell used a magnetochemical method for the determination of hemoglobin concentration. This method is more convenient and probably more accurate than the conventional gasometric method. The procedure is as follows:

The hemoglobin solution is reduced to ferrohemoglobin with sodium dithionite, $Na_2S_2O_4$. Then Δw, the apparent change in weight on application of the field in a Gouy balance is determined. The solution is now saturated with carbon monoxide, and Δw is redetermined. The change in Δw corresponds to a change in molar susceptibility per heme of $12{,}290 \times 10^{-6}$ at 24° C., the effective moment of ferrohemoglobin being taken as 5.46 Bohr magnetons. Let Δw for the ferrohemoglobin $= \Delta w_{\mathrm{Hb}}$, for the carbonmonoxyhemoglobin $= \Delta w_{\mathrm{HbCO}}$ and for the solution being studied $= \Delta w$. Then the molal susceptibility per heme at 24° for the solution under investigation is

$$\chi_M = \frac{\Delta w - \Delta w_{\mathrm{HbCO}}}{\Delta w_{\mathrm{Hb}} - \Delta w_{\mathrm{HbCO}}} \times 12{,}290 \times 10^{-6}$$

and the effective moment per heme $= \mu = \left(\frac{\Delta w - \Delta w_{\mathrm{HbCO}}}{\Delta w_{\mathrm{Hb}} - \Delta w_{\mathrm{HbCO}}} \right)^{\frac{1}{2}} \times 5{\cdot}46$ Bohr magnetons. The method is particularly elegant because of the automatic cancellation of the diamagnetic corrections.

Methods such as the above, and the technique of magnetic titration, would appear to have many applications in chemistry. The only difficulty is the time necessary to fill and reset the sample tubes. Perhaps this trouble could be eliminated by using a method whereby the sample is measured indirectly. Such methods are the Rankine balance, and, more promising, the modification of the Gouy method in which the sample is made the surrounding atmosphere instead of the actual moving tube.

A substance closely related to hemoglobin is myoglobin, or muscle hemoglobin. The oxygen saturation curve for this substance is a rectangular hyperbola rather than a sigmoid curve. It also has a much higher affinity for oxygen than hemoglobin. In spite of these differences the magnetic moment of the iron in myoglobin and in ferrimyoglobin

[111] The existence of "inactive" iron in the blood had previously been established by orthodox chemical tests.

(metamyoglobin) is the same as in the corresponding hemoglobins.[112a] The iron atoms must therefore be held by essentially ionic bonds. Another substance related to hemoglobin is cytochrome.[112b] Ferrous and ferric cytochrome *c* and their derivatives have magnetic properties not unlike those of the corresponding hemoglobin compounds.

An important and curious commentary on our use of the word "ionic" in reference to chemical bonds is found in some recent experiments on exchange reactions with radioactive iron as a tracer element.[113a-b] There can be made a convenient isotope of iron, having a half-life of 47 days. This iron in the form of Fe^{+++} ions does not exchange with the supposedly ionic iron in ferriheme or ferrihemoglobin. On the other hand, Fe^{++} ions do exchange, slowly but easily measurably, with supposedly covalent iron in ferrous *o*-phenanthroline, and ferrous dipyridyl sulfate. The observations may require some modification of our definitions of the terms "ionic" and "covalent." Perhaps the explanation lies in the greater importance of structural relationships than of bond type for exchange reactions. The "fused ring" structures may not permit exchange because the metal atom is, in a sense, boxed in. But in the "open rings" such as the phenanthroline and dipyridyl complexes there is no stereochemical obstacle to exchange, even though the bond type may not be especially favorable towards it.

In all this computation of magnetic moments for hemoglobin and related compounds it has been implied that the Curie law is obeyed. That this should be the case is of considerable importance because it is idle to interpret magnetic data in terms of bond type unless the moments are known with some certainty. There is also the question of possible magnetic interaction between the iron in adjacent hemes. For those compounds such as iron enneacarbonyl in which we feel reasonably certain that interaction does take place, the magnetic properties of the iron are profoundly altered. It is a little surprising therefore that not more attention has been paid to the temperature coefficient of susceptibility of these substances. Cambi and Szegö [114] have measured the susceptibility of hemin from 84° to 294° K. and find that it obeys the Curie law. Extension of these observations to other hemoglobin derivatives is greatly to be desired.

[112a] D. S. Taylor, *J. Am. Chem. Soc.*, **61**, 2150 (1939).

[112b] H. Theorell, *J. Am. Chem. Soc.*, **63**, 1820 (1941).

[113a] S. Ruben, M. D. Kamen, M. B. Allen, and P. Nahinsky, *J. Am. Chem. Soc.*, **64**, 2297 (1942).

[113b] P. F. Hahn, W. F. Bale, J. F. Ross, R. A. Hettig, and G. H. Whipple, *Science*, **92**, 131 (1940).

[114] L. Cambi and L. Szegö, *Rend. ist. lombardo sci.*, **67**, 275 (1934).

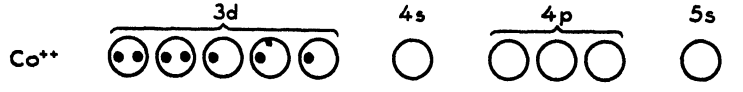
It will be recalled that the *ortho-para*hydrogen conversion is catalyzed by paramagnetic substances. It is probably inevitable, therefore, that the conversion on porphyrin compounds should have been studied. Eley [115] has investigated the heterogeneous conversion of *para*hydrogen from − 80° to 120° C. on hemoglobin, hematin, and hemin, as well as on metal-free phthalocyanine and on copper phthalocyanine. As expected, the conversion is catalyzed by the paramagnetic substances but not by the diamagnetic.

The magnetic behavior of catalase has been studied by Michaelis and Granick.[116] The measurements are difficult because of the small iron content. At first it was thought that this compound was another example of iron with three unpaired electrons as in ferrihemoglobin hydroxide, but later measurements render this uncertain.[117]

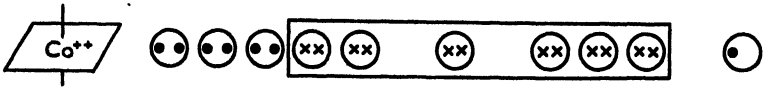
No mention has been made in this discussion of iron complexes of the ferrites and ferrates. Ferrites are generally ferromagnetic and will be referred to in Chap. VIII. The salts of ferric acid, H_2FeO_4, seem to have escaped magnetochemical investigation.

5. Cobalt

The cobaltous ion has a moment corresponding to three unpaired electrons, with perhaps an unusually large orbital contribution. But complex compounds involving divalent cobalt are much less stable than those in which the valence is three. This is, of course, just the reverse of the situation with simple cobalt compounds. The reason for this stabilization of trivalent cobalt seems first to have been suggested by Dr. J. L. Hoard.[118] The cobaltous ion has the electronic configuration shown. Octahedral covalent bond formation leads to ejection of a single

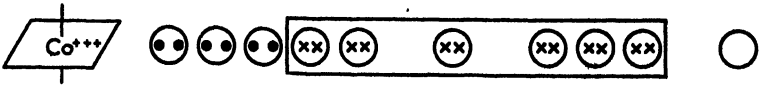


electron to the unstable 5s orbital where it is easily lost, resulting in



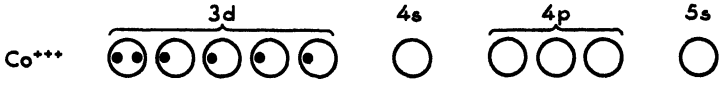
oxidation to the much more stable trivalent complex.

[115] D. D. Eley, *Trans. Faraday Soc.*, **36**, 500 (1940).
[116] L. Michaelis and S. Granick, *J. Gen. Physiol.*, **25**, 325 (1941).
[117] Private communication from Dr. L. Michaelis.
[118] L. Pauling, *op. cit.*,[8] p. 93.



It will be clear that hexacoordinated cobaltous complexes will have a moment corresponding to one unpaired electron, provided the bonds are covalent, and that octahedral complexes of trivalent cobalt should be diamagnetic. This seems to be true with the possible exception of the hexafluoride and of some nitroso complexes to which reference will be made later.

In most work on cobaltic complexes it is assumed that the free Co^{+++} ion would have a moment corresponding to four unpaired electrons. Unfortunately it is difficult to establish this experimentally. It will be



recalled (p. 113) that cobaltic fluoride gives a moment which varies with temperature from 1.60 at 90° K. to 2.46 at 293° K. Other efforts to obtain the moment of trivalent cobalt have been made by Bommer [119] and by Rây and Sen.[120] $Co_2(SO_4)_3 \cdot 18H_2O$ is prepared by electrolytic oxidation but it seems impossible to obtain the salt free from cobaltous cobalt. The Indian workers obtained a moment of 3.2 Bohr magnetons for the anhydrous salt. Bommer claims that the pure hydrated compound would be diamagnetic and is therefore a covalent aquo-complex. Rubidium cobaltic sulfate is diamagnetic. Cobaltic cyanide, $Co(CN)_3$, exists in a blue form with a moment of 2.7, and a red hydrated form with $\mu = 3.0$. It is clear that all these compounds are complexes and that we do not yet have any good experimental data on the simple cobaltic ion.

In spite of the instability of cobaltous complexes a surprisingly large amount of work has been done on them. Some of the results are summarized by Mellor and Goldacre.[121] Several of these complexes exist in two forms, sometimes with large differences in susceptibility. The magnetic measurements show that the tendency is for divalent cobalt to form essentially ionic octahedral and tetrahedral complexes when the groups are attached through nitrogen or oxygen atoms or through both. For instance Table XXX shows a few cobaltous complexes and their magnetic moments.

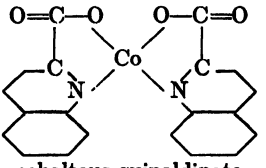
[119] H. Bommer, *Z. anorg. allgem. Chem.*, **246**, 275 (1941).
[120] P. Rây and D. C. Sen, *J. Indian Chem. Soc.*, **12**, 190 (1935).
[121] D. P. Mellor and R. J. Goldacre, *J. Proc. Roy. Soc. N. S. Wales*, **73**, 233 (1940).

TABLE XXX

EFFECTIVE MOMENTS OF SOME COBALTOUS COMPLEXES

Substance	μ_{eff} in Bohr Magnetons
$Co(NH_3)_6Cl_2$	4.96
$[Co(ethylenediamine)_3]Cl_2$	3.82
$Co(C_9H_8N_2)_2Cl_2 \cdot H_2O$	4.79
$Na_2[Co\{C_6H_4(CO_2)_2\}] \cdot H_2O$	5.35
$(NH_4)_2Co(CNS)_4 \cdot 4H_2O$	4.16
$[CoCl_2(NH_3)_2]\alpha$	5.50
$[CoCl_2(NH_3)_2]\beta$	5.41
$Co(N_2H_4)_2Cl_2$	4.93
$Co\{CH(COCH_3)_2\}_2$	4.18–4.34
$Co(pyridyl)_2Cl_2$ violet	5.34
$Co(pyridyl)_2Cl_2$ blue	4.60

Other examples of paramagnetic cobaltous complexes are the quinaldinate,[122] the disalicylaldehyde,[123] the kojate,[124] bis-salicylaldehyde



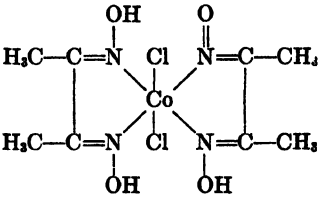
cobaltous quinaldinate

propylenediamine, and bis-(formylcamphor) dihydrate.[125] The blue cobaltous bis-pyridyl compounds[126,127] with a moment of 4.6 undergo a change in a few days with the moment rising to 5.3, owing to conversion to the violet form. Cobaltocyanides are diamagnetic.[128]

Complexes of trivalent cobalt are generally diamagnetic. $K_3[CoF_6]$, which has a moment of 5.3, is an exception, but the substitution of as few as three ammonia molecules as in $[Co(NH_3)_3F_3]$ leads to diamagnetism.[129] A few other representative ammines in which the cobalt has zero moment are $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5 \cdot H_2O]_2(C_2O_4)_3$, $[Co(ethylenediamine)_2Cl_2]Cl$, $[Co(NH_3)_3(NO_2)_2Cl]$.

[122] N. K. Dutt, *J. Indian Chem. Soc.*, **14**, 572 (1937).
[123] G. N. Tyson, Jr. and S. C. Adams, *J. Am. Chem. Soc.*, **62**, 1228 (1940).
[124] J. W. Wiley, G. N. Tyson, Jr., and J. S. Steller, *J. Am. Chem. Soc.*, **64**, 963 (1942).
[125] D. P. Mellor, *J. Proc. Roy. Soc. N. S. Wales*, **75**, 157 (1942).
[126] E. D. P. Barkworth and S. Sugden, *Nature*, **139**, 374 (1937).
[127] D. P. Mellor and C. D. Coryell, *J. Am. Chem. Soc.*, **60**, 1786 (1938).
[128] D. M. Bose, *Z. Physik*, **65**, 677 (1930).
[129] L. Pauling, *op. cit.*,[8] p. 109.

Cobalt salts of glyoximes have been studied by Sen and Rây,[130] and by Cambi.[131] When crystalline cobaltous chloride is added to dimethylglyoxime in acetone solution a green compound is formed. This is diamagnetic; Sen and Rây propose the formula



which contains trivalent cobalt. A red compound of substantially the same composition is obtained from dimethylglyoxime and anhydrous cobaltous chloride. This is paramagnetic with a moment of 3.8 Bohr magnetons, corresponding with the expected moment for the cobaltous ion. The structure is probably $[H_2D = Co = DH_2]Cl_2$, H_2D standing for dimethylglyoxime. Further measurements and interpretations, however, are given by Cambi.

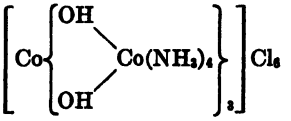
Cobalticyanides are diamagnetic unless associated with a paramagnetic ion in the positive part of the salt. Thus the cobalt has zero moment in $K_3Co(CN)_6$, $K_4[Co(CN)_5S_2O_3]$; but approximately normal moments for the positive ion are found in the cobalticyanides of copper,[132] the rare earth elements,[133] nickel, and of cobalt itself.[134]

$Co(CO)_3NO$ is diamagnetic although some other nitrosyl derivatives have some rather peculiar properties. For instance, hydrated $CoCl_2$ and $Co(NO_3)_2$, in ammoniacal solution, when treated with nitric oxide give respectively black $[Co(NH_3)_5NO]Cl_2O \cdot 5H_2O$, and red $[Co(NH_3)_5NO](NO_3)_2O \cdot 5H_2O$. The first is paramagnetic with $\mu = 1.7$, but the second is diamagnetic.[135] A somewhat higher susceptibility is reported by Frazer and Long[136] for the first compound. Since all other known ammines of trivalent cobalt are diamagnetic it is assumed that the red compound is a true nitroso derivative of trivalent cobalt. The structure of the black compound cannot be given with certainty. Frazer and Long state that the nitroso complex $K_3[CoNO(NO_2)_5]$ is diamagnetic at low fields but paramagnetic at high fields. The reverse

[130] D. C. Sen and P. Rây, *J. Indian Chem. Soc.*, **11**, 899 (1934).
[131] L. Cambi, *Rend. ist. lombardo sci.*, **71**, 85 (1938).
[132] M. A. Rollier and E. Arreghini, *Gazz. chim. ital.*, **69**, 499 (1939).
[133] T. Karantassis, K. Basileiados, and N. Perakis, *Compt. rend.*, **208**, 1720 (1939).
[134] J. Richardson and N. Elliott, *J. Am. Chem. Soc.*, **62**, 3182 (1940).
[135] J. L. Milward, W. Wardlaw, and W. J. R. Way, *J. Chem. Soc.*, **1938**, 233.
[136] J. H. Frazer and N. O. Long, *J. Chem. Phys.*, **6**, 462 (1938).

of this is often found in cases where slight amounts of ferromagnetic impurities are present, but the effect described is a very peculiar one.

Several binuclear complexes of trivalent cobalt have been studied. These compounds, of which

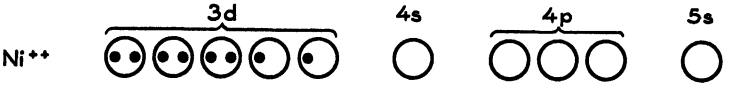


is an example, are all diamagnetic.[137]

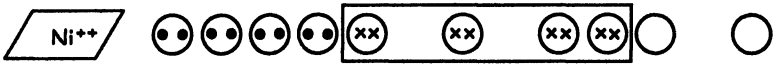
Not very much work has been done on the magnetic anisotropy of cobalt complexes. Strock [138] has investigated the anisotropy of a few ammines. Krishnan and Mookherji [139] report that cobalt is strongly anisotropic in compounds in which the coordination number is six, but only feebly anisotropic when the coordination number is four as in $Cs_2[CoCl_4]$. Possibly this difference may serve as an aid in some structural studies.

6. Nickel

The divalent nickel atom has two unpaired electrons, with a normal



moment of about 3 Bohr magnetons. In a tetrahedral complex involving ionic bonds or only the 4s and 4p orbitals in weak covalent bonds, the moment remains unchanged. But for the formation of four planar dsp^2 covalent bonds, there are only four 3d orbitals available for eight electrons. The square planar nickel complexes are therefore diamagnetic.

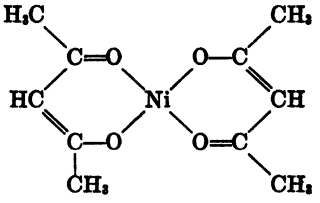


The classification of nickel complexes as tetrahedral or planar is thus readily made on the basis of magnetic measurements.

The tetrahedral ionic type is found in such compounds as $Ni(N_2H_4)_2SO_3$, $Ni(N_2H_4)_2(NO_2)_2$, $Ni(NH_3)_4SO_4$, $[Ni\{C_2H_4(NH_2)_2\}_2](SCN)_2 \cdot H_2O$, and nickel acetylacetonate, all of which have magnetic moments of from about 2.6 to 3.2. Most of the data are from Rosenbohm.[16] Nickel

[137] S. Berkman and H. Zocher, *Z. physik. Chem.*, **124**, 318 (1926).
[138] L. W. Strock, *Z. physik. Chem.*, **B23**, 235 (1933); *Z. Krist.*, **88**, 238 (1934).
[139] K. S. Krishnan and A. Mookherji, *Phys. Rev.*, **51**, 528, 774 (1937).

bis-acetylacetone is a good example of a paramagnetic complex with coordination number four.[140]



nickel bis-acetylacetone

Other examples of this type are nickel bis-nicotinylacetone, nickel bis-salicylaldehyde, potassium nickel oxalate, and ammonium nickel malonate. Hexa-coordinated ammines such as $Ni(NH_3)_6SO_4$ are also paramagnetic.[141] Still other examples will be indicated later.

On the other hand the cyanides $K_2Ni(CN)_4$ and $K_2Ni(CN)_4 \cdot H_2O$ are diamagnetic and hence contain planar $Ni(CN)_4^{=}$ groups, a result which is supported by studies of isomorphism. There are many examples of this type, including the nickel glyoximes, potassium nickel dithiooxalate, nickel diacetyldioxime, nickel ethylxanthogenate, nickel ethyldithiocarbamate, bis-phenylethylenediamine nickel nitrate, potassium nickel succinimide, and bis-xanthic acid nickel. Mellor and Craig list many others, to some of which reference will be made below.

Nickel cyanide heptahydrate, $Ni(CN)_2 \cdot 7H_2O$, has a normal moment for the Ni^{++} ion, but on dehydration the paramagnetism undergoes a curious diminution. $Ni(CN)_2$ containing between two and four molecules of water has a moment of only about one half that for ionic nickel compounds. This suggests that these hydrates contain approximately equal numbers of planar covalent, $Ni(CN)_4^{=}$, complexes and ionic $Ni(OH_2)_4^{++}$ or $Ni(OH_2)_6^{++}$ groups. Still further dehydration yields a substance with an apparent moment of about 0.5 Bohr magnetons or even less.[142,143] Bose concludes that completely dehydrated nickel cyanide would be diamagnetic. It is not yet possible to predict whether a given coordinating group will form a square or a tetrahedral complex with nickel. Some progress has, however, been made in this direction and will be referred to below.

[140] L. Cambi and L. Szegö, *Ber.*, **64**, 2591 (1931).

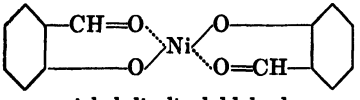
[141] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 475 (1941). This paper contains an extensive summary on nickel complexes.

[142] D. M. Bose, *Nature*, **125**, 708 (1930).

[143] L. Cambi, A. Cagnasso, and E. Tremolada, *Gazz. chim. ital.*, **64**, 758 (1934).

Nickel carbonyl, $Ni(CO)_4$, and related compounds such as $Ni(CO)_2$-*o*-phenanthroline have been shown by Oxley,[144] Klemm [145] and others to be diamagnetic. At first glance this would suggest that $Ni(CO)_4$ should be a square complex. That it is not, does not constitute a contradiction for the magnetic criterion because the neutral nickel atom has two more electrons than the Ni^{++} ion. As a consequence the 3d orbitals are all filled with electron pairs and the compound has four sp^3 covalent bonds.

A few other nickel compounds which have been studied are the dithiocarbamates which are diamagnetic,[140,146] the disalicylaldehyde [147,148]



nickel disalicylaldehyde

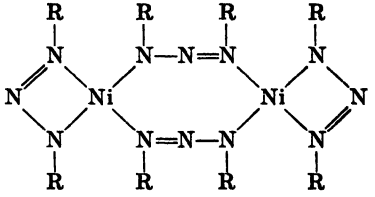
and the kojate,[149] in which the nickel atoms have moments of 3.1 and 3.2, respectively. The structures are probably tetrahedral. Nickel disalicylaldehyde in solution is a light green color. On hydrogenation it turns to a yellow liquid with a brownish cast, but magnetic measurements indicate the same moment for the nickel in each form.

Nickel complexes with *o*-phenanthroline and dipyridyl are diamagnetic,[150] as are the related compounds nickel dimethylmesoporphyrin [151] and nickel protoporphyrin.[152] All these presumably have the dsp^2 covalent square structure. Nickel phthalocyanine also belongs to this group.[93]

Nickel glyoximes have been studied by Cambi and Szegö,[140] and by Sugden.[153,154] Without exception they are diamagnetic and have the planar structure. The triazene complexes of nickel have been investi-

[144] A. E. Oxley, *Proc. Cambridge Phil. Soc.*, **16**, 102 (1911).
[145] W. Klemm, H. Jacobi, and W. Tilk, *Z. anorg. allgem. Chem.*, **201**, 1 (1931).
[146] L. Malatesta and A. A. Mella, *Gazz. chim. ital.*, **67**, 738 (1937).
[147] G. N. Tyson, Jr. and S. C. Adams, *J. Am. Chem. Soc.*, **62**, 1228 (1940).
[148] M. A. Fobes and G. N. Tyson, Jr., *J. Am. Chem. Soc.*, **63**, 3530 (1941).
[149] J. W. Wiley, G. N. Tyson, Jr., and J. S. Steller, *J. Am. Chem. Soc.*, **64**, 963 (1942).
[150] L. Cambi and A. Cagnasso, *Atti. accad. Lincei*, **19**, 458 (1934).
[151] F. Haurowitz and W. Klemm, *Ber.*, **68**, 2312 (1935).
[152] L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci.*, **22**, 159 (1936).
[153] S. Sugden, *J. Chem. Soc.*, **1932**, 246.
[154] H. J. Cavell and S. Sugden, *J. Chem. Soc.*, **1935**, 621.

gated by Dwyer and Mellor.[155] Bis-diazoaminobenzene nickel and bis-4,4-dimethyldiazoaminobenzene nickel are both diamagnetic. Molecular weight determinations indicate dimerization. The structures probably contain square covalent nickel atoms as shown. Dissolving



the compounds in pyridine, however, produces octahedral complexes, the moment for bis-pyridine-bis-4,4-dimethyldiazoaminobenzene nickel being 3.38 Bohr magnetons, suggesting two unpaired electrons.

There have been several efforts to find the factors which determine whether nickel complexes will assume the diamagnetic square or the paramagnetic tetrahedral configuration. Sulfur atoms in the coordinating groups often form diamagnetic complexes, for instance the oxalo complexes are paramagnetic but the thio-oxalo complexes are not. For nitrogen and oxygen atoms in the coordinating group there may be some relationship between the number and arrangement of the double bonds in the group and the tendency to form diamagnetic or paramagnetic complexes.

At one time it was thought that an important relation had been discovered between the color and the configuration of nickel complexes. Phenylated ethylenediamines such as nickel distilbenediamine chloride and nickel diphenylethylenediamine nitrate form two series of complexes, a blue paramagnetic form and a yellow diamagnetic form. These colored salts readily undergo transformation from blue to yellow or the reverse.[156,157] Two types of nickel acyloin oximes[158] have also been prepared, a green paramagnetic form and a red diamagnetic form. But while it is true that many paramagnetic nickel complexes are some shade of green or blue, and the diamagnetic complexes often range from bright red through red-brown to yellow, yet little reliance can be placed in this rule. For instance vermillion bis-1-hydroxyacridine nickel has a moment of 3.2, and green bis-formylcamphorethylenediamine nickel is diamagnetic, at least in the solid.[159]

[155] F. P. Dwyer and D. P. Mellor, *J. Am. Chem. Soc.*, **63**, 81 (1941).

[156] I. Lifschitz, J. G. Bos, and K. M. Dyjkema, *Z. anorg. allgem. Chem.*, **242**, 97 (1939).

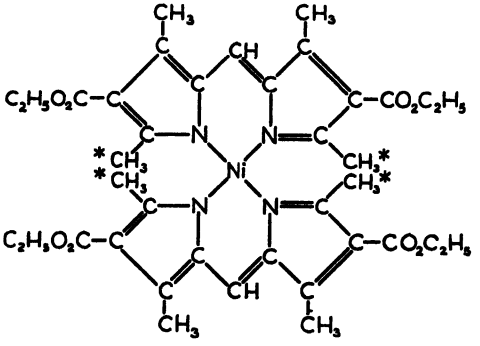
[157] I. Lifschitz and K. M. Dyjkema, *Rec. trav. chim.*, **60**, 581 (1941).

[158] L. Malatesta, *Gazz. chim. ital.*, **68**, 319 (1938).

[159] J. E. Mills and D. P. Mellor, *J. Am. Chem. Soc.*, **64**, 181 (1942).

Another idea is that the electronegativities of the attached groups may determine the configuration of the complex.[160] An exhaustive study of the available data, however, leads Mellor and Craig to the conclusion that while electronegativity may be important, other factors, such as the nature of the functional group in which the atom bonded to nickel occurs, are also significant.

The explanation which seems most promising at present is the effect of bond-angle distortion on the configuration of the complex.[161–165] All nickel complexes in which nickel is bonded to four nitrogen atoms irrespective of whether these nitrogen atoms belong to pyrrole rings, oxime, or triazene groups have proved to be diamagnetic. But if, for some reason, the chelate groups are prevented from assuming a coplanar configuration, it is to be expected that the resulting distortion will be reflected in the magnetic moment of the metal ion. Such is the case in the nickel derivative of 3,3′,5,5′-tetramethyl-4,4′-dicarbethoxydipyrromethene in which the methyl groups indicated (*) mutually prevent



assumption of a coplanar structure. Owing to the large van der Waals radius of the methyl groups no amount of distortion of the C—CH_3 bonds could accommodate chelating pyrromethene groups in square coordinated positions. This compound has been shown by Mellor and Lockwood to be paramagnetic. The nickel has a moment of 3.2 Bohr magnetons corresponding to two unpaired electrons. From this it may be inferred that the nickel-nitrogen bonds have been forced out of their normal square configuration into an essentially ionic tetrahedral structure.

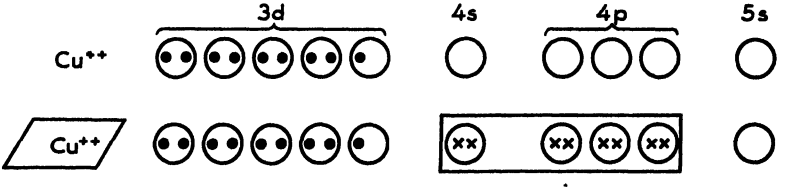
[160] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 479 (1941).
[161] D. P. Mellor and W. H. Lockwood, *Nature*, **145**, 862 (1940).
[162] D. P. Mellor, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 129 (1940).
[163] D. P. Mellor and W. H. Lockwood, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 141 (1940).
[164] D. P. Mellor, *J. Proc. Roy. Soc. N. S. Wales*, **75**, 157 (1942).
[165] H. S. French, M. Z. Magee, and E. Sheffield, *J. Am. Chem. Soc.*, **64**, 1924 (1942).

A curious case which may be due to the same effect is found for bis-formylcamphor ethylenediamine nickel. This compound is stated by French, Magee, and Sheffield to be diamagnetic in the solid (which is confirmed by Mellor), but is paramagnetic with an apparent moment of 1.9 in methyl alcohol solution. It may be that the compound is a square covalent complex in the solid, but tends, owing to bond distortion, toward the ionic tetrahedral in solution. Why this should be so is not clear, but if the rather low apparent moment of 1.9 indicates an equilibrium between planar and tetrahedral forms it would be interesting to have the temperature coefficient of the equilibrium, as well as measurements in other solvents.

Complexes in which nickel has a valence other than two have apparently received little attention. A supposed complex compound of trivalent nickel and benzamide oxime has been shown by Malatesta and Monti [166] to be of doubtful composition.

7. Copper and Related Elements

Copper, with a valence of one, has no unpaired electrons, as a consequence of which all cuprous compounds including the cuprocyanides $K_3Cu(CN)_4$ and $KCu(CN)_2$ are diamagnetic.[167,168] Although cupric copper has one unpaired electron with a moment close to 1.73, yet the magnetic criterion is not of much service in determining the structure of cupric complexes. The reason for this is that covalent copper still has one unpaired electron regardless of the configuration of the bonds.



Thus ammines of the type $[Cu(NH_3)_4](NO_3)_2$ and $[Cu(NH_3)_4(OH_2)_2]SO_4$ were shown by Rosenbohm [169] to have a moment of almost exactly 1.73 Bohr magnetons. The same is true of the cuprichlorides such as $K_2CuCl \cdot 2H_2O$.

In spite of this drawback there have been a number of magnetochemical studies of copper complexes recently. Sometimes it is possible to postulate a structure by analogy with the corresponding nickel com-

[166] L. Malatesta and F. Monti, *Gazz. chim. ital.*, 70, 842 (1940).
[167] W. Biltz, *Z. anorg. allgem. Chem.*, 170, 161 (1928).
[168] D. M. Bose, *Z. Physik*, 65, 677 (1930).
[169] E. Rosenbohm, *Z. physik. Chem.*, 93, 693 (1919).

plex. Tyson and Adams [170] give the moment of cupric disalicylaldehyde as 1.9. When the green cupric disalicylaldehyde is dissolved in pyridine a solution of the same color results. After hydrogenation the solution becomes a deep ruby-red. At one time it was thought that this change might involve reduction of the copper to Cu^+ but Tyson and Vivian [171] show that the magnetic moment after hydrogenation is exactly the same as before. Hydrogenation of the compound may involve a stereochemical change in the coordinated groups. Like the disalicylaldehyde, the cupric disalicylaldehyde-propylenediamine, and the disalicylaldimine have moments corresponding to one unpaired electron and are probably planar. The same is true of bis(formylcamphor) copper dioxanate.[172] Cupric kojate [173] has a moment of 1.9 but here the structure, at least by analogy, is probably tetrahedral.

The binuclear copper derivative of diphenylmethylarsine exists in a blue and a brown form. These have the same moments of 1.78 magnetons for the $Cu_2Cl_3(Ph_2MeAs)_3$ molecule.[174] Copper phthalocyanine has also been shown by Mellor [172] to have a moment of 1.72.

Studies on the dithiocarbamates [175] and on the sulfamates and disulfamates [176] of copper show that here, too, the moment of the copper is normal. The same is probably true of the nitrosyl chloride complex $CuCl \cdot ClNO$.[177]

The common silver Ag^+ ion is, of course, diamagnetic. Mention has already been made of certain paramagnetic complexes of divalent silver (p. 102). The possible divalence of silver and of gold in $Cs_2AgAuCl_6$ and in $Cs_2Au_2Cl_6$ has been examined by Elliott.[178] Both compounds are diamagnetic. Paramagnetism is found, however, in the silver compound produced by action of ozone on strongly acidified silver nitrate solution.[179] The moment found corresponds most closely to that expected for Ag^{++} which should have one unpaired electron. The possibility of Ag^{+++} is

[170] G. N. Tyson, Jr. and S. C. Adams, *J. Am. Chem. Soc.*, **62**, 1228 (1940).

[171] G. N. Tyson, Jr. and R. E. Vivian, *J. Am. Chem. Soc.*, **63**, 1403 (1941).

[172] D. P. Mellor, *J. Proc. Roy. Soc. N. S. Wales*, **75**, 157 (1942).

[173] J. W. Wiley, G. N. Tyson, Jr., and J. S. Steller, *J. Am. Chem. Soc.*, **64**, 963 (1942).

[174] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S. Wales*, **75**, 27 (1941). This paper was not available to the writer. It is not entirely clear from the abstract, but the implication is that only one unpaired electron is present in each molecule.

[175] L. Malatesta and A. A. Mella, *Gazz. chim. ital.*, **67**, 738 (1937).

[176] L. Lecuir, *Ann. chim.*, **15**, 33 (1941).

[177] R. W. Asmussen, *Z. anorg. allgem. Chem.*, **243**, 127 (1939).

[178] N. Elliott, *J. Chem. Phys.*, **2**, 419 (1934).

[179] A. A. Noyes, K. S. Pitzer, and C. L. Dunn, *J. Am. Chem. Soc.*, **57**, 1229 (1935).

not completely excluded because it is not entirely certain whether this ion would be diamagnetic like Pd^{++} or paramagnetic like Ni^{++}. The former seems more probable. Divalent paramagnetic silver in such complexes as $[Ag_xCd_y(C_5H_5N)_4]S_2O_8$ has been studied by Perakis and Capatos.[180]

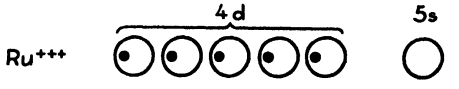
The mercurous ion is diamagnetic because it always forms a double ion, Hg_2^{++} (p. 140). The mercuric ion has no unpaired electrons. The statement that the mercuriiodide ion is paramagnetic [181] seems to be an error, because a group of mercuriiodides in several solvents investigated by Gallais [182] are, without exception, diamagnetic.

In the International Critical Tables, Vol. 6, page 357, the mercury alkyls are listed as having diamagnetic susceptibilities of the order of -40×10^{-6}. This is obviously a mistake and probably is the value for the molar susceptibilities of these compounds.

8. The Palladium and Platinum Groups

It will be recalled (p. 000) that the ions of this group have, with the exception of Ru^{+++}, very small or zero moments. This is even true of substances like palladous nitrate in solution, palladous chloride, and of platinum di- and tetrachlorides. The magnetic method is obviously not of much service in determining the structures of substances such as these.

Ruthenium is an exception. Complexes of trivalent ruthenium such as $[Ru(NH_3)_4Br_2]Br \cdot H_2O$, $[Ru(NH_3)_4C_2O_4]S_2O_6$, and $[Ru(NH_3)_4Cl_2]$-$Cl \cdot 3/4H_2O$ all have moments in the neighborhood of two Bohr magnetons corresponding to one unpaired electron.[183] If the electronic configuration of trivalent ruthenium is as shown, then the bonding in the ammines



must correspond to that in the ferricyanides. The corresponding compounds of iron would be almost completely ionic. We must conclude, therefore, that ruthenium enters into covalent bonding more readily than does iron. This tendency is developed to a remarkable degree in the other elements of the palladium and platinum groups. Nitroso thio salts of ruthenium such as the nitrosoruthenium dialkyldithiocarbamates in which ruthenium has a valence of four are diamagnetic. The ruthe-

[180] N. Perakis and L. Capatos, *J. phys. radium*, 9, 27 (1938).

[181] S. S. Bhatnagar and K. N. Mathur, *Physical Principles and Applications of Magnetochemistry*. MacMillan and Co., Ltd., London 1935, p. 69.

[182] F. Gallais, *Compt. rend.*, 205, 1052 (1937).

[183] K. Gleu and W. Breuel, *Z. anorg. allgem. Chem.*, 237, 326 (1938).

nium, Ru^{+++}, ion itself may have a small, presumably temperature independent, paramagnetism in these compounds.[184]

A series of complex rhodium compounds has been studied by Christiansen and Asmussen.[185] All of these are diamagnetic.

In addition to those palladium compounds already mentioned the following have been investigated by Janes:[186] $PdCl_2 \cdot 2NH_3$, K_2PdCl_4, $K_2Pd(CN)_4$, K_2PdI_4, $K_2Pd(SCN)_2$, $K_2Pd(NO_2)_4$, Pd dimethylglyoxime, $[Pd(NH_3)_2Cl_2]_2$, K_2PdCl_6, $PdCl_4 \cdot 2NH_3$. Without exception they are diamagnetic. The palladium derivative of 3,3′,5,5′-tetramethyl-4,4′-dicarbethoxydipyrromethene is also diamagnetic,[163] a result by no means unexpected.

Osmium and iridium complexes seem to have received little attention, except, of course, in the sense that all compounds of these elements must be considered as covalent rather than ionic substances. Bose and Bhar[187] claim that iridium tetrachloride has a moment corresponding approximately to one unpaired electron, other complexes of both osmium and iridium are all diamagnetic.[188]

Amongst the platinum complexes which have been shown to be diamagnetic are $[Pt(NH_3)_4Cl_2]Cl_2$, $[Pt(NH_3)_3Cl_3]Cl$, $[Pt(NH_3)_2Cl_4]$, K_2PtCl_4, K_2PtCl_6, $Pt(NH_3)_4SO_4$,[189] $PtCl_2 \cdot 2CO$, and $PtCl_2 \cdot CO$.[190]

[184] L. Cambi and L. Malatesta, *Rend. ist. lombardo sci.*, **71**, 118 (1938).

[185] J. A. Christiansen and R. W. Asmussen, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **12**, No. 10 (1934).

[186] R. B. Janes, *J. Am. Chem. Soc.*, **57**, 471 (1935).

[187] D. M. Bose and H. G. Bhar, *Z. Physik*, **48**, 716 (1928).

[188] D. M. Bose, *Z. Physik*, **65**, 677 (1930).

[189] W. Biltz, *Z. anorg. allgem. Chem.*, **170**, 161 (1928).

[190] W. Klemm, H. Jacobi, and W. Tilk, *Z. anorg. allgem. Chem.*, **201**, 1 (1931).

CHAPTER SEVEN

METALLIC DIA- AND PARAMAGNETISM

1. Introduction to Metallic Magnetism

Although the magnetic properties of metals are sometimes of the greatest technological importance, they have not assumed very much significance in the solution of strictly chemical problems. There are indications that this situation is changing and that the structure of alloys, of intermetallic compounds, and of catalytically active metal surfaces will all be studied in connection with their magnetic properties.

Most metals are either diamagnetic or paramagnetic. A very few are ferromagnetic. Ferromagnetic metals and compounds will be treated in the next chapter. There is, however, no very fundamental difference between ferromagnetic substances and paramagnetic. All ferromagnetic substances become paramagnetic if heated above the Curie point. Many paramagnetic substances develop field strength dependence of susceptibility, and other suggestions of incipient ferromagnetism, if cooled to very low temperatures.

Metallic magnetism is discussed by Seitz.[1,2] Paramagnetism is a characteristic of the short series of the periodic table, and of those elements preceding the eighth group triads. Metals following the eighth group elements are diamagnetic. Metallic paramagnetism has been treated in a semi-quantitative manner by Pauli,[3] and more completely by Seitz (*op. cit.*, p. 599). Metallic diamagnetism due to free electrons has been treated by Landau,[4] and Peierls [5] has extended the theory to the case of quasi-bound electrons. A further extension is given by Wilson.[6] An interpretation of the magnetic properties of metals in terms of the interatomic forces is given by Pauling.[7]

[1] F. Seitz, *The Modern Theory of Solids*. McGraw-Hill Book Company, Inc., New York 1940.

[2] See also M. Fallot, *Rev. sci.*, 79, 418 (1941).

[3] W. Pauli, *Z. Physik*, 41, 81 (1927).

[4] L. Landau, *Z. Physik*, 64, 629 (1930).

[5] R. Peierls, *Z. Physik*, 81, 186 (1933).

[6] A. H. Wilson, *Theory of Metals*. Cambridge University Press, London 1936, p. 108.

[7] L. Pauling, *Phys. Rev.*, 54, 899 (1938).

It must be pointed out that the susceptibilities of many metals is so small that the presence of ferromagnetic impurities in extremely small amount may completely conceal the true susceptibilities. It is always advisable, in making magnetic measurements on solids, to work at two or more field strengths. In this way any trace of ferromagnetism, such as might be due to traces of iron, will at once become apparent. It is not accurate to correct for ferromagnetic impurities simply by subtracting from the measured susceptibility that corresponding to the total impurity content as determined by chemical analysis. Iron, for instance, may be present either as a ferromagnetic or as a paramagnetic constituent. The method of Honda [8] and of Owen [9] consists of measuring the susceptibility at fields larger than those required to give ferromagnetic saturation. If $\chi = \chi_\infty + i/H$ where i is the saturation intensity of the ferromagnetic impurity, and χ is the measured susceptibility, then χ_∞ will be the susceptibility of the impurity-free specimen. Furthermore, the susceptibility often seems to depend on the previous mechanical history of the specimen, although this may be due to impurities and to their precipitation on cold-working. Some authors have reported a dependence of metallic susceptibilities on particle size. This question has been reviewed by Bhatnagar, Verma, and Anwar-ul-Haq [10] who find that in general the magnetic susceptibility of metals is independent of particle size. Of course, oxidation, contamination, or change of microcrystalline structure may affect the susceptibility and these may sometimes be rather difficult to avoid when fine powders are dealt with. This question will be mentioned again in connection with specific metals.

The susceptibilities of metals differ widely in their temperature dependence. For some, such as the alkali metals, the susceptibility is almost independent of temperature. For many others the susceptibility increases with decreasing temperature, but often in a somewhat irregular way.[11] Some diamagnetic elements such as bismuth show a marked positive thermal coefficient of susceptibility. Changes of susceptibility during melting and during allotropic change are discussed by Shimizu.[12]

Susceptibility measurements of alloys are beginning to be used for the solution of structural problems, some of which will be discussed in Chap. IX, in connection with catalytic activity and magnetism. Other cases will be referred to under one of the principal constituents in this chapter. For

[8] K. Honda, *Ann. Physik*, **32**, 1027 (1910).

[9] M. Owen, *Ann. Physik*, **37**, 657 (1912).

[10] S. S. Bhatnagar, M. R. Verma, and M. Anwar-ul-Haq, *Kolloid-Z.*, **78**, 9 (1937).

[11] W. J. de Haas and P. M. van Alphen, *Proc. Acad. Sci. Amsterdam*, **36**, 263 (1933).

[12] Y. Shimizu, *Science Repts. Tôhoku Imp. Univ., First Ser.*, **25**, 921 (1937).

true solid solutions of metals miscible in all proportions the susceptibility generally varies uniformly with concentration, although the variation is seldom linear. For other types of alloys markedly irregular susceptibility-composition curves are the rule. Some general references to this field are given below.[13–15]

In the following sections the metals are discussed in Periodic Table order. The literature up to 1934 is reviewed by Stoner.[16]

2. Alkali Metals

The alkali metals are all paramagnetic, though at one time it was thought that cesium might be diamagnetic. Lithium is reported by Rao and Sriraman [17] to have a susceptibility of 2.6×10^{-6}. This is considerably different from the value 0.5×10^{-6} considered most probable by Owen. Starr and Kaufmann [18] have recently reported a still higher value of 3.73×10^{-6} at 20° C. They find that between 300° K. and 13.9° K. the susceptibility per cubic centimeter is given by $\kappa \times 10^6 = 1.90 + 7.8/T$. There is some doubt as to whether or not the major part of the temperature dependent term may be caused by dissolved iron as an impurity.

TABLE XXXI

ATOMIC SUSCEPTIBILITIES OF THE ALKALI METALS AT ROOM TEMPERATURE
($\chi_A \times 10^6$)

	− 183° C.	− 78°	20°	100°
Li	25.9	25.4	25.2	—
Na	15.2	15.4	15.6	16.4
K	20.0	20.3	21.5	20.4
Rb	21.5	21.5	19.2	18.2
Cs	34.5	—	29.9	26.5

Values for the other alkali metals are reviewed by Klemm and Hauschulz,[19] and by Böhm and Klemm.[20] The best data are given in Table XXXI.

[13] H. Jones, *Helv. Phys. Acta*, 7, Suppl. II, 84 (1934).

[14] E. Vogt, *Z. Metallkunde*, 27, 40 (1935).

[15] W. L. Bragg, C. Sykes, and A. J. Bradley, *Proc. Phys. Soc. London*, 49, 96 (1937).

[16] E. C. Stoner, *Magnetism and Matter*. Methuen and Co., Ltd., London 1934, p. 498, *et seq.*

[17] S. R. Rao and S. Sriraman, *Proc. Indian Acad. Sci.*, 5A, 343 (1937).

[18] C. Starr and A. R. Kaufmann, *Phys. Rev.*, 59, 476 (1941).

[19] W. Klemm and B. Hauschulz, *Z. Elektrochem.*, 45, 346 (1939).

[20] B. Böhm and W. Klemm, *Z. anorg. allgem. Chem.*, 243, 69 (1939).

Various efforts have been made to calculate the susceptibilities of metals from theoretical considerations. Some of these have been fairly successful. For instance, Sampson and Seitz [21] calculate the atomic susceptibilities of lithium and of sodium to be 23×10^{-6} and 16×10^{-6} respectively. It will be noticed that the susceptibilities, with a possible exception for potassium, are dependent on temperature. But for sodium the temperature coefficient is positive, while for rubidium and cesium it is negative.

The magnetic properties of alkali metal amalgams have been studied by Franke and Katz,[22] Aravamuthachari,[23] Rao and Aravamuthachari,[24] and by Klemm and Hauschulz.[19] In most cases the maxima and minima and changes in direction of susceptibility plotted against concentration correspond to compounds. These compounds are also indicated by thermoanalysis, although there are a few cases in which the two methods disagree. As an example of the work done by Klemm and Hauschulz it may be mentioned that magnetic measurements clearly indicate the existence of KHg_9, K_2Hg_9, KHg_8, KHg_2, and KHg as compounds in potassium amalgam.

A related field is the behavior of alkali metals toward one another. Magnetic measurements on mixed alkali metal systems by Böhm and Klemm [20] show that formation of intermetallic compounds or mixed crystals decreases the susceptibility. The system Na-K shows a susceptibility linear with concentration at 20° and at − 78° C. But at − 183° C. there is a slight minimum at the atomic ration Na_2K. Other systems such as Na-Cs, and K-Cs show fairly large negative deviations from linearity. (Fig. 44.) Certain regularities in the data may be correlated with atomic sizes.

Another study of considerable interest is that of alkali metals dissolved in liquid ammonia.[25–27] The problem has been reviewed by Sugarman and Freed.[28] The solubility of alkali and alkaline earth metals in liquid ammonia permits observation of a continuous change in electron density. When these solutions are concentrated they are metallic in appearance and conductance. But when they are diluted they become blue and

[21] J. B. Sampson and F. Seitz, *Phys. Rev.*, 58, 633 (1940).
[22] W. Franke and H. Katz, *Z. anorg. allgem. Chem.*, 231, 63 (1937).
[23] S. Aravamuthachari, *Current Sci.*, 7, 179 (1938).
[24] S. R. Rao and S. Aravamuthachari, *Proc. Indian Acad. Sci.*, 9A, 181 (1939).
[25] E. Huster and E. Vogt, *Physik. Z.*, 38, 1004 (1937).
[26] E. Huster, *Ann. Physik*, 33, 477 (1938).
[27] S. Freed and H. G. Thode, *J. Chem. Phys.*, 7, 85 (1939).
[28] N. Sugarman and S. Freed, Abstracts of the Atlantic City Meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, p. 23 (1941).

develop electrolytic conductance. The molal susceptibility of potassium in liquid ammonia is small for high concentrations, approaching the value for the metal as the concentration increases. But for dilute solutions the susceptibility approaches that classically predicted for a material gas. In the latter case the electron is no longer free, as it is in more concen-

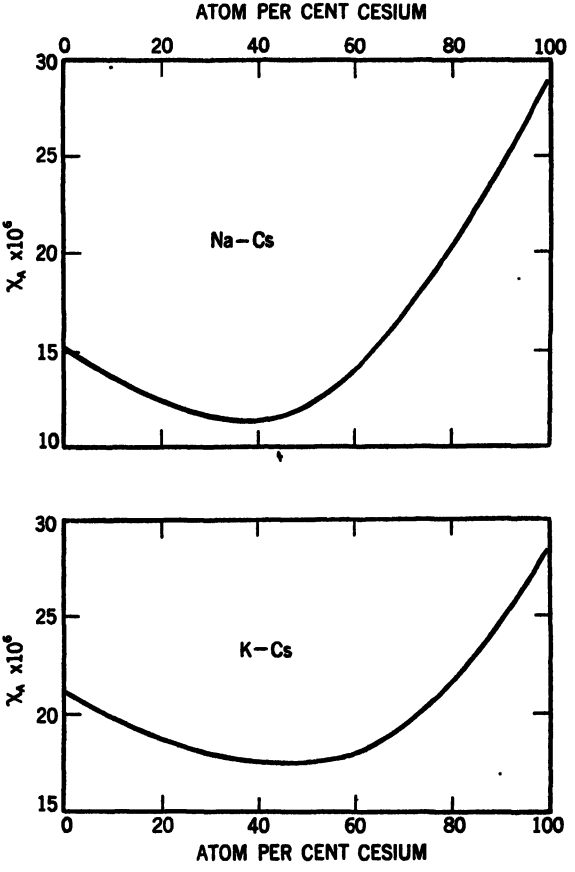


FIG. 44.—Deviations from additivity in the susceptibilities of sodium-cesium and of potassium-cesium alloys.

trated solutions, but is bound to a heavy center, such as a molecule of ammonia.

3. Copper, Silver, and Gold

The atomic susceptibilities of these elements are given in Table XXXII. As pointed out by Stoner, an interesting feature of these results

TABLE XXXII

ATOMIC SUSCEPTIBILITIES OF THE COINAGE METALS AT ROOM TEMPERATURE

Metal	$\chi_A \times 10^6$
Cu	− 54
Ag	− 21
Au	− 29

is that, although the metals are diamagnetic, they are less so than the corresponding ions, indicating that there is a definite paramagnetic contribution from the free electrons in the metals.

Colloidal copper is stated by Rao [29] to have a somewhat larger diamagnetism than massive copper, but the whole question of the influence of particle size on magnetic properties must be regarded as unsettled.

Copper amalgams have been studied by Bhatnagar, Kapur, and Mittal.[30] The susceptibilities are approximately linear with concentration when first prepared, but they decrease with aging and hardening of the amalgam. This is possibly due to compound formation. Silver amalgams have been studied by Bates and Ireland.[31]

Alloys of the coinage metals with one another and with other nonferromagnetic metals generally have susceptibilities which are linear with concentration or nearly so. Whenever mixed crystals are formed this is almost exactly true. Solid solutions show, as a rule, regular deviations from linearity, and intermetallic compounds are often indicated by rather striking maxima or minima or change of direction of the susceptibility-concentration curve. Alloys with ferromagnetic metals such as iron or nickel may show continuous increase of ferromagnetism with increasing concentration of the ferromagnetic constituent. This is true of iron-copper alloys. In fact it is sometimes difficult to obtain copper which has no field strength dependence of susceptibility. On the other hand nickel-copper alloys are paramagnetic or even diamagnetic for low concentrations of nickel but become ferromagnetic as the nickel concentration is increased. Certain alloys containing copper are ferromagnetic even though they contain no metal which is ferromagnetic in the pure state. These will be discussed in the following chapter.

[29] S. R. Rao, *Proc. Indian Acad. Sci.*, 2A, 249 (1935).

[30] S. S. Bhatnagar, P. L. Kapur, and G. L. Mittal, *Current Sci.*, 7, 279 (1938); *Proc. Indian Acad. Sci.*, 10A, 45 (1939).

[31] L. F. Bates and A. W. Ireland, *Proc. Phys. Soc. London*, 49, 642 (1937).

References are given below to some of the many alloys studied by the magnetic method.[32–55]

4. Alkaline Earth Metals

The best available data on these elements are summarized in Table XXXIII. Considerable doubt may be justified for these values. The difficulties of preparation of magnetically pure specimens is great, and the accuracy of corrections for diamagnetic impurities may not be high.

TABLE XXXIII

ATOMIC SUSCEPTIBILITIES OF BERYLLIUM AND THE ALKALINE EARTH ELEMENTS AT ROOM TEMPERATURE

Metal	$\chi_A \times 10^6$
Be	− 9
Mg	+ 6
Ca	+ 44
Sr	+ 92
Ba	+ 20
Ra	—

[32] R. Gans and A. Fonseca, *Ann. Physik*, 61, 742 (1920). (Ni-Cu)
[33] C. H. Johansson and J. O. Linde, *Ann. Physik*, 5, 762 (1930). (Au-Pt)
[34] J. W. Shih, *Phys. Rev.*, 38, 2051 (1931). (Fe-Au)
[35] E. H. Williams, *Phys. Rev.*, 38, 828 (1931). (Ni-Cu)
[36] K. E. Grew, *Proc. Leeds Phil. Lit. Soc. Sci. Sect.*, 2, 217 (1931). (Ni-Cu)
[37] Y. Shimizu, *Science Repts. Tôhoku Imp. Univ., First Ser.*, 21, 826 (1932).
[38] E. Vogt, *Ann. Physik*, 14, 1 (1932).
[39] B. Svensson, *Ann. Physik*, 14, 699 (1932). (Cu-Pd, Ag-Pd)
[40] H. J. Seemann, *Z. Metallkunde*, 24, 299 (1932). (Cu-Au, Cu-Pd, Cu-Pt)
[41] E. Vogt, *Ann. Physik*, 18, 771 (1933).
[42] C. G. Montgomery and W. H. Ross, *Phys. Rev.*, 43, 358 (1933). (Pb-Ag)
[43] E. Vogt and H. Krueger, *Ann. Physik*, 18, 755 (1933). (Comprehensive)
[44] H. Auer, E. Riedl, and H. J. Seemann, *Z. Physik*, 92, 291 (1934). (Au-Ag)
[45] K. E. Grew, *Proc. Roy. Soc. London*, A145, 509 (1934). (Ni-Cu)
[46] C. S. Smith, *Physics*, 6, 47 (1935). (γ-brass structures, Cu-Zn, Cu-Cd, Ag-Zn, Ag-Cd)
[47] H. Auer, *Z. Metallkunde*, 28, 164 (1936). (Cu-Al)
[48] C. T. Lane, *Applied Phys.*, 8, 693 (1937). (γ-brasses)
[49] E. Hildebrand, *Ann. Physik*, 30, 593, (1937). (Au-Co, Cu-Co, Pt-Rh)
[50] D. Shoenberg, *Nature*, 142, 874 (1938). (Au-Bi)
[51] W. Broniewski, S. Franczak, and R. Witkowski, *Ann. phys.*, 10, 5 (1938). (Au-Cu, Au-Ag, Ag-Cu, and Cu-Ni)
[52] G. Rienäcker and H. Gaubatz, *Naturwissenschaften*, 28, 534 (1940). (Cu-Pt)
[53] A. R. Kaufmann and C. Starr, *Phys. Rev.*, 59, 690 (1941). (Cu-Ni)
[54] N. Sibata, *J. Inst. Metals Japan*, 5, 46 (1941). (Cu-Sb-Ni)
[55] A. Knappworst and H. Nowotny, *Z. Metallkunde*, 33, 153 (1941). (Al-Cr-Cu)

About all that may be said for the results is that they represent some advance over Honda's extensive compilation in the International Critical Tables.

Strontium has been studied by Rao and Savithri.[56] A specimen of 99.8% purity gave an average susceptibility at room temperature of $+ 1.05 \times 10^{-6}$. Over the temperature range 0° to 65° C. the susceptibility increases from 1.02 to 1.09×10^{-6}, and then decreases slowly to $+ 0.73 \times 10^{-6}$ at 260° C.

Barium has been shown by Lane[57] to have a susceptibility rather markedly dependent on temperature. At 20° C. $\chi = 0.147 \times 10^{-6}$, and at 400° it has risen to 0.415×10^{-6}. There is a slight discontinuity at 350°, which parallels an anomaly in the electrical conductivity of barium at that temperature.

Alkaline earth metal amalgams have not received very much attention. The liquid ammonia solutions of these metals have, however, been examined by Freed and his co-workers.

5. Zinc, Cadmium, and Mercury

The best values for the atomic susceptibilities of these metals are given in Table XXXIV.

TABLE XXXIV

ATOMIC SUSCEPTIBILITIES OF ZINC, CADMIUM, AND MERCURY AT ROOM TEMPERATURE

Metal	$\chi_A \times 10^6$
Zn	− 10
Cd	− 19.6
Hg	− 33.8

The only recent work on zinc appears to be that of McLennan, Ruedy, and Cohen,[58] and of Rao.[59] The first group measured the magnetic anisotropy of single crystals of zinc and of cadmium. Rao found a slight decrease of diamagnetism in cold-working single crystals of zinc. Single crystals of cadmium have also been studied by Rao and Sriraman.[59] The experimentally determined susceptibility for the polycrystalline state is $- 0.1746 \times 10^{-6}$. Traces of lead alter the susceptibility normal to the

[56] S. R. Rao and K. Savithri, *Proc. Indian Acad. Sci.*, **14A**, 584 (1941).

[57] C. T. Lane, *Phys. Rev.*, **44**, 43 (1933).

[58] J. C. McLennan, R. Ruedy, and E. Cohen, *Proc. Roy. Soc. London*, **A121**, 9 (1928).

[59] S. R. Rao and S. Sriraman, *Proc. Roy. Soc. London*, **A166**, 325 (1938); *Proc. 25th Indian Sci. Congr.*, Part 3, 2 (1938); S. R. Rao, *Proc. Indian Acad. Sci.*, **4A**, 186 (1936).

C-axis but do not affect the susceptibility parallel to this axis. Cadmium amalgams have been studied by Ramiah.[60]

Mercury has been the object of some very careful studies. Bates and Baker [61] report that mercury purified by the Hulett process (distillation under reduced pressure in a current of air) gives an irregular temperature coefficient of susceptibility. But after the mercury has been boiled for two hours under reduced pressure the susceptibilities lie on a smooth curve. At 18.5° C. $\chi = -0.1681 \times 10^{-6}$, and at 287.5° C. $\chi = -0.1637 \times 10^{-6}$. Rao and Aravamuthachari [24] report a susceptibility for mercury of -0.1660×10^{-6} at room temperature. Single crystals of mercury have been studied by Vogt.[62]

6. Group III Metals

Atomic susceptibilities of these elements are given in Table XXXV. For reasons to be discussed below some of these data must be used with caution.

TABLE XXXV

ATOMIC SUSCEPTIBILITIES OF GROUP III ELEMENTS AT ROOM TEMPERATURE

Element	$\chi_A \times 10^6$	Element	$\chi_A \times 10^6$	Element	$\chi_A \times 10^6$
Boron	− 6.7	Europium	30,400	Actinium	—
Aluminum	16.7	Gadolinium	75,500	Gallium	− 16.8
Scandium	315	Terbium	115,000	Indium	− 12.6
Yttrium	191	Dysprosium	102,000	Thallium(α)	− 49
Lanthanum	140	Holmium	68,200		
Cerium	2300	Erbium	44,500		
Praseodymium	3520–5150	Thulium	25,600		
Neodymium	5600	Ytterbium	250		
Samarium	1820	Lutecium	—		

The magnetic properties of boron have been studied by Li Klemm [63] who reports a susceptibility of -0.62×10^{-6} at 20° C. and -0.63×10^{-6} at − 183° C. Values for the susceptibility of aluminum are not in very good agreement. Weiss and Klemm [64] who studied the effect of small amounts of iron and of silicon on the magnetic properties of aluminum give $\chi = +0.61 \times 10^{-6}$. Auer gives $\chi = 0.645 \times 10^{-6}$. He studied

[60] H. S. V. Ramiah, *J. Mysore Univ.*, 1, 155 (1941).
[61] L. F. Bates and C. J. W. Baker, *Proc. Phys. Soc. London*, 50, 409 (1938).
[62] E. Vogt, *Ann. Physik*, 21, 791 (1935).
[63] L. Klemm, *Z. Elektrochem.*, 45, 354 (1939).
[64] P. Weiss and W. Klemm, *Z. anorg. allgem. Chem.*, 245, 288 (1940).
[65] H. Auer, *Z. Physik*, 92, 283 (1934).

mixed crystals of aluminum with small amounts of manganese, indium, germanium, gallium, copper, silver, zinc, lithium, and magnesium. The susceptibility varies linearly with concentration but the results are not strictly additive.

Scandium, yttrium, and lanthanum have been studied by Bommer.[66] The susceptibilities are all dependent on temperature, that of scandium being considerably more so than the others. At 19° C. χ for scandium is 7.0×10^{-6}, at $-183°$ C. $\chi = 8.2 \times 10^{-6}$. Lanthanum has also been studied by Trombe.[67] His results are not in very good agreement with those of Bommer.

The susceptibilities of the remaining rare earth metals are of exceptional interest because they show extremely high paramagnetism. The effective moments of the metals are substantially equal to the moments of the corresponding ions. This must be because the 4f electrons, which are responsible for most of the paramagnetism are shielded from external influence to almost as great an extent in the metal as in compounds. This is a situation quite different, of course, from the transition group elements.

Metallic cerium has been studied by Vereshchagin, Shubnikov, and Lazarev;[68] by Yanus;[69] Trombe;[70] and by Starr and Kauffman.[71] As with other metals of this group, some difficulty is experienced in making proper corrections for iron impurity. At low temperatures cerium shows unusual magnetothermal properties, including some hysteresis, but this may be due to impurities.

Praseodymium and neodymium have been studied by Klemm and Bommer,[72] the latter also by Trombe.[70] These elements both follow the Curie law fairly closely.

The most interesting metal of this group is gadolinium which was discovered by Urbain, Weiss, and Trombe [73,74] to be ferromagnetic at room temperature. It is well known that for substances which obey the Weiss law $\chi = C/(T + \Delta)$, incipient ferromagnetism often appears when $T + \Delta$ becomes very small or negative. The molecular field constant Δ, when expressed in degrees with reversed sign is then approximately equal

[66] H. Bommer, *Z. Elektrochem.*, 45, 357 (1939).

[67] F. Trombe, *Compt. rend.*, 198, 1591 (1934).

[68] L. F. Vereshchagin, L. V. Shubnikov, and B. G. Lazarev, *Physik. Z. Sowjetunion, Arb. Gebiete Tiefer Temp. Special No.*, 107 (June, 1936).

[69] R. I. Yanus, *Physik. Z. Sowjetunion*, 12, 729 (1937).

[70] F. Trombe, *Ann. phys.*, 7, 385 (1937).

[71] C. Starr and A. R. Kaufmann, *Phys. Rev.*, 58, 657 (1940).

[72] W. Klemm and H. Bommer, *Z. anorg. allgem. Chem.*, 231, 138 (1937); 241, 264 (1939).

[73] G. Urbain, P. Weiss, and F. Trombe, *Compt. rend.*, 200, 2132 (1935).

[74] F. Trombe. *Compt. rend.*, 201, 652 (1935).

to the Curie temperature. Néel [75] has listed the Curie points of several rare earth metals of the yttrium series as shown in Table XXXVI. It

TABLE XXXVI

CURIE POINTS OF THE YTTRIUM EARTH METALS

Metal	Curie Point
Gadolinium	302° K.
Terbium	205
Dysprosium	150
Holmium	86 (calc.)
Erbium	40
Thulium	10

is clear that gadolinium will become ferromagnetic in the neighborhood of room temperature. The Curie point is not especially sharp and is given by Trombe as 16 ± 2° C. Gadolinium shows all the characteristic properties of a ferromagnetic metal. The intensity of magnetization at saturation is actually higher than that of iron. Above the Curie point the metal is paramagnetic with a fairly normal susceptibility-temperature curve. The effective moment is almost exactly the same as that for the Gd^{+++} ion.

Holmium seems to be the only other rare earth metal which has been studied very thoroughly from a magnetic standpoint. Bommer [76] finds that below 195° C. the susceptibility is somewhat dependent on field strength. At higher temperatures $\chi = C/(T - 87°)$.

The magnetic properties of gallium and indium have not received much study since the work of Honda and Owen, but considerable attention has been given to thallium. Polycrystalline thallium has been studied by Nevgi.[77] The magnetic anisotropy of single crystals is given by Rao and Narayanaswamy,[78] and by Rao and Subramaniam.[79] Thallium exists in two crystalline forms, a hexagonal (α), stable at normal temperatures, and a face-centered cubic (β), stable above 235° C. The crystals show a very high anisotropy up to 235° C., the transition temperature. The polycrystalline α form has $\chi = -0.25 \times 10^{-6}$, the β form -0.19×10^{-6}, and the liquid -0.17×10^{-6}. The drop in diamagnetism which occurs on the melting of thallium amounts to nearly

[75] L. Néel, *Z. Elektrochem.*, **45**, 378 (1939).

[76] H. Bommer, *Z. anorg. allgem. Chem.*, **242**, 277 (1939).

[77] M. B. Nevgi, *J. Univ. Bombay*, **7**, Part 3, 19 (1938).

[78] S. R. Rao and A. S. Narayanaswamy, *Current Sci.*, **6**, 276 (1937).

[79] S. R. Rao and K. C. Subramaniam, *Nature*, **136**, 336 (1935); *Phil. Mag.*, **21**, 609 (1936).

10 per cent. This, however, is not unusual, especially among elements in the lower center of the periodic table.

Alloys of thallium with bismuth and with cadmium have been studied by David and Spencer.[80] The Bi-Tl susceptibility-concentration curve (Fig. 45) is a good example of the use of magnetic measurements in the

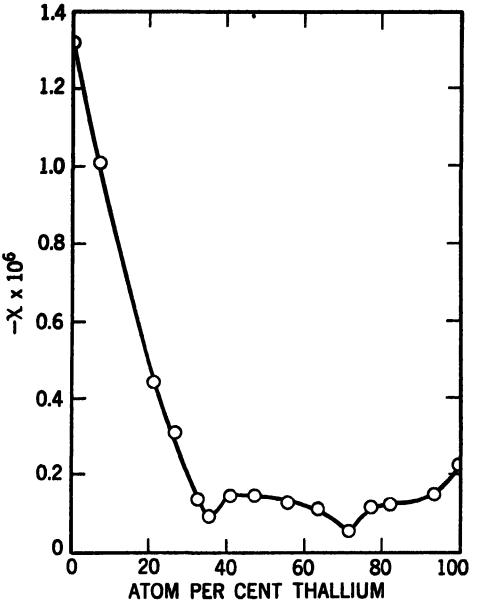


FIG. 45.—Thallium-bismuth alloy.

study of intermetallic compounds. The results clearly indicate compounds at 36 and at 71 per cent Tl, which correspond respectively to the compounds Bi_5Tl_3 and Bi_2Tl_3. The existence of such compounds is supported by thermal and other data. There is no sign of compound formation in the corresponding Cd-Tl curve.

7. Graphite and Group IV Metals

Graphite is included in this section because it shows metallic conductivity and because the magnetic properties are, to a remarkable degree, similar to those found in some metals. The atomic susceptibilities for these elements are listed in Table XXXVII.

Attention has already been drawn to the fact that graphite has a large diamagnetic anisotropy.[81, 82] This substance shows an outstanding ex-

[80] A. W. David and J. F. Spencer, *Trans. Faraday Soc.*, **32**, 1512 (1936).

[81] K. S. Krishnan, *Nature*, **133**, 174 (1934).

[82] B. C. Guha and B. P. Roy, *Indian J. Phys.*, **8**, 345 (1934).

TABLE XXXVII

ATOMIC SUSCEPTIBILITIES OF GROUP IV METALS AT ROOM TEMPERATURE

Element	$\chi_A \times 10^6$	Element	$\chi_A \times 10^6$
Graphite (polycryst.)	42	Germanium	− 8.9
Titanium	150	Tin (white)	4.4
Zirconium	120	Lead	− 24
Hafnium	—		
Thorium	130		

ample of free-electron diamagnetism which is restricted to one plane only. Ganguli and Krishnan [83] have determined the anisotropy over a wide temperature range for some exceptionally good crystals of Ceylon graphite. Perpendicular to the hexagonal axis χ = about -0.5×10^{-6} or nearly the same as for diamond. But along the hexagonal axis $\chi = -21.5 \times 10^{-6}$ at room temperature. Variation of the anisotropy with temperature [84] is shown in Fig. 46 where $\chi_{\parallel} - \chi_{\perp} = \chi_e$, that is, the difference in dia-

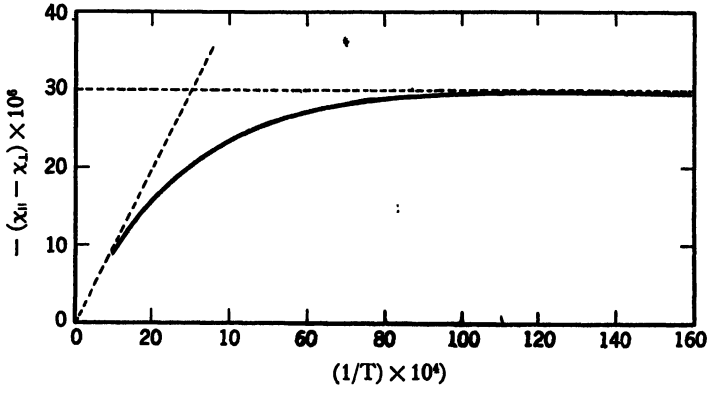


FIG. 46.—Diamagnetic anisotropy, $\chi_{\parallel} - \chi_{\perp}$, plotted against temperature for a single crystal of graphite.

magnetism along the hexagonal axis and perpendicular to it, is plotted against temperature. It will be seen that at very high temperatures (1270° K.) χ_e tends asymptotically to reach $-0.010/T$, while at low temperatures (90° K.) it approaches a temperature-independent value of -30×10^{-6}.

[83] N. Ganguli and K. S. Krishnan, *Proc. Roy. Soc. London*, **A177**, 168 (1941).

[84] K. S. Krishnan and N. Ganguli, *Nature*, **139**, 155 (1937), *Z. Krist.*, **A100**, 530 (1939).

It may be shown that this very large diamagnetism along the hexagonal axis is due to one free electron per carbon atom, and that this electron is completely free in the basal plane but highly restricted in the perpendicular direction. Each layer of carbon atoms may be thought of as a giant aromatic molecule. This, incidentally, constitutes proof that the bonds in aromatic molecules are not localized, that is, it establishes the basic concept of the resonance theory as applied to such substances.

In order to explain the non-appearance of free-electron paramagnetism in graphite it is suggested by Ganguli and Krishnan that all occupied energy levels in graphite must contain pairs of electrons, and that no such levels contain single electrons. It follows that the energy of spin coupling must be large compared to kT even at 1270° K.

The abnormal diamagnetic anisotropy of graphite is largely destroyed by partial oxidation in nitric plus sulfuric acids to form "blue graphite." [85]

Titanium and zirconium have been studied by Li Klemm and by Squire and Kaufmann.[86] The susceptibilities of these elements are peculiar. With increasing temperature, as shown in Fig. 47, the susceptibilities increase until an anomalous region is reached in the neighborhood of 1200° K. for titanium and of 1000° K. for zirconium. These anomalies are not associated with hysteresis, and are entirely reproducible. They are doubtless associated with a change of crystal structure. For zirconium the change is especially striking because the susceptibility increases almost vertically as the temperature approaches 1100° K., and then suddenly becomes almost independent of temperature. These changes parallel changes in the electrical conductivity, specific heat, and thermal conductivity at the corresponding temperature. The sample of zirconium investigated by Squire and Kaufmann showed increasing susceptibility below 50° K. but this may have been due to ferromagnetic impurities. The same workers [87] have also examined the effect of dissolved hydrogen on the susceptibilities of titanium and zirconium. The presence of dissolved hydrogen reduces by about 40 per cent the susceptibility of zirconium at 295° K. when the hydrogen is present in the proportion 2 H atoms for 1 Zr. Hydrogen also alters the high-temperature anomaly in zirconium and lowers the temperature of maximum susceptibility to about 900° K. A rather interesting observation is that a trace of dissolved iron may precipitate and regain its ferromagnetism in the presence of dissolved oxygen.

[85] K. S. Krishnan and N. Ganguli, *Current Sci.*, 3, 472 (1935).

[86] C. F. Squire and A. R. Kaufmann, *J. Chem. Phys.*, 9, 673 (1941).

[87] J. Fitzwilliam, A. R. Kaufmann, and C. F. Squire, *J. Chem. Phys.*, 9, 678 (1941).

The diamagnetism of germanium has been reported by Stöhr and Klemm [88] to depend somewhat on temperature, χ being -8.9×10^{-6} at room temperature and -10.6×10^{-6} at $-183°$ C. At slightly lower temperature, 75° K., germanium goes through a transition during which

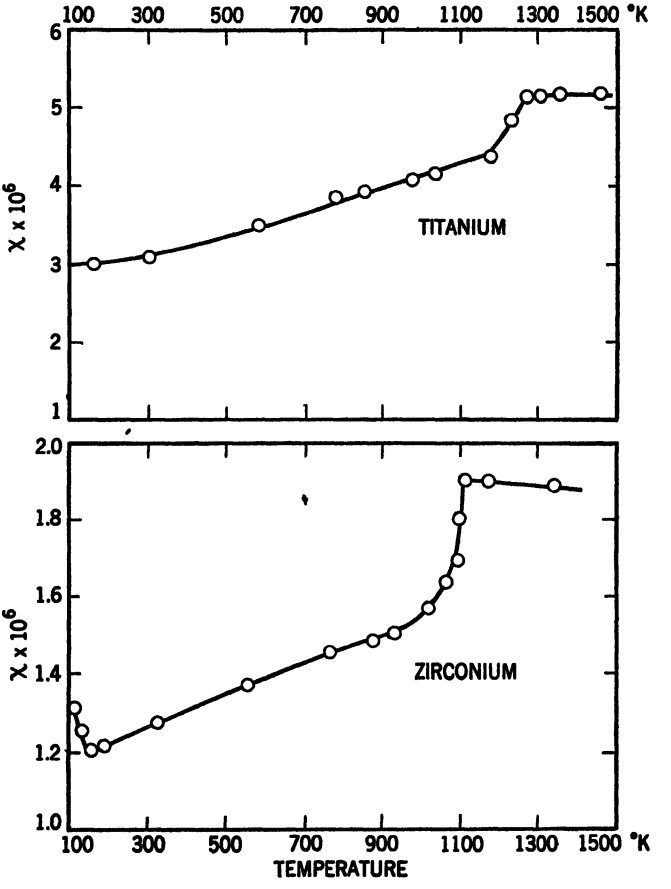


FIG. 47.—Susceptibilities of titanium and zirconium at various temperatures.

the diamagnetism increases about one hundred fold.[89] Stöhr and Klemm also used magnetic measurements to study alloys of germanium with arsenic, antimony, and bismuth. Germanium alloys have been studied by others as indicated below.[90, 91]

[88] H. Stöhr and W. Klemm, *Z. anorg. allgem. Chem.*, **244**, 205 (1940).

[89] C. F. Squire, *Phys. Rev.*, **58**, 202 (1940).

[90] H. Stöhr and W. Klemm, *Z. anorg. allgem. Chem.*, **241**, 305 (1939). (Ge-Al, Ge-Sn)

[91] K. Ruttewit and G. Masing, *Z. Metallkunde*, **32**, 52 (1940). (Ge-Sb, Ge-Bi)

Tin has some interesting magnetic properties. Rao and Subramaniam confirm earlier observations that the white variety is paramagnetic with χ = about 0.038×10^{-6} at 30° C., but at the melting point, 233° C., there is a sharp change to diamagnetism, with $\chi = -0.043 \times 10^{-6}$. The change is reversible. A small change occurs on the transition from white tin to gray.[92] Honda and Shimizu [93] interpret these changes as being due to (*1*) a diminution of free electrons due to the expansion, and (*2*) an increase in the number of bound electrons. The influence of particle size on the susceptibility of tin has been studied by Rao [94] who finds that as the particle size decreases the metal becomes diamagnetic. His results would appear to be valid because on melting and recrystallizing the tin from the colloidal powders, the paramagnetism was restored.

Single crystals of tin alone and with added antimony, cadmium, and gallium have been studied by Hoge.[95]

8. Group V Metals

Except for antimony and bismuth these metals have not recently received much attention, and for their atomic susceptibilities we must rely chiefly on the early values given in the International Critical Tables.

TABLE XXXVIII

ATOMIC SUSCEPTIBILITIES OF GROUP V ELEMENTS AT ROOM TEMPERATURE

Element	$\chi_A \times 10^6$	Element	$\chi_A \times 10^6$
Vanadium	230	Arsenic	− 5.5
Columbium	121?	Antimony	− 107
Tantalum	145?	Bismuth	− 285
Protoactinium	—		

Vanadium has been studied by Li Klemm and has exactly the same susceptibility at − 183° C. as at 20° C.

Arsenic is reported by Stöhr [96] to be slightly paramagnetic at − 183° C. The different allotropic modifications of arsenic all have about the same susceptibility.

Explosive antimony [97] has a susceptibility of -0.3×10^{-6}, compared with -0.88×10^{-6} for the ordinary polycrystalline metal. The suscepti-

[92] S. R. Rao, *Proc. Indian Acad. Sci.*, **1A**, 123 (1934).
[93] K. Honda and Y. Shimizu, *Nature*, **136**, 393 (1935).
[94] S. R. Rao, *Nature*, **134**, 288 (1934).
[95] H. J. Hoge, *Phys. Rev.*, **48**, 615 (1935).
[96] H. Stöhr, *Z. anorg. allgem. Chem.*, **242**, 138 (1939).
[97] C. C. Coffin, *Can. J. Research*, **13A**, 120 (1935).

bility of single crystals of the metal has been studied by Schoenberg and Uddin.[98] Both principal susceptibilities are independent of field strength, down at least to 44° K. The numerical value of the principal susceptibility parallel to the trigonal axis decreases with increasing temperature, but that perpendicular to the trigonal axis is independent of temperature. The susceptibility of antimony, like that of bismuth is very sensitive to the addition of small quantities of foreign elements. Single crystals of antimony alloyed with small amounts of tin, germanium, lead, and tellurium have been studied by Hart,[99] and by Browne and Lane.[100] Changes of electron concentration caused by such additions have a profound effect on the anisotropy of the antimony, even causing reversal of sign of $\chi_{\parallel}/\chi_{\perp}$. This reversal is caused by a change of principal susceptibility parallel to the trigonal axis from diamagnetic to paramagnetic at 1.17 atomic per cent of tin or 1.25 atomic per cent of germanium. The perpendicular susceptibility changes but little.

Bismuth has been the object of much magnetic study. It is remarkable for its high diamagnetism, for its temperature coefficient of susceptibility, for its structure-sensitivity, and for its curious field-strength dependence of susceptibility at low temperatures. Among the more recent investigations of this element are those of Goetz and Focke.[101,102] Over a fairly wide temperature range the atomic susceptibility of bismuth may be represented by

$$\chi_{A(T)} = \chi_{A(T_0)} + \alpha(T - T_0)$$

at the melting point (271° C.) the atomic susceptibility drops sharply from about -213×10^{-6} to -17×10^{-6}. As for antimony the magnetic anisotropy is large, and is dependent on temperature and on the presence of small amounts of foreign elements.[103] Very thin deposits of evaporated bismuth apparently have a slightly smaller diamagnetism than massive bismuth. Lane [104] shows that below 0.5μ, χ decreases somewhat with decreasing film thickness. The curious de Haas-van Alphen effect, the periodic variation of susceptibility with field strength, for bismuth crystals at low temperatures has already been discussed in Chap. IV (p. 93).

[98] D. Shoenberg and M. Z. Uddin, *Proc. Cambridge Phil. Soc.*, 32, 499 (1936).
[99] H. M. Hart, *Phys. Rev.*, 52, 130 (1937).
[100] S. H. Browne and C. T. Lane, *Phys. Rev.*, 59, 939; 60, 895, 899 (1941).
[101] A. Goetz and A. B. Focke, *Phys. Rev.*, 45, 170 (1934) (large bibliography).
[102] A. Goetz, O. Stierstadt and A. B. Focke, *Z. Physik*, 98, 118 (1935).
[103] W. J. John, *Z. Krist.*, 101, 337 (1939).
[104] C. T. Lane, *Nature*, 130, 999 (1932); *Phys. Rev.*, 51, 863 (1937).

9. Chromium and Other Group VI Metals

The atomic susceptibilities of these metals, so far as they are known, are shown in Table XXXIX.

TABLE XXXIX

ATOMIC SUSCEPTIBILITIES OF GROUP VI METALS AT ROOM TEMPERATURE

Element	$\chi_A \times 10^6$	Element	$\chi_A \times 10^6$
Chromium	160	Selenium	− 26.5
Molybdenum	54?	Tellurium	− 40.8
Tungsten	40?	Polonium	—
Uranium	620		

Metallic chromium has recently been studied by Bates and Baqi.[105] The preparation of iron-free specimens of this metal is not easy. It may be achieved by electrolytic preparation of chromium amalgam from which the mercury may be distilled in vacuum. Even then the samples gave erratic results until they had been evacuated at 1200° C. for two hours. Such preparations have a susceptibility almost independent of temperature between 90 and 620° K.

The intermetallic compound, CrSb, shows antiferromagnetism.[106]

Chromium amalgam, along with amalgams of manganese, bismuth, and copper have been examined by Bates and Tai [107] who point out that earlier work, including that given in the International Critical Tables, is vitiated by use of an incorrect susceptibility for mercury. The apparent atomic susceptibility of chromium in dilute amalgams is $+ 23 \times 10^{-6}$, in contrast to manganese the paramagnetism of which increases enormously when the metal is dissolved in mercury.

Bommer [108] reports that metallic uranium shows an irregular temperature dependent paramagnetism, corresponding somewhat to antiferromagnetism.

Haraldsen and Nygaard [109] have made magnetic measurements on the system Cr-As, which is discussed in comparison with corresponding studies on Cr-S, Cr-Se, and Cr-Te.

Selenium and tellurium have been the object of considerable study by Indian workers. Dharmatti [110,111] reviews the literature on the effect of

[105] L. F. Bates and A. Baqi, *Proc. Phys. Soc. London*, **48**, 781 (1936).
[106] G. Foëx and M. Graff, *Compt. rend.*, **209**, 160 (1939).
[107] L. F. Bates and L. C. Tai, *Proc. Phys. Soc. London*, **48**, 795 (1936).
[108] H. Bommer, *Z. anorg. allgem. Chem.*, **247**, 249 (1941).
[109] H. Haraldsen and E. Nygaard, *Z. Elektrochem*, **45**, 686 (1939).
[110] S. S. Dharmatti, *Nature*, **134**, 497 (1934).
[111] M. Prasad and S. S. Dharmatti, *Indian J. Phys.*, **11**, 1 (1937).

fine powdering on magnetic properties. There is no doubt that prolonged powdering of selenium results in a large change of susceptibility, in some cases even resulting in a change of sign. But the major portion of this change seems to be due to adsorption of impurities. Perhaps some change is due to conversion of gray selenium into an allotropic modification. Similarly tellurium,[112] on very slow thorough grinding, finally became paramagnetic. But grinding under paraffin oil produced negligible changes in susceptibility, and fusing of the powdered mass did not restore the initial susceptibility. It is probable that here too the apparent change is due to adsorbed impurities. The crystal diamagnetism of tellurium has been studied by Rao and Govindarajan.[113]

10. Manganese and Rhenium

The first of these metals is of particular importance because, although it is paramagnetic, its structure lacks very little of that necessary for the establishment of ferromagnetism. The atomic susceptibilities at room temperature are manganese $\chi_A = 527 \times 10^{-6}$ for the crystalline α form, possibly somewhat less for the β form. For rhenium $\chi_A = 68.7 \times 10^{-6}$.

Pure manganese metal has recently been studied by Shimizu;[114] Wheeler;[115] Grube and Winkler;[116] Serres;[117] and by Bates and Pantulu.[118] There still remains some doubt as to the exact form of the susceptibility-temperature curve. If sufficient pains are taken to insure the absence of impurities, both solid and gaseous, the susceptibility is apparently nearly independent of temperature, at least from $-183°$ C. to $+600°$ C. Above 600° there appears to be some very erratic temperature dependence, which may not be entirely reversible. The possibility, however, of oxidation or of nitride formation cannot be completely ruled out. Amorphous manganese prepared by Bates and Pantulu by vacuum distillation of the amalgam under most rigid conditions has a susceptibility somewhat higher than is reported for the massive form. Over the range 90 to 600° K. this substance follows the Weiss law $\chi = 2.174 \times 10^{-2}/(T + 1540)$. In very dilute amalgams the atomic susceptibility of manganese is reported by Bates and Tai[119] to reach the very large value of $13{,}700 \times 10^{-6}$ at room temperature. This value is in substantial agreement with that found for

[112] M. Prasad and S. S. Dharmatti, *Indian J. Phys.*, 11, 393 (1938).
[113] S. R. Rao and S. R. Govindarajan, *Proc. Indian Acad. Sci.*, 10A, 235 (1939).
[114] Y. Shimizu, *Science Repts. Tôhoku Imp. Univ., First Ser.*, 19, 411 (1930).
[115] M. A. Wheeler, *Phys. Rev.*, 41, 331 (1932).
[116] G. Grube and O. Winkler, *Z. Elektrochem.*, 42, 815 (1936).
[117] A. Serres, *J. phys. radium*, 9, 377 (1938).
[118] L. F. Bates and D. V. R. Pantulu, *Proc. Phys. Soc. London*, 47, 197 (1935).
[119] L. F. Bates and L. C. Tai, *Proc. Phys. Soc. London*, 49, 230 (1937).

manganese in alloys with copper, silver, or gold, although the susceptibility depends on concentration and on choice of solvent.[120]

The effect of dissolved hydrogen on the susceptibility of manganese has been studied by Wheeler,[121] and the effect of nitrogen by Bates, Gibbs, and Pantulu.[122] Definite hysteresis curves are obtained from the material prepared by heating manganese in an atmosphere of nitrogen. This reaction takes place as low as 300° C. with finely divided manganese prepared from the amalgam. But it is not clear whether the nitrogen forms a true compound with the manganese or whether it acts merely by expansion of the lattice. Pure manganese is probably not ferromagnetic in any sense, but it is peculiarly sensitive to traces of impurities.[123]

Our knowledge of the magnetic properties of metallic rhenium comes from Perakis and Capatos.[124] The susceptibility is 0.369×10^{-6} and is independent of temperature from -79 to $+20°$ C.

11. The Platinum Group Metals

The atomic susceptibilities of these elements are shown in Table XL.

TABLE XL

ATOMIC SUSCEPTIBILITIES OF THE PLATINUM GROUP METALS AT ROOM TEMPERATURE

Element	$\chi_A \times 10^6$	Element	$\chi_A \times 10^6$
Ruthenium	44	Osmium	7.6
Rhodium	113	Iridium	25
Palladium	580	Platinum	200

Palladium and platinum are the most extensively studied of these elements.[125–127] Over a limited temperature range the susceptibilities of all the metals follow the Weiss law. Takatori [128] reports a diminution in

[120] G. Gustafsson, *Ann. Physik*, 25, 545 (1936); L. Weil, *Cahiers phys.*, 1941, No. 4, IV–49.

[121] M. A. Wheeler, *Phys. Rev.*, 49, 642 (1936).

[122] L. F. Bates, R. E. Gibbs, and D. V. R. Pantulu, *Proc. Phys. Soc. London*, 48, 665 (1936).

[123] R. Ochsenfeld, *Ann. Physik*, 12, 353 (1932).

[124] N. Perakis and L. Capatos, *Compt. rend.*, 196, 611 (1933); 198, 1905 (1934).

[125] A. N. Guthrie and L. T. Bourland, *Phys. Rev.*, 37, 303 (1931).

[126] P. Collet and G. Foëx, *J. phys. radium*, 2, 290 (1931).

[127] E. Vogt, "Magnetismus der Metallischen Elemente," *Ergeb. exact. Naturw.*, 11, 323 (1932).

[128] N. Takatori, *Science Repts. Tôhoku Imp. Univ., First Ser.*, 25, 489 (1936).

the susceptibility of platinum when the metal is reduced to a fine powder. The effect of small amounts of foreign substances on the magnetic properties of platinum has been studied by Theron.[129] Palladium-manganese alloys have very complicated magnetic properties. Grube and Winkler [116] show that at about 40 atomic per cent of manganese the susceptibility becomes extremely high owing to the existence of Pd_3Mn_2 which is ferromagnetic below 350° C. The compound PdMn is also ferromagnetic although only weakly so. Measurements on this system have been carried up to 1400° C.

The magnetic susceptibility of hydrogenized palladium is an old problem, first studied by Graham.[130] More recently Svensson [131] has found that the susceptibility of palladium diminishes linearly with increase of hydrogen content and finally reaches a value just below zero for a volume ratio of H/Pd of 800/1. Substantially the same form of change is shown by Sieverts and Danz [132] to occur when deuterium is substituted for hydrogen. These changes are also discussed by Michel and Gallissot.[133]

[129] R. Theron, *Compt. rend.*, 208, 1634 (1939).
[130] T. Graham, *Ann. chim. phys.*, 16, 197 (1869).
[131] B. Svensson, *Ann. Physik*, 18, 299 (1933).
[132] A. Sieverts and W. Danz, *Z. physik. Chem.*, B38, 61 (1937).
[133] A. Michel and M. Gallissot, *Compt. rend.*, 208, 434 (1939).

CHAPTER EIGHT

FERROMAGNETISM

1. Introduction to Ferromagnetism

This topic is of the utmost technological importance but it has not yet played a very important part in chemistry. There is considerable evidence that ferromagnetism is not as rare in nature as was once believed and that the structure of many chemical substances may be revealed by examination of their ferromagnetic properties. Ferromagnetism is difficult to define simply and precisely. With Bitter [1] we shall be content to say that a ferromagnetic substance is one whose magnetic properties are like those of iron. How, in general, this differs from diamagnetism and paramagnetism should be sufficiently clear from the following discussion to serve the purposes of most readers.

Ferromagnetic substances are chiefly distinguished by the facts that the susceptibility at low field strengths may be enormous, and that the susceptibility is a function of field strength up to the field at which the substance is said to be saturated. This field is generally readily attainable. Many ferromagnetic substances show the phenomena of hysteresis, and of residual magnetism. A typical hysteresis curve is shown in Fig. 11, on p. 17. This also shows the interrelationships among the various quantities used in discussions of ferromagnetic substances.

There are many excellent texts and reviews on ferromagnetism. A few recent references with some definite bearing on chemical problems are given below.[2–8]

The permeability and other magnetic properties of a ferromagnetic substance depend on temperature in a complicated, poorly understood manner. Sometimes the coefficient is positive, sometimes negative. Es-

[1] F. Bitter, *Introduction to Ferromagnetism.* McGraw-Hill Book Company, Inc., New York 1937.

[2] L. W. McKeehan, *Am. Inst. Mining Metal. Engrs., Tech. Publ.*, No. 554, (1934).

[3] O. v. Auwers, *Ergeb. exakt. Naturw.*, **16**, 133 (1937).

[4] E. Vogt, *Angew. Chem.*, **51**, 361 (1938).

[5] H. Bittel and W. Gerlach, *Physik. regelmäss. Ber.*, **7**, No. 3, 119 (1939).

[6] A. Kussmann, *Z. Ver. deut. Ing.*, **83**, 445 (1939).

[7] L. F. Bates, *Modern Magnetism.* The University Press, Cambridge 1939.

[8] W. Döring, *Z. Elektrochem.*, **45**, 621 (1939).

pecially in the neighborhood of transition points the thermal effects may be large. Previous thermal history also has an effect on magnetic properties. The most striking change of magnetization with changing temperature occurs at the Curie point. At this temperature the substance loses its ferromagnetism and becomes paramagnetic. The changes in ferromagnetic properties at this temperature are not complete but continue over a definite temperature interval.[9] It has already been implied that the Curie temperature is related to the molecular field constant, Δ, in the expression $\chi(T + \Delta) = C$. Unfortunately the negative of Δ expressed in degrees does not always give the exact temperature at which ferromagnetism disappears or begins to disappear.[10, 11] There has therefore come into use the term "ferromagnetic Curie point" as distinguished from $-\Delta$. There is often a difference of 10° or 15° between the two temperatures. Above the Curie point ferromagnetic substances become normal paramagnetics although the temperature plotted against reciprocal of susceptibility may not approach a straight line until the Curie point has been greatly exceeded. The behavior of metallic gadolinium in this respect was mentioned in the previous chapter. Paramagnetic magneton numbers of the common ferromagnetic metals have been determined by Sucksmith and Pearce.[12] Their results are shown in Table XLI.

TABLE XLI

PARAMAGNETIC MAGNETON NUMBERS OF IRON, COBALT, AND NICKEL

		$-\Delta$	$C = \chi(T + \Delta)$	μ_{eff}
Ni	500–850°	377° C.	0.00548	1.61
	925–1200°	265	0.00685	1.78
Co	1230–1450°	1130–1155	0.02080	3.15
Fe from Fe-V alloys			0.02270	3.20
Fe from δ phase		820	0.02200	3.15

The magneton numbers obtained in the conventional way from the slope of the $1/\chi$ versus T curves are considerably greater than those calculated from the saturation intensity of magnetization at low temperatures. The point is discussed by Stoner.[13] Earlier work on the same topic is also

[9] W. Gerlach, *Z. Elektrochem.*, **45**, 151 (1939).

[10] R. Forrer, *J. phys. radium*, **1**, 49 (1930).

[11] L. F. Bates, *Proc. Phys. Soc. London*, **43**, 87 (1931).

[12] W. Sucksmith and R. R. Pearce, *Nature*, **140**, 970 (1937); *Proc. Roy. Soc. London*, **A167**, 189 (1938).

[13] E. C. Stoner, *Proc. Leeds Phil. Lit. Soc. Sci. Sect.*, **3**, 457 (1938).

reviewed by Stoner,[14] who gives details of the calculation of magneton numbers in ferromagnetics. (*Op. cit.*, p. 352).

The magnetic properties of single crystals of ferromagnetic substances do not greatly concern us. Stoner (*op. cit.*, p. 435) lists many earlier references. More recent theoretical and experimental work in this field is reported by McKeehan,[15] by Elmore,[16] and by Van Vleck.[17]

The effect of mechanical deformation and of time lags in the study of ferromagnetism are discussed by Bitter (*op. cit.*,[1] p. 25). A host of magneto-optical and other magnetic effects will be found described in Williams' "Magnetic Phenomena." [18]

The origin of ferromagnetism has been the object of considerable theoretical study. The earliest attempt to explain the subject from a quantitative standpoint is due to Weiss who introduced the concept of the "molecular field." [19] The modern theory is due to Heisenberg.[20] Discussions of the various theories, their successes, and their limitations are given by Van Vleck;[21] Stoner (*op. cit.*,[14] p. 350); Bates (*op. cit.*,[7] p. 239); and by many others.[22–24c] Such discussions lie outside the scope of this book.

As already mentioned, ferromagnetism is fairly rare in nature, occurring in only a few metals, alloys and compounds. In Heisenberg's model the essential condition [25] for ferromagnetism is that the wave functions of electrons in neighboring atoms should only slightly overlap each other near the nuclei. Owing to the angular distribution of electrons in an atom in a crystal, there is a tendency to limit ferromagnetism to crystals of elements in the latter part of a period in the periodic table.

Ferromagnetism is not an atomic property. It is therefore of interest to know the minimum size of ferromagnetic particles. Various theo-

[14] E. C. Stoner, *Magnetism and Matter*. Methuen and Co., Ltd., London 1934, p. 378.

[15] L. W. McKeehan, *Phys. Rev.*, 52, 18 (1937); 53, 301 (1938).

[16] W. C. Elmore, *Phys. Rev.*, 51, 982 (1937).

[17] J. H. Van Vleck, *Phys. Rev.*, 52, 1178 (1937).

[18] S. R. Williams, *Magnetic Phenomena*. McGraw-Hill Book Company, Inc., New York 1930.

[19] P. Weiss, *J. phys.*, 6, 661 (1907).

[20] W. Heisenberg, *Z. Physik*, 49, 619 (1928).

[21] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*. Clarendon Press, Oxford 1932, p. 316.

[22] T. Hirone, *Science Repts. Tôhoku Imp. Univ., First Ser.*, 23, 523 (1934).

[23] J. C. Slater, *Phys. Rev.*, 52, 198 (1937).

[24a] J. H. Van Vleck, *J. Chem. Phys.*, 6, 105 (1938).

[24b] V. Firgau, *Ann. Physik*, 40, 295 (1941).

[24c] Y. Takagi, *Proc. Phys.-Math. Soc. Japan*, 23, 553 (1941).

[25] D. R. Inglis, *Phys. Rev.*, 45, 128 (1934).

retical estimates have been made to determine the size of the unit magnetic cell. The obvious experimental approach is to find the magnetization of ferromagnetic powders as a function of particle size. Beischer and Winkel [26] prepared aerosols of nickel and of iron by thermal decomposition of the carbonyls in an atmosphere of nitrogen. The individual grains so formed consist of crystals whose dimensions, for nickel, are $35 \times 60 \times 210$ Å. as determined by x-ray methods. These tiny crystals are definitely ferromagnetic and form chains about 0.5 mm. long. This work does not, however, establish a lower limit for the size of the elementary ferromagnetic particle. Winkel and Haul,[27] and Haul and Schoon [28] oxidized iron carbonyl at several temperatures in order to obtain progressively increasing grain size of Fe_2O_3. The γ form of this oxide is ferromagnetic and it is this form which seems to have been obtained in every case. The susceptibility is shown in Fig. 48 to remain nearly

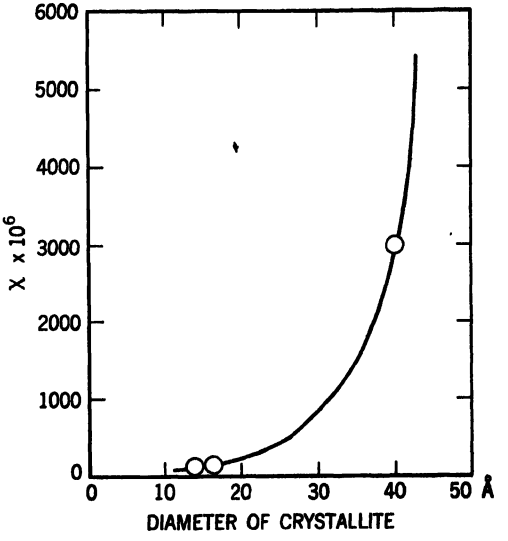


FIG. 48.—Ferromagnetism as a function of particle size for γ-Fe_2O_3.

constant up to 30–40 Å. diameter but above this size ferromagnetism sets in and the susceptibility rises very sharply. The field strength dependence of susceptibility supports this evidence, being negligible below a grain size of 30–40 Å. This experimentally determined value marks the lowest

[26] D. Beischer and A. Winkel, *Naturwissenschaften*, 25, 420 (1937).
[27] A. Winkel and R. Haul, *Z. Elektrochem.*, 44, 823 (1938).
[28] R. Haul and T. Schoon, *Z. Elektrochem.*, 45, 663 (1939).

elementary particle in which spontaneous magnetization occurs. The question is further discussed by Klemm.[29]

In the following sections the complicated magnetic properties of ferromagnetic alloys will be referred to under each element. Some partially successful efforts have been made to relate structure and composition to magnetic properties. Among the many contributions to this field, those of Dehlinger [30] and of Auwers [31] may be mentioned. Ferromagnetism of alloys is to be expected only in alloys containing at least one of the elements chromium, manganese, iron, cobalt, and nickel. An effect of the alloying element on the Curie temperature and on the maximum magnetic moment is to be expected only when the element is highly soluble in the parent lattice. Small amounts of alloy, however, often greatly change the coercive force and the remanence. Binary alloys of nickel, cobalt, iron, and manganese with elements that obey the Hume-Rothery rule and possess body-centered cubic phases generally lose their ferromagnetism. Alloys of the transition elements with those elements that do not obey the Hume-Rothery rule may be ferromagnetic.

2. Iron

The magnetic properties of ferromagnetic substances depend on impurities and other factors to such a remarkable degree that their study is often hampered by the difficulty of obtaining pure specimens. The preparation of pure iron is no exception. This problem is very ably discussed by Yensen.[32] The purest iron is obtained by thermal decomposition of the liquid iron pentacarbonyl

$$Fe(CO)_5 \rightarrow Fe + 5CO$$

(not the enneacarbonyl as erroneously stated by Yensen). If this substance is decomposed in a heated chamber, so that it does not touch the walls before decomposition occurs, the product will be very pure. A trace of carbon may be removed by heating the iron with a measured quantity of iron oxide, also prepared from iron carbonyl. The purity of such iron is better than 99.9 per cent. There is some question as to whether or not the best electrolytic iron may not be even purer than carbonyl iron.

The magnetic properties of iron are often greatly changed by annealing. In many cases this is essentially a diffusion process leading to elimination of gaseous impurities. In impure iron the solubility and dis-

[29] W. Klemm, *Z. Elektrochem.*, **46**, 296 (1940).
[30] U. Dehlinger, *Z. Metallkunde*, **29**, 388 (1937).
[31] O. v. Auwers, *Wiss Veröffentl. Siemens-Werken*, **17**, 74 (1938).
[32] T. D. Yensen in Bitter's, *Introduction to Ferromagnetism.* (*Op. cit.*,[1] p. 67).

tribution of impurities may be modified by heat treatment. Magnetic properties, particularly hysteresis, are also influenced by grain size and lattice orientation, which depend in turn on the presence of impurities and on the previous heat treatment. The magnetism also depends on time. The reason for this "aging" process seems to lie in the presence of impurities and to their alteration or diffusion with time. Extensive references to this field are given by Yensen. The effect seems definitely to be absent in pure iron.[33]

The purer iron can be obtained the higher its permeability and the lower its hysteresis loss. A B–H curve for nearly pure iron is shown in Fig. 49, together with curves for several common commercial irons and steels. A thorough introduction to this subject is that of Auwers.[34]

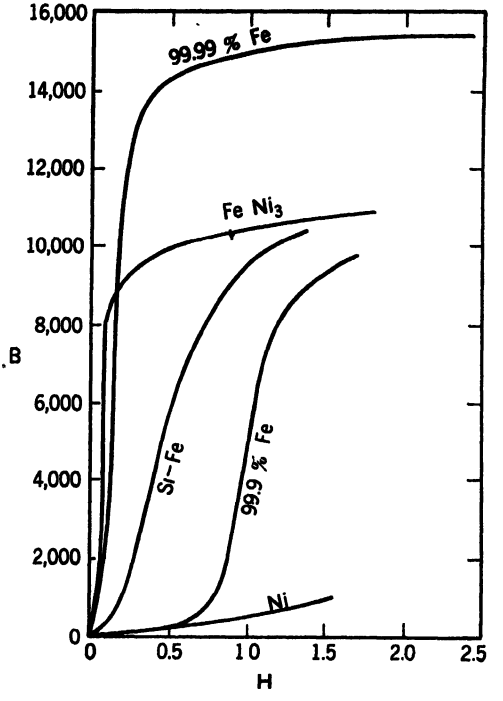


FIG. 49.—B-H curves for pure iron and for several alloys.

Single crystals of pure iron have been studied especially in connection with the domain concept of ferromagnetism first advanced by Weiss.

[33] J. L. Snoek, *Physica*, 6, 161 (1939).

[34] O. v. Auwers, "*Magnetische und Elektrische Eigenschaften des Eisens und seiner Legierungen*" in Gmelin's *Handbuch der Anorganischen Chemie*. Verlag Chemie, Berlin 1937.

The domain theory and its present status are discussed by Becker,[35] by Becker and Döring,[36] and by Brown.[37] The idea is that small domains which may or may not correspond to the metallographic grains possess an intrinsic permanent magnetization, but because of their random orientation the domains do not lead to magnetization of the whole crystal except in the presence of an external field.

Ferromagnetic crystals are anisotropic and often show very different ease of magnetization along different crystallographic axes. There have been many studies of this effect. A few of them are listed below.[38–45]

Very thin layers of iron deposited electrolytically seem to have somewhat different magnetic properties from iron in bulk.[46] This to be expected if ferromagnetism is a property of massive form rather than of atomic particles.

There have been some differences of opinion expressed on the effect of dissolved hydrogen on the magnetic properties of iron. Some authors regard the changes occurring on heat treatment in the presence of hydrogen as being due solely to the elimination of impurities. Reber [47] has, however, shown a rather definite magnetic hardening to take place when hydrogen is electrolyzed into iron.

3. Ferrous Alloys

There is a wealth of data on ferromagnetic alloys of iron. Most of the work in this field has been done with a view to producing new and improved alloys for specific purposes. The use of thermomagnetic methods for structural studies [48] is, however, receiving increasing attention, and some of these methods will be reviewed in the following chapter. Such studies furnish a sensitive means for quantitative evaluation of heterogeneity in a ferromagnetic solid solution. Efforts have been made to place the study of such substances on a sound theoretical basis and

[35] R. Becker, *Probleme der technischen Magnetisierungskurve.* J. Springer, Berlin 1938.

[36] R. Becker and W. Döring, *Ferromagnetismus.* J. Springer, Berlin 1939.

[37] W. F. Brown, *J. Applied Phys.*, **11**, 160 (1940).

[38] K. Honda and S. Kaya, *Science Repts. Tôhoku Imp. Univ., First Ser.*, **15**, 721 (1926).

[39] N. S. Akulov, *Z. Physik*, **67**, 794 (1931).

[40] R. Gans, *Physik. Z.*, **33**, 924 (1932).

[41] F. Bitter, *Phys. Rev.*, **42**, 697 (1932).

[42] H. Schlechtweg, *Ann. Physik*, **27**, 573 (1936).

[43] K. Honda and T. Nishina, *Z. Physik*, **103**, 728 (1936).

[44] R. M. Bozorth and L. W. McKeehan, *Phys. Rev.*, **51**, 216 (1937).

[45] K. Honda and T. Hirone, *Z. Physik*, **111**, 477 (1939).

[46] S. Procopiu and G. d'Albon, *Compt. rend.*, **205**, 1373 (1937).

[47] R. K. Reber, *Physics*, **5**, 297 (1934).

[48] P. Chevenard, *14me Congr. chim. ind.*, Paris, Oct. 1934.

some success in this direction has been achieved.[49–51] When pure, transition elements generally show ferromagnetism or at least paramagnetism independent of temperature. But in dilute solution in diamagnetic noble metals, transition group metals often exhibit almost free moments. Whether or not the Curie law is obeyed under such circumstances seems to depend partly on electron density. A good introduction to magnetization of ferrous alloys as a function of chemical composition is given by Messkin and Kussmann.[52]

In all work on iron and iron alloys it is imperative to bear in mind that oxygen in amounts less than 0.1 per cent, and carbon in amounts less than 0.01 per cent can profoundly alter the magnetic characteristics of the metal. The large effect of carbon traces may be due to lattice distortions brought about by carbon atoms or to Fe_3C in the lattice of the iron. The ferromagnetic Curie point for pure iron is at 769° C. The change is referred to as a transition from α to β iron although both forms have the same crystal structure. At 900° C. a true transition occurs from the body-centered to the face-centered cubic or γ form. Addition of carbon lowers the $\beta - \gamma$ transition temperature to 710° C. Austenite is generally paramagnetic but a ferromagnetic form has been obtained by Tarasov and Parker.[53] The room temperature characteristics of iron are dependent not only on the percentage of carbon present but also on the rate of cooling which determines the relative proportions of carbon remaining in solid solution or precipitating as cementite, Fe_3C.

Iron-silicon alloys are much used commercially. Silicon up to a few per cent has a markedly beneficial effect on the hysteresis and eddy losses of transformer steel. This improvement is stated by Yensen (*op. cit.*,[1] p. 107) to be due to an indirect effect of the silicon. This element is very soluble in iron and it promotes the precipitation of carbon as graphite and at the same time combines vigorously with dissolved oxygen. Silicon therefore owes its beneficial effects primarily to its scavenging action. Alloys of iron high in silicon are paramagnetic.[54] Single crystals of such alloys have been studied by Williams.[55] Various other elements such as aluminum, arsenic, tin, and vanadium, alone or in combination, produce effects similar to those of silicon.

Alloys of iron with the other common ferromagnetic metals, cobalt

[49] E. Vogt, *Ann. Physik*, **18**, 771 (1933).

[50] A. Kussmann, *Chem. Ztg.*, **59**, 285 (1935).

[51] W. Messkin and J. M. Margolin, *Z. Physik*, **101**, 456 (1936).

[52] W. Messkin and A. Kussmann, *Die Ferromagnetischen Legierungen*. J. Springer, Berlin 1932.

[53] L. P. Tarasov and E. R. Parker, *Phys. Rev.*, **56**, 379 (1939).

[54] C. Bedel, *Compt. rend.*, **196**, 262 (1933).

[55] H. J. Williams, *Phys. Rev.*, **52**, 747 (1937).

and nickel, have also been very thoroughly studied. Some of these,[56,57] such as hypernik, Fe_2Ni_2, and permalloy, $FeNi_3$, have remarkably useful magnetic properties. These alloys have exceedingly high permeabilities. Others containing iron, cobalt, and nickel, such a perminvar, have a constant permeability for low magnetizing fields. Still others, containing principally iron and cobalt are useful for permanent magnets. In some such alloys the Curie point exhibits a sort of thermal hysteresis, that is, on rising temperature the ferromagnetism may be lost at, say, 600° C., but on falling temperature the ferromagnetism is not regained until far below 600°. In general, the alloying of one ferromagnetic metal with another yields a ferromagnetic alloy. But the permeability, saturation, hysteresis, and other magnetic properties may be very greatly modified. Still further modification is possible by heat treatment and working. In iron-nickel alloys, both the saturation magnetization and the ferromagnetic anisotropy are affected by the order-disorder transformation involving Ni_3Fe. Similar considerations probably apply to many other alloys.[58]

Manganese and chromium are, of course, paramagnetic, but they stand just on the border of ferromagnetism. Small changes in atomic distances shift these two elements into the other classification and many of their alloys and compounds are found to be ferromagnetic. Some of these have important technological uses. Similarly many base metals are used as subsidiary alloying agents for iron.

Iron, when present as a minor constituent with non-ferromagnetic metals, generally imparts ferromagnetism to the whole mass. In very dilute solution this must be due to precipitation of the iron. The ferromagnetism of such alloys may sometimes be destroyed by quenching from a temperature high enough to dissolve all the iron. This, however, is not always possible. Bates and Illsley [59a] find that iron amalgams retain their ferromagnetism even at very low iron concentrations.

Quenched, supersaturated solutions of iron in gold, containing 37 atomic per cent of iron are ferromagnetic.[59b]

Iron alloys with the platinum group metals have been studied chiefly by Fallot.[60–64] The diagrams are complex.

[56] G. W. Elmen, *Bell System Tech. J.*, **8**, 435 (1929).
[57] A. J. Corson, *Gen. Elec. Rev.*, **45**, 573 (1942).
[58] E. M. Grabbe, *Phys. Rev.*, **57**, 728 (1940).
[59a] L. F. Bates and P. F. Illsley, *Proc. Phys. Soc. London*, **49**, 611 (1937).
[59b] S. T. Pan, A. R. Kaufmann, and F. Bitter, *J. Chem. Phys.*, **10**, 318 (1942).
[60] M. Fallot, *Compt. rend.*, **199**, 128 (1934). (Fe-Pt)
[61] L. Graf and A. Kussmann, *Physik. Z.*, **36**, 544 (1935). (Fe-Pt)
[62] M. Fallot, *Compt. rend.*, **205**, 227 (1937). (Fe-Ru) (Fe-Os)
[63] M. Fallot, *Compt. rend.*, **205**, 517 (1937). (Fe-Ir)
[64] M. Fallot, *Compt. rend.*, **205**, 558 (1937). (Fe-Rh)

4. Nickel

The magnetic properties of nickel are not as pronounced as those of iron, yet the pure metal, its single crystals, and its alloys have been the object of possibly even more intensive study. Pure nickel may be prepared by electrolytic deposition, or by thermal decomposition of the carbonyl, $Ni(CO)_4$. Impurities found in the best nickel commercially available are discussed by Yensen (*op. cit.*,[1] p. 74).

Nickel has the smallest saturation permeability of the four ferromagnetic elements. Two fairly recent reviews of the magnetic properties of this metal and of nickel-rich alloys are given by Hirone [65] and by Gerlach, Bittel, and Velayos.[66] Next to gadolinium, nickel has the lowest Curie point of the ferromagnetic metals. The ferromagnetic Curie point is about 358° C. The properties of pure nickel near the Curie point have been described by Neel [67] and by Gerlach.[68]

Single crystals of nickel have been very extensively studied by S. Kaya.[69] A long bibliography on this subject is given by Stoner (*op. cit.*,[14] p. 435). Some more recent studies are those of Gerloff [70] and of Brukhatov and Kirenskii.[71]

Thin films of nickel and nickel colloids have been studied respectively by Malmstrom [72] and by Rao.[73] The thin films show a decreasing coercive force with decreasing film thickness in the range from 140 to 60mμ. The colloids showed an intensity of magnetization of from 70 to 85 per cent of the value for solid nickel.

One of the most interesting magnetochemical studies recently made on nickel is that of Post and Ham [74] who measured the diffusion of hydrogen into nickel in relation to magnetic properties. The temperature range covered was 150° to 1100° C. The rate of diffusion is regular over all that range except for a definite discontinuity at the Curie point. Variation of hydrogen concentration does not measurably change the Curie point. The authors believe that these experiments prove that loss of magnetism at the Curie point is essentially an atomic rather than a

[65] T. Hirone, *Science Repts. Tôhoku Imp. Univ., First Ser.*, 27, 101 (1938).

[66] W. Gerlach, H. Bittel, and S. Velayos, *Sitzber. math.-naturw. Abt. bayer. Akad. Wiss. München*, 1936, 81.

[67] L. Néel, *J. phys. radium*, 6, 27 (1935).

[68] W. Gerlach, *Science Repts. Tôhoku Imp. Univ., First Ser.*; K. Honda Ann. Vol. 1936, p. 248.

[69] S. Kaya, *Science Repts. Tôhoku Imp. Univ., First Ser.*, 17, 639 (1928).

[70] G. Gerloff, *Z. Physik*, 99, 585 (1936).

[71] N. L. Brukhatov and L. V. Kirenskii, *Physik. Z. Sowjetunion*, 12, 602 (1937).

[72] H. E. Malmstrom, *Proc. Iowa Acad. Sci.*, 38, 214 (1931).

[73] S. R. Rao, *Current Sci.*, 1, 170 (1932).

[74] C. B. Post and W. R. Ham, *J. Chem. Phys.*, 6, 598 (1938).

"cooperative" phenomenon of atomic aggregates. It seems difficult to reconcile this view with the experiments on particle size and elementary ferromagnetic "domains." Nevertheless it is a remarkable fact that there should be any type of discontinuity at the Curie point in the complete absence of an external magnetic field. Such changes are, however, by no means unusual. Specific heat and coefficients of thermal expansion both change sharply at the Curie point. It seems most probable that Post and Ham's results can be explained in terms of the peculiar thermal expansion [75] maximum observed for nickel in the neighborhood of 360° C.

5. Nickel Alloys

Alloys of nickel with other ferromagnetic metals are themselves ferromagnetic. Addition of a non-ferromagnetic metal to nickel generally results in a diminution of ferromagnetism of the alloy, although the alloy does not as a rule lose all its ferromagnetism until the nickel concentration becomes quite low. Various attempts have been made to relate the magnetic properties of nickel alloys to their composition. Dorfman,[76] for instance, has pointed out the relation between atomic moments in solid solution and the number of valence electrons. Extensive theoretical studies on this subject are also reported by Neel [77] and by Hirone.[65] Relationships between the composition and the Curie temperature of nickel alloys are reported by Marian [78] and by Niessen.[79] The Curie point and the saturation moment are roughly linear functions of the valence multiplied by the mole fraction of nickel.

Alloys of nickel and cobalt show no particular magnetic anomalies, except possibly in regard to the anisotropy of single crystals.[80, 81] Shih [82] shows that these crystals have a reversal of the direction of easiest magnetization between about 10 and 20 per cent of cobalt.

Nickel-manganese alloy is unusual.[83] The saturation magnetization passes through two peaks as the percentage of manganese is increased. The hysteresis curves are also unusual, and are markedly dependent on heat treatment.[84] Thompson [85] has shown that the magnetization, elec-

[75] C. Williams, *Phys. Rev.*, **46**, 1011 (1934).
[76] J. Dorfman, *Physik. Z. Sowjetunion*, **3**, 399 (1933).
[77] L. Néel, *Compt. rend.*, **198**, 1311 (1934); **201**, 135 (1935).
[78] V. Marian, *J. phys. radium*, **8**, 313 (1937); *Ann. phys.*, **7**, 59 (1937).
[79] K. F. Niessen, *Physica*, **6**, 1011 (1939).
[80] C. Sadron, *Ann. phys.*, **17**, 371 (1932).
[81] W. Broniewski and W. Pietrek, *Compt. rend.*, **201**, 206 (1935).
[82] J. W. Shih, *Phys. Rev.*, **50**, 376 (1936).
[83] S. Kaya and A. Kussmann, *Z. Physik*, **72**, 293 (1931).
[84] S. Valentiner and G. Becker, *Z. Physik*, **93**, 795 (1935).
[85] N. Thompson, *Proc. Phys. Soc. London*, **52**, 217 (1940).

trical resistance, and specific heat of the alloy all indicate that at 510° C. an order-disorder transformation takes place involving Ni_3Mn. The ordered structure is ferromagnetic with Curie point at 460° C.

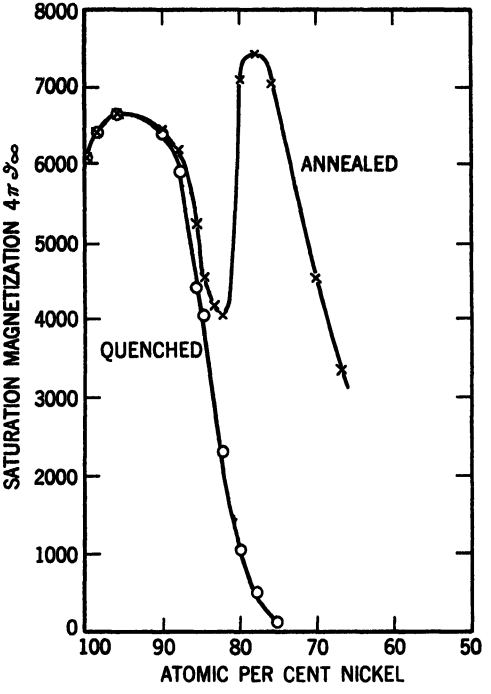


FIG. 50.—Saturation magnetization as a function of concentration for nickel-manganese alloy.

Some of the many publications on alloys of nickel with non-ferromagnetic metals are listed below.[86–100] A few of the main results achieved will be discussed briefly.

[86] C. Manders, *Ann. Phys.*, **5**, 167 (1936). (Ag, Zr, Pb, Au, Al, Ti, Si, Sn, Sb, V, As, Cr, Mo, W, Mn, Ru, Pd, Pt)
[87] E. Vogt and H. Krueger, *Ann. Physik*, **18**, 755 (1933). (Au)
[88] R. Gans and A. Fonseca, *Ann. Physik*, **61**, 742 (1920). (Cu)
[89] E. H. Williams, *Phys. Rev.*, **38**, 828 (1931). (Cu)
[90] K. E. Grew, *Proc. Roy. Soc. London*, **A145**, 509 (1934). (Cu)
[91] W. H. Ross, *Phys. Rev.*, **46**, 46 (1934). (Cu)
[92] G. Gustafsson, *Ann. Physik*, **28**, 121 (1937). (Cu)
[93] W. Gerlach, *Z. Metallkunde*, **28**, 80, 183 (1936). (Be)
[94] J. Schramm, *Z. Metallkunde*, **30**, 327 (1938). (Zn)
[95] Y. G. Dorfman and S. Sidorov, *Compt. rend. acad. sci. URSS*, **19**, 381 (1938). (Zn)
[96] L. F. Bates and J. H. Prentice, *Proc. Phys. Soc. London*. **51**. 419 (1939). (Hg)

For many nickel alloys the susceptibilities are reasonably well represented by the equation $\chi = a + C/(T + \Delta)$. In the copper alloys, for instance, the results indicate that there exists for nickel a strong paramagnetism independent of temperature. Relationships between the atomic susceptibility and temperature for various nickel concentrations are shown in Fig. 51, and the atomic susceptibility of nickel as a function of nickel concentration in Fig. 52.

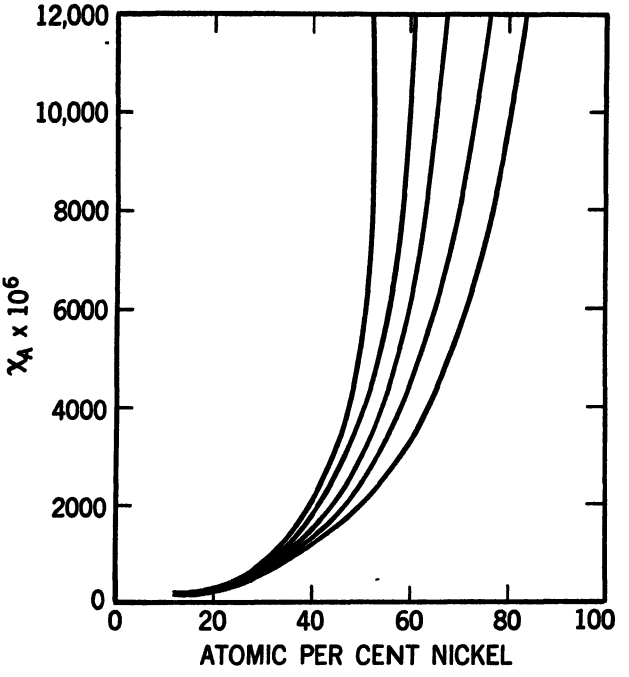


FIG. 51.—Relationship between atomic susceptibility and nickel concentration at several temperatures, for nickel-copper alloys.

In nickel-zinc alloys the γ-phase has an abnormally high diamagnetism suggesting zero moment for nickel. Extremely high diamagnetism is found in other γ-phases, for instance in brass.[101]

Nickel amalgams are interesting. When first prepared the amalgams are diamagnetic, in sharp contrast to those of iron and of cobalt which are

[97] L. F. Bates and C. J. W. Baker, *Proc. Phys. Soc. London*, **52**, 436, 443 (1940). (Hg)

[98] A. Foster, *Proc. Leeds Phil. Lit. Soc. Sci. Sect.*, **2**, 401 (1933). (Cr)

[99] G. Grube and O. Winkler, *Z. Elektrochem.*, **44**, 423 (1938). (Mo)

[100] A. Kussmann and H. Nitka, *Physik. Z.*, **39**, 373 (1938). (Pt)

[101] H. Endo, *Science Repts. Tôhoku Imp. Univ., First Ser.*, **14**, 479 (1925).

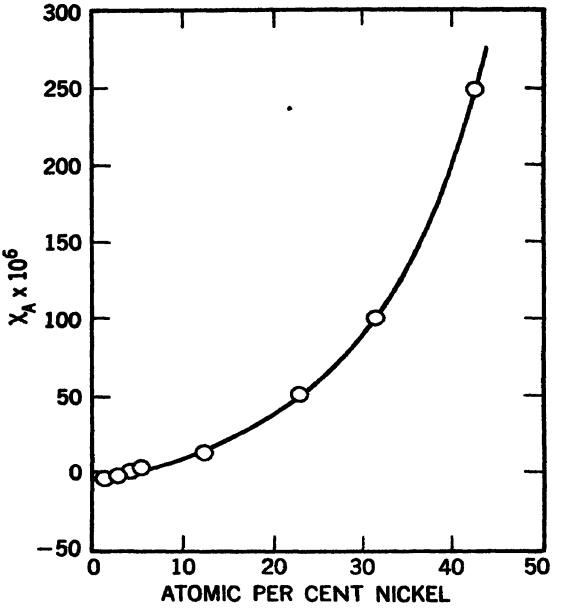


FIG. 52.—Atomic susceptibility of nickel as a function of nickel concentration in nickel-copper alloys.

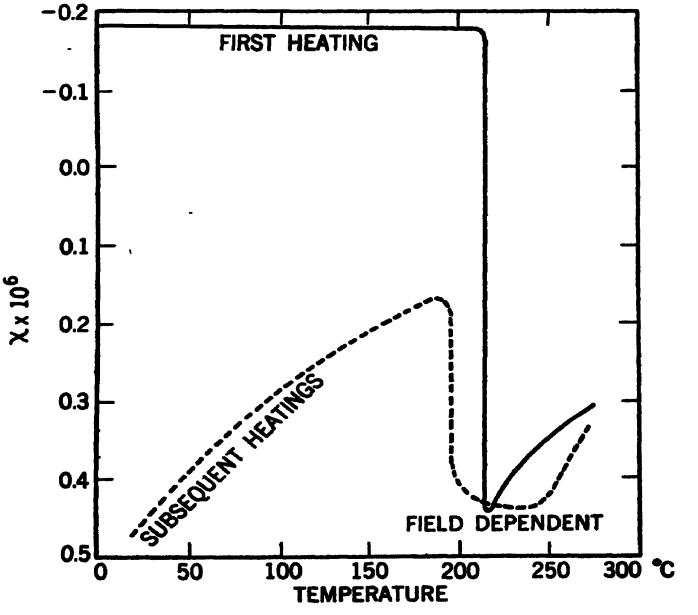


FIG. 53.—Nickel amalgam.

invariably ferromagnetic. But when the nickel amalgam is heated to 225° it changes irreversibly to ferromagnetism. This transition is shown in Fig. 53.

Nickel-molybdenum alloys show rather complicated magnetic characteristics. The Curie temperatures of the ferromagnetic solid solutions decrease linearly with molybdenum content and reach 0° C. when the proportion of molybdenum reaches 10.5 per cent.

6. Cobalt and Cobalt Alloys

The intensity of magnetization of cobalt at saturation lies between that of iron and of nickel. The ferromagnetic Curie point is given as 1120° ± 20° C. by Stoner (*op. cit.*,[14] p. 384) who surveys the literature on the subject. Farcas[104] gives 1145° C. As for the other ferromagnetic metals the magnetic properties are dependent on the previous history of the specimen. The magnetothermal characteristics of cobalt in polycrystalline and in single crystal form have been studied by Kaya,[102] and by Honda and Masumoto.[103]

Some recent publications on cobalt alloys are listed below.[104–107] Addition of chromium, aluminum, tungsten, or molybdenum in all cases results in progressive lowering of the magnetic moment of the cobalt. According to Farcas alloys of cobalt with tungsten and molybdenum are not ferromagnetic. Cobalt amalgams like those of iron are ferromagnetic. The cobalt may be concentrated into a single small globule with the aid of a magnet.

7. Oxides and Hydroxides of Iron

Ferromagnetism is by no means limited to metals and alloys. Various oxides, hydroxides, and salts of the ferromagnetic elements exhibit this property, as do a few compounds of elements near iron in the periodic table. From the chemist's standpoint these substances are often of as much or more interest than the metals and alloys. They have not as yet, however, assumed anything like the same technological importance. Apart from its scientific interest, the study of such ferromagnetic com-

[102] S. Kaya, *Science Repts. Tôhoku Imp. Univ., First Ser.*, **17**, 1157 (1928).

[103] K. Honda and H. Masumoto, *Science Repts. Tôhoku Imp. Univ., First Ser.*, **20**, 323 (1931).

[104] T. Farcas, *Ann. phys.*, **8**, 146 (1937). (Cr, Al, W, Mo); *Ann. sci. univ. Jassy*, **23**, I, 125 (1937). (Curie points)

[105] L. F. Bates and C. J. W. Baker, *Proc. Phys. Soc. London*, **52**, 443, (1940). (Hg)

[106] F. W. Constant, *Phys. Rev.*, **34**, 1217 (1929); **35**, 116 (1930); **36**, 1654 (1930). (Pt, Pd)

[107] G. Grube and O. Winkler, *Z. Elektrochem.*, **41**, 52 (1935). (Pd)

pounds is important in the magnetic concentration of minerals,[108,109] and in the construction of permanent oxide magnets.[110,111] The magnetic properties of natural and artificial iron-oxygen compounds, and the relationships among the hydrates and oxides of iron are reviewed by Luyken and Kraeber,[112] and by Welo and Baudisch.[113]

The ferromagnetism of magnetite, Fe_3O_4, has been known since the earliest times. Socrates refers to it in one of the Platonic dialogues, and, even earlier, Thales of Miletus, in the sixth century before Christ, is supposed to have had knowledge of the mineral. Stoner (*op. cit.*,[14] p. 1) gives an interesting account of the history of magnetite. It occurs widely distributed in nature. The name is perhaps derived from Magnesia, the region in Asia Minor where the mineral was found in abundance.

Artificial magnetite may be prepared as follows:[114] a solution containing 1 mole of $FeSO_4$ and 2 moles of $Fe_2(SO_4)_3$ is poured into excess boiling solution of NaOH. The precipitate of Fe_3O_4 is washed free from alkali and dried in a desiccator. An alternative preparation yielding very near the stoichiometric Fe_3O_4 ratio is obtained by burning $Fe(CO)_5$ in a limited supply of air.

Magnetite prepared in different ways has rather different magnetic characteristics and may differ quite sharply from natural magnetite. The ferromagnetic Curie point is about 590° C. The intensity of magnetization at saturation is about the same as that of nickel, or less than a third of that of electrolytic iron. The hysteresis of precipitated magnetite has been studied by Welo and Baudisch.[115,116] Lattice discontinuities affect the magnetic properties, including the hysteresis.[117] Age-hardening produces an increase in the hysteresis constants as do the temperature and nature of the reducing agent if the magnetite is prepared by reduction of hematite. There appear to be two forms of natural magnetite one of which is capable of adding chlorine, the other not. The latter has a discontinuity in the magnetization curve at − 138° C. This is attributed

[108] C. W. Davis, *U. S. Bur. Mines, Repts. Investigations Tech. Papers*, No. 3268, 91 (1935).

[109] E. T. Hayes, *U. S. Bur. Mines, Repts. Investigations Tech. Papers*, No. 3570 (1941).

[110] Y. Kato and T. Takai, *J. Inst. Elec. Engrs. Japan*, 53, 408 (1933).

[111] Y. Kato, T. Takai, N. Kawai, and H. Aikawa, *J. Chem. Soc. Japan*, 55, 584 (1934).

[112] W. Luyken and L. Kraeber, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, 16, 169 (1934); 17, 149 (1936).

[113] L. A. Welo and O. Baudisch, *Am. J. Sci.*, 28, 139 (1934); *Chem. Rev.*, 15, 45 (1934). This excellent article is the source of most of the information in this section.

[114] L. A. Welo and O. Baudisch, *Phil. Mag.*, 50, 399 (1925).

[115] O. Baudisch and L. A. Welo, *Naturwissenschaften*, 14, 1005 (1926).

[116] L. A. Welo and O. Baudisch, *Phil. Mag.*, 3, 396 (1927).

[117] D. J. Doan, *U. S. Bur. Mines Repts. Investigations Tech. Papers*, No. 3400, 65 (1938).

by Forrer [118] to direct bonds between pairs of Fe^{++} ions which are ruptured at $-$ 138° C. Such bonds are supposed to be absent in the other form of magnetite.

Magnetite, although cubic, exhibits ferromagnetic anisotropy, a fact which was discovered by Weiss.[119] Theoretical reasons for this are discussed by McKeehan.[120] As mentioned above, magnetite prepared in different ways has somewhat different magnetic characteristics and this is also true of natural magnetites from different sources.[121] The almost unique magnetic position of magnetite amongst minerals, and its possible uses are discussed by Dean and Davis.[122]

Colloidal magnetite has been examined by Elmore.[123]

Ferric oxide, Fe_2O_3, has been studied extensively. It has some interesting and complicated magnetic properties. There is a strongly ferromagnetic cubic form, γ-Fe_2O_3, and an extremely weakly ferromagnetic rhombohedral form, α-Fe_2O_3 which is the mineral hematite. Possibly still other forms exist. Our knowledge of these complex interrelationships is due mostly to Welo and Baudisch, and in part to Forrer.

If Fe_3O_4 is oxidized in oxygen at 220° C. there is a change of color from black to red accompanied by no appreciable change of magnetic properties. If the temperature is now raised, at about 550° C. an irreversible change takes place with the loss of almost all of the ferromagnetism and the formation of α-Fe_2O_3. But if Fe_3O_4 is heated in the absence of oxygen it retains its ferromagnetism up to its Curie point and it may even be heated above 800° C. without destroying the reversibility of its magnetothermal characteristics. The permeabilities of the various phases are shown in Fig. 54. The magnetic properties of γ-Fe_2O_3 appear to be almost identical with those of Fe_3O_4, and the Fe_2O_3 derived by oxidation of Fe_3O_4 at low temperature retains the magnetite structure. Fe_3O_4 and γ-Fe_2O_3 differ, therefore, only in color and in the presence of extra oxygen atoms which seem to be without influence on the magnetic properties. Sachsse [124] reports that each iron atom is surrounded by eight nearest neighbors both in Fe_3O_4 and in γ-Fe_2O_3 but not in α-Fe_2O_3. There is no ferrous iron in γ-Fe_2O_3. This observation seems to dispose of the suggestion that its magnetic properties are due to solid solution of magnetite in

[118] R. Forrer, *Compt. rend.*, **207**, 281 (1938).

[119] P. Weiss, *J. phys.*, **5**, 435 (1896).

[120] L. W. McKeehan, *Phys. Rev.*, **53**, 307 (1938).

[121] F. Y. Levinson-Lessing, *Centr. Minerat. Geol.*, A1932, 369; O. N. Al'Thauzen, *Compt. rend. acad. sci., URSS*, **31**, 566 (1941).

[122] R. S. Dean and C. W. Davis, *Am. Inst. Mining Met. Engrs., Tech. Pub.*, No. 795 (1937).

[123] W. C. Elmore, *Phys. Rev.*, **54**, 1092 (1938).

[124] H. Sachsse, *Z. physik. Chem.*, B9, 83 (1930).

rhombohedral α-Fe_2O_3.[125] Haul and Schoon [126] show that the unit cell of γ-Fe_2O_3 is $Fe_{24}O_{36}$. The oxidation reaction is therefore

$$\underset{\text{(magnetite)}}{Fe_{24}O_{32}} + 2O_2 \rightarrow \underset{\gamma\text{-}(Fe_2O_3)}{Fe_{24}O_{36}}$$

No essential difference was found in lattice constants or intensity distribution for γ-Fe_2O_3 prepared in several different ways. On chemical

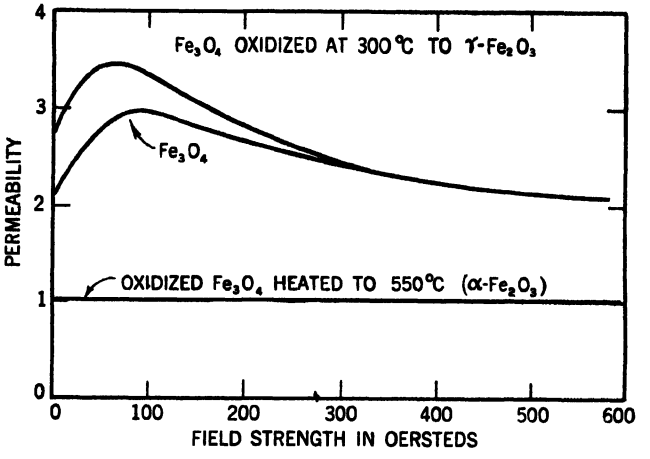
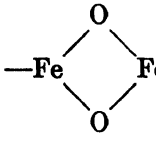


FIG. 54.—Permeability as a function of field strength for Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3.

grounds Krause [127] suggests that all ferromagnetic iron oxides contain the



group.

Various magnetic characteristics of γ-Fe_2O_3 are given by Koenigsberger.[128] There is some doubt as to the Curie point. Welo and Baudisch give 620° C. Other values range down to 500° C. The precise transition point for the change from cubic γ-Fe_2O_3 to rhombohedral α-Fe_2O_3 is also indefinite and depends on the method of purification. The ferromagnetic oxide may be stabilized by introduction of sodium hydroxide, alumina, or silica,[129] but the ferromagnetism of this substance is slowly diminished on standing.

[125] A. Michel and A. Girard, *Compt. rend.*, **201**, 64 (1935).
[126] R. Haul and T. Schoon, *Z. physik. Chem.*, **B44**, 216 (1939).
[127] A. Krause, *Z. physik. Chem.*, **B26**, 58 (1934).
[128] J. G. Koenigsberger, *Naturwissenschaften*, **22**, 90 (1934).
[129] J. Huggett, *Ann. chim.*, [10], **11**, 447 (1929).

Magnetic measurements have been used by Lille [130] to follow the rate of oxidation of magnetite in a stream of oxygen and nitrogen.

Magnetite and γ-Fe_2O_3 are by no means the only ferromagnetic oxides of iron which have been reported. There is a group of oxide hydrates which will be discussed below, and there are also several oxides of rather doubtful status. Michel and Gallissot [131] suggest that the variable Curie points found for some of these substances may be due to a dependence of Curie point on the size of the crystallites. So far as the writer knows, however, this view is not supported by any direct studies of the influence of particle size on the Curie point. Bhargava and Prakash [132] state that the oxides resulting from heating ferrous oxalate in air are strongly paramagnetic, but that the oxides prepared from ferric oxalate or ferric benzoate are ferromagnetic. Hilpert, Maier, and Hoffmann [133] claim that hydrolysis of basic iron chloride, FeOCl, followed by dehydration at 250° C. yields a new ferromagnetic iron oxide. This view is supported by Forrer [134] who shows, however, that rapid dehydration at 275° C. yields an oxide of only slight ferromagnetism, but slow dehydration yields a strongly ferromagnetic oxide whose Curie point is 350° C. If this is heated more strongly another ferromagnetic state results with Curie point 520° C. Finally, on heating at 600° C. a non-ferromagnetic product results. The first strongly ferromagnetic form is the only one with the cubic lattice of γ-Fe_2O_3, all the others being rhombohedral. Glemser and Gwinner [135] claim the preparation of a new ferromagnetic hexagonal ferric oxide by oxidation of a ferrous salt after addition of excess sodium hydroxide. Whether or not these various products represent distinct chemical substances is uncertain. Chaudron and Michel [136a] insist that there are only two varieties of Fe_2O_3: a rhombohedral, stable, feebly ferromagnetic form with Curie point 675° C.; and a cubic, unstable, strongly ferromagnetic form, transformable into the rhombohedral form at about 500° C., and readily dissociated in a vacuum into Fe_3O_4 and oxygen.

Ferric oxide forms two hydrates α-$Fe_2O_3 \cdot H_2O$, or α-FeOOH, which is the mineral goethite, and γ-$Fe_2O_3 \cdot H_2O$, or γ-FeOOH, which is lepidocrocite.[136b, 136c] The magnetic and crystallographic properties of these

[130] R. Lille, *Compt. rend.*, 208, 1891 (1939).

[131] A. Michel and M. Gallissot, *Compt. rend.*, 207, 140 (1938).

[132] L. N. Bhargava and S. Prakash, *Z. anorg. allgem. Chem.*, 217, 27 (1934).

[133] R. S. Hilpert, K.-H. Maier, and A. Hoffmann, *Ber.*, 71B, 2676 (1938).

[134] R. Forrer, *Compt. rend.*, 207, 670 (1938).

[135] O. Glemser and E. Gwinner, *Naturwissenschaften*, 26, 739 (1938); *Z. anorg. allgem. Chem.*, 240, 161 (1939).

[136a] G. Chaudron and A. Michel, *Compt. rend.*, 208, 90 (1939).

[136b] O. Baudisch and L. A. Welo, *Naturwissenschaften*, 21, 659 (1933).

[136c] L. A. Welo and O. Baudisch, *Phil. Mag.*, 17, 753 (1934).

substances have been studied by Albrecht.[137] Both these substances are paramagnetic with the same susceptibility of 42×10^{-6}. Both substances obey the Curie law.[138,139] The dehydration of hydrated γ-ferric oxide at moderate temperatures yields ferromagnetic γ-Fe_2O_3, a fact first observed long ago by von Kobell.[140] Further heating above about 500° C. will, of course, yield α-Fe_2O_3. The transition of lepidocrocite to γ-Fe_2O_3 has been carefully investigated by Welo and Baudisch.[141,142] It appears that the compounds γ- and α-FeOOH may be intermediates in the transition γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$.[143] γ-Fe_2O_3, the ferromagnetic form, is very readily converted to α-Fe_2O_3 if heated with water in a sealed tube. Further studies on the preparation and magnetic properties of lepidocrocite are reported by Michel and Gallissot.[144] Colloidal Fe_2O_3 (siderac) has been studied by Elmore,[123] and by Boutaric and Bonneviale.[145] Baudisch reports on the use of colloidal γ-Fe_2O_3 as a biological indicator.[146]

Hematite, α-Fe_2O_3, is commonly regarded as being paramagnetic with a susceptibility of about 20×10^{-6}. But careful studies by Hayes [109] and others show that it may actually be ferromagnetic with an extremely low saturation permeability. Hayes points out that (*a*) its susceptibility is dependent on field strength, (*b*) it shows residual magnetism, (*c*) it requires a definite coercive force to reduce the residual magnetism to zero, and (*d*) it has a Curie point. These characteristics are probably not attributable to ferromagnetic impurities. But samples of the oxide prepared in different ways give varying susceptibilities at room temperature. Michel [147] points out that the variations depend on the temperature to which the oxide has been heated, and that treatment at 1300° C. is necessary before the thermomagnetic curves become reversible. Chevallier and Bégui [148] state that the Curie point is between 690° and 700° C. Above this point the susceptibility is 19×10^{-6} which is characteristic of all iron oxides at high temperatures. Hematite does not follow the Curie law, the susceptibility is almost independent of temperature. No difficulty is experienced in the artificial preparation of α-Fe_2O_3. It is the normal

[137] W. H. Albrecht, *Ber.*, **B62**, 1475 (1929).
[138] W. H. Albrecht and E. Wedekind, *Z. anorg. allgem. Chem.*, **202**, 205; 209 (1931).
[139] R. Chevallier and S. Mathieu, *Compt. rend.*, **207**, 58 (1938).
[140] F. von Kobell, *Grundzüge der Mineralogie, Nürnberg*, **1838**, p. 304.
[141] L. A. Welo and O. Baudisch, *Phil. Mag.*, **17**, 753 (1934).
[142] O. Baudisch and L. A. Welo, *Naturwissenschaften*, **21**, 659 (1933).
[143] L. A. Welo and O. Baudisch, *Phil. Mag.*, **24**, 80 (1937); **31**, 103 (1941).
[144] A. Michel and M. Gallissot, *Compt. rend.*, **206**, 1252 (1938).
[145] A. Boutaric and R. Bonneviale, *Bull. soc. chim. mém.*, **2**, 1998 (1935).
[146] O. Baudisch, *Naturwissenschaften*, **23**, 512 (1935).
[147] A. Michel, *Compt. rend.*, **202**, 1769 (1936).
[148] R. Chevallier and Z. E. Bégui, *Bull. soc. chim. mém.*, **4**, 1735 (1937).

oxide obtained on precipitation of ferric hydroxide from a nitrate solution, followed by ignition. A variation of susceptibility with grain size is reported by Chevallier and Mathieu.[149] The same problem, and that of solid solution formation among the oxides of iron, is discussed by Michel.[150] Solid solutions of FeO and Fe_2O_3 are also discussed, together with the effect of added silica, by Leitgebel and Bockemühl.[151] A possible method of detecting Fe_2O_3 in glass sand by measurement of its susceptibility is outlined by Charlesworth and Long.[152]

Pure ferrous oxide hydrate is stated by Welo and Baudisch to be paramagnetic with χ about 20×10^{-6}. On standing, it changes spontaneously into α-Fe_2O_3.

There is some doubt as to whether ferric hydroxide, $Fe(OH)_3$, actually exists in a ferromagnetic form. Quartaroli [153] finds that a compound with susceptibility a hundred times greater than normal $Fe(OH)_3$ may be obtained by precipitation from Mohr's salt followed by hydrogen peroxide oxidation. Further study of this substance seems called for. The adsorbtive properties of the hydroxide parallel its abnormally high susceptibility.[154] There seems little doubt that the magnetic properties of ferric hydroxide are influenced by the amount and concentration of base used in the precipitation.[155] The preparation of ferromagnetic gels of $Fe(OH)_3$ is claimed by Katsurai and Yamasaki.[156]

There exist, in addition to the compounds already described, a large number of substances formed by the union of iron oxide and other metal oxides. Some of these will be discussed in the following section.

8. Other Ferromagnetic Compounds of Iron

Compounds formed by the replacement of FeO in $FeO \cdot Fe_2O_3$ by other metal oxides are called ferrites. Some of these substances have received very intensive study by Hüttig, reference to whose work will be made in the following chapter. Some of the ferrites have complicated and often irreversible magnetic behavior, but most of them are definitely ferromagnetic. Michel [150] has studied the ferrites of barium, strontium, lead, nickel, magnesium, copper, calcium, beryllium, silver, mercury, and

[149] R. Chevallier and S. Mathieu, *Compt. rend.*, **204**, 854 (1937).

[150] A. Michel, *Ann. chim.*, **8**, 317 (1937).

[151] W. Leitgebel and K. Bockemühl, *Z. anorg. allgem. Chem.*, **225**, 209 (1935).

[152] G. Charlesworth and F. A. Long, *Proc. Leeds Phil. Lit. Soc., Sci. Sect.*, **3**, 515 (1939).

[153] A. Quartaroli, *Gazz. chim. ital.*, **63**, 279 (1933).

[154] E. Vallesi, *Gazz. chim. ital.*, **64**, 161 (1934).

[155] R. Chevallier and S. Mathieu, *Compt. rend.*, **206**, 1469, 1955 (1938).

[156] T. Katsurai and K. Yamasaki, *Kolloid-Z.*, **84**, 311 (1938).

lithium. Other references are indicated below.[157–165a] For manganese ferrite Kussmann and Nitka state that ferromagnetism is associated with a solid solution stable at high temperature and having a face-centered cubic (spinel) structure. Reproducible results are rather difficult to obtain with these substances. If the preparations are obtained in the usual way by prolonged heating at high temperatures of the oxides, then the susceptibility and magnetothermal curves often depend on the time and temperature of heating. Raychaudhuri reports that nickel ferrite, $NiFe_2O_4$, exhibits the phenomenon of "magnetic viscosity" or a time lag in the attainment of maximum magnetization in a given field. This is of an entirely different order from the familiar time lag in the magnetization of iron. Redslob and Forestier state that tin and cadmium ferrites are not ferromagnetic. For the ferromagnetic ferrites the Curie temperatures all lie between 400° and 600° C. When a ferromagnetic component and a non-magnetic component coexist, the Curie point is constant and the saturation intensity varies linearly with concentration. With regard to the coercive force of such substances it seems safe to conclude that a high coercive force indicates a heterogeneous mixture and a low one a homogeneous phase.[165b]

It is commonly thought that ferromagnetic substances have high electrical conductivity, but this is not invariably true. Manganese ferrite, which is ferromagnetic, has, for instance, a specific resistivity of 10^5 at room temperature.[165c]

Some sulfides of iron also exhibit ferromagnetism. Hilpert, Maier, and Hoffmann [166] prepared thiomagnetite, $FeS \cdot Fe_2O_3$, by heating equimolar amounts of FeS and Fe_2O_3 in an atmosphere of nitrogen. The compound has a Curie point at 580° C. It also shows an anomaly at − 138° to − 118° C., similar to that shown by one variety of magnetite.

[157] A. Michel and G. Chaudron, *Compt. rend.*, 200, 2171 (1935). (Ba, Pb)

[158] A. Kussmann and H. Nitka, *Physik. Z.*, 39, 208 (1938). (Mn)

[159] D. P. Raychaudhuri, *Indian J. Phys.*, 9, 417, 425 (1935). (Mn, Co, Cu, Zn, Ni).

[160] S. Hilpert and A. Wille, *Z. physik. Chem.*, B18, 291 (1932). (Many different ferrites)

[161] H. Forestier, *Compt. rend.*, 201, 45 (1935). (Ba, Sr, Pb, Ca, Cd)

[162] T. Takai, T. Yasuda, and S. Isihara, *J. Inst. Elec. Engrs. Japan*, 59, 568 (1939). (Cu, Co)

[163] A. Schulze, *Tech. Blätter*, 28, 410 (1938). (Mn)

[164] F. Redslob and H. Forestier, *Compt. rend.*, 206, 250 (1938). (Sn, Cd)

[165a] H. Forestier and R. Lille, *Compt. rend.*, 205, 848 (1937). (Mg, Sr, Ni, Cu, Ba, Pb)

[165b] A. Kussmann and B. Scharnov, *Z. Physik*, 54, 1 (1929).

[165c] J. L. Snoek, *Physica*, 3, 463 (1936).

[166] R. S. Hilpert, K.-H. Maier, and A. Hoffmann, *Ber.*, 71B, 2682 (1938).

Ferrous sulfide, FeS, is probably ferromagnetic [167] (see Stoner, *op. cit.*,[14] p. 529) although Miyahara [168] claims that the presence or absence of ferromagnetism depends on the amount of dissolved sulfur in the compounds. This is not impossible as somewhat similar behavior is exhibited by non-stoichiometric nickel oxide. It is not entirely clear from Miyahara's paper what condition favors the establishment of ferromagnetism. Weiss and Forrer give the Curie point as 320° C. The saturation intensity is not high. Compounds of the type of iron pyrites, FeS_2, and pyrrhotite, Fe_7S_8, are also ferromagnetic although not greatly so. They have been studied by Michel [150] and by others. Pyrrhotite [169,170] is very peculiar in its magnetic properties. Its ferromagnetism is practically restricted to the base of the hexagonal plane. It is paramagnetic along other planes.

Among other ferromagnetic compounds of iron the carbides, nitrides, and borides may be mentioned. Cementite, Fe_3C, is of considerable interest from the part it plays in influencing the magnetic properties of steel. It has a fairly high saturation intensity, and its Curie point is about 215° C. It is probable that still other compounds of iron will show ferromagnetism, especially those which are "magnetically concentrated." In fact as has already been shown, incipient ferromagnetism, especially at low temperatures, is a fairly general phenomenon.

9. Non-ferrous Ferromagnetic Substances

Ferromagnetism has been reported for a large variety of substances. These all contain, if not one or more of the ferromagnetic elements, at least manganese or chromium. There is a possibility that even vanadium or titanium compounds or alloys might show ferromagnetism, especially at low temperatures.

Compounds of the pyrites structure such as MnS_2 and NiS_2 both have susceptibilities slightly dependent on field strength.[169] The corresponding cobalt compound containing slightly less than the stoichiometric amount of sulfur is quite definitely ferromagnetic at 90° K. but not at higher temperatures. Nickel oxide, NiO, has often been reported as being ferromagnetic, but this seems to be due to metallic nickel. The question will be discussed further in the following chapter. Similarly it is not entirely clear if cobaltous oxide, CoO, is ferromagnetic, although Bhat-

[167] P. Weiss and R. Forrer, *Ann. phys.*, 12, 279 (1929). (This paper includes data on several other ferromagnetic compounds)

[168] S. Miyahara, *Proc. Phys.-Math. Soc. Japan*, 22, 358 (1940).

[169] H. Haraldsen and W. Klemm, *Z. anorg. allgem. Chem.*, 223, 409 (1935).

[170] D. R. Inglis, *Phys. Rev.*, 45, 118 (1934). (Theoretical)

nagar, Prakash, and Qayyum [171] state that the oxide obtained by heating metallic cobalt in nitric oxide is so. The oxide, Co_3O_4, sometimes exhibits ferromagnetism but this may be due to partial reduction to the metal. Bose and Raychaudhuri [172] have reported both CoO and Co_3O_4 as being paramagnetic.

Manganese forms several ferromagnetic substances in addition to hauerite, MnS_2. The best known of these are the "Heusler alloys" [173a,b] which consist of aluminum, copper, and manganese. The maximum intensity of magnetization at saturation is about the same as that for nickel, and the Curie temperature is about 330° C. In these alloys the aluminum may be replaced by tin, arsenic, antimony, bismuth, or boron. The copper may be replaced by silver. The intermetallic compounds $SnMn_4$ and $SnMn_2$ are also ferromagnetic.[174]

Ferromagnetism has been reported for the following compounds, MnP, Mn_5P_2, MnAs, Mn_3As_2, Mn_2Sb, Mn_3Sb_2, MnSb, MnBi, MnB, Mn_3C, Mn_3N_2, Mn_6N_2, and Mn_7N_2, and MnS. Selenides, tellurides, silicides, and possibly hydrides of manganese also have ferromagnetic properties.[175–182]

Ferromagnetism is also observed in some chromium compounds such as the telluride, hydride, arsenides, and possibly certain oxides.[183–186] Bates and Taylor [187] find that when powdered chromium, obtained from chromium amalgam, is heated with sulfur in vacuum ferromagnetic com-

[171] S. S. Bhatnagar, B. Prakash, and M. A. Qayyum, *J. Indian Chem. Soc.*, **18**, 540 (1941).

[172] A. K. Bose and D. P. Raychaudhuri, *Science and Culture*, **3**, 246 (1937).

[173a] S. Valentiner and G. Becker, *Z. Physik*, **83**, 371 (1933).

[173b] L. A. Carapella and R. Hultgren, *Trans. Am. Inst. Mining Met. Engrs.*, No. 1405 (1941).

[174] H. H. Potter, *Proc. Phys. Soc.*, **41**, 135 (1939); *Phil. Mag.*, **12**, 255 (1931).

[175] O. von Auwers, *Z. anorg. allgem. Chem.*, **108**, 49 (1919).

[176] L. F. Bates, *Proc. Roy. Soc. London*, **A117**, 680 (1928); *Phil. Mag.*, **8**, 714 (1929); *Proc. Phys. Soc. London*, **42**, 441 (1930); **43**, 87 (1931); *Phil. Mag.*, **13**, 393 (1932); **16**, 657 (1933). (As)

[177] A. Kussmann and B. Scharnov, *Z. Physik*, **47**, 770 (1928).

[178] R. Ochsenfeld, *Ann. Physik*, **12**, 353 (1932). (N)

[179] B. G. Whitmore, *Phil. Mag.*, **7**, 125 (1929). (As, P)

[180] E. Persson, *Naturwissenschaften*, **16**, 613 (1928); *Z. Physik*, **57**, 115 (1929).

[181] K. Thielmann, *Ann. Physik*, **37**, 41 (1940). (Bi)

[182] W. Messkin and A. Kussmann, *Die Ferromagnetischen Legierungen.* J. Springer, Berlin 1932.

[183] V. M. Goldschmidt, *Ber.*, **60**, 1263 (1927); see also Ochsenfelder (*loc. cit.*).

[184] L. F. Bates and A. Baqi, *Proc. Phys. Soc. London*, **48**, 781 (1936).

[185] H. Nowotny and O. Arstadt, *Z. phys. Chem.*, **B38**, 461 (1938).

[186] T. Soné and T. Ishiwara, *Science Repts. Tôhoku Imp. Univ., First Ser.*, **3**, 271 (1914).

[187] L. F. Bates and G. G. Taylor, *Proc. Phys. Soc. London*, **51**, 33 (1939).

pounds are formed. At least two combinations of uncertain composition occur. Their Curie points are at 30° and 90–100° C. Chromium-platinum alloys are generally paramagnetic, but Friederick and Kussmann find that in the concentration range 7 to 20 per cent chromium the alloys are ferromagnetic with Curie points ranging from 50° C. on the platinum side to 900° C. on the chromium side.[188]

Mention has already been made in the previous chapter of metallic gadolinium which is ferromagnetic below about 16° C.

[188] E. Friederick and A. Kussmann, *Physik. Z.*, **36**, 185 (1935).

CHAPTER NINE

APPLIED MAGNETOMETRIC ANALYSIS

In the previous chapters many applications of magnetochemistry have been presented. There remain, however, a group of studies not readily classified with any topics yet covered. Some of these make up active branches of magnetochemistry, others refer to quite obscure and little known phenomena. References to a few review articles in this field are given below.[1–7]

1. Magnetometric Analysis of the Rare Earths

The familiar reactions of analytical chemistry have little application to the analysis of rare earth mixtures. Recourse must in most instances be made to physical methods, some of which are unique in this field. Because of the large differences in susceptibilities, magnetic methods are well suited for the quantitative analysis of rare earth mixtures. The method is in general, however, limited to binary mixtures and must often be supplemented by use of the absorption spectra and other criteria.

Magnetic analysis of rare earth mixtures is frequently accomplished with the Curie-Chéneveau balance (p. 10) although more elaborate instruments may be used. The method is based on the Wiedemann mixture law $\chi = \chi_1 p_1 + \chi_2 p_2 + \cdots \chi_n p_n$, where χ is the susceptibility of the mixture and χ_1, p_1 etc., the susceptibilities and weight fractions of the respective constituents of the mixture. The temperature coefficient of susceptibility for most paramagnetic substances is only about 1/300 at room temperature. No careful temperature control is therefore necessary unless accuracy greater than one per cent is aimed at, and this will seldom be attained with the Curie-Chéneveau balance.

Table XLII gives susceptibilities per gram for the known rare earth sesquioxides at 20° C. It will be recalled that cerium, praseodymium, and terbium are often found in the form of their higher oxides,

[1] A. Kussmann, *Z. Metallkunde*, **25**, 259 (1933).
[2] W. Klemm, *Angew. Chem.*, **48**, 617 (1935).
[3] H. Haraldsen, *Tids. Kjemi Bergvesen*, **18**, 69 (1938).
[4] S. S. Bhatnagar, *Science and Culture*, **3**, 466 (1938).
[5] W. Klemm, *Z. Elektrochem.*, **45**, 583 (1939).
[6] H. Bittel and W. Gerlach, *Physik. regelmäss Ber.*, I., No. 3, 119 (1939).
[7] P. W. Selwood, *J. Chem. Education*, **19**, 181 (1942).

TABLE XLII

MAGNETIC SUSCEPTIBILITIES OF THE RARE EARTHS AT 20° C.

Oxide	$\chi \times 10^6$	Oxide	$\chi \times 10^6$
Y_2O_3	+ 0.5*	Tb_2O_3	—†
La_2O_3	− 0.4	Dy_2O_3	219
Ce_2O_3	—†	Ho_2O_3	229
Pr_2O_3	(29)†	Er_2O_3	189
Nd_2O_3	30	Tu_2O_3	—
Sm_2O_3	5.8	Yb_2O_3	38
Eu_2O_3	30	Lu_2O_3	(− 0.3)
Gd_2O_3	135		

* Yttrium oxide might certainly be expected to be diamagnetic, but the small positive value given in the International Critical Tables has recently been checked by Mr. H. Cutforth in the author's laboratory. He worked with a sample of "atomic weight purity" Y_2O_3 obtained from the University of Illinois.

† Cerium, praseodymium, and terbium commonly form higher oxides, for some of which magnetic data are available. The value given for Pr_2O_3 is estimated. It is astonishing that after so much research in the field of the magnetic properties of the rare earths we are still without adequate data for several of these substances.

and that samarium, europium, and ytterbium are fairly readily reducible. Valence changes make a profound change in the susceptibilities under investigation, but apart from this difficulty the sesquioxides are readily obtainable by ignition of the precipitated oxalates and are most convenient for magnetic analysis.

The method is most useful when the two constituents of a mixture differ widely in susceptibility, as do europium and gadolinium, or especially when one constituent is diamagnetic, as in the elimination of ytterbium from lutecium. In a few cases the method may be applied to ternary mixtures. When the object of the study is the preparation of pure samples of one of the diamagnetic earths, La_2O_3 or Lu_2O_3, the magnetic method may be made extremely searching by carrying the susceptibility measurements to low temperatures. For instance, commercial lanthanum oxide is generally paramagnetic or at least shows a pronounced temperature coefficient of susceptibility. By prolonged and careful purification it is possible to obtain samples whose susceptibilities are virtually, of not quite, independent of temperature. This method is so powerful that until it has been applied, no atomic weight determination on lanthanum or lutecium should be considered complete.

Rare earths are generally purified by a tedious process of fractional crystallization. Approaching purity may be determined by plotting the magnetic susceptibility, or apparent equivalent weight, against fraction

number. A horizontal region in such a plot is evidence for isolation of a pure compound. On the other hand it may correspond to the establishment of a mixture that cannot be resolved by the particular fractionation process being used.

2. Detection of Ferromagnetic Impurities

In Chap. I reference was made to the necessity for eliminating all ferromagnetic impurities in the determination of magnetic susceptibilities. This is particularly important in the study of alloys. But magnetic measurements may also be used for the detection and estimation of ferromagnetic impurities. A simple way to do this is to measure the susceptibility over a range of field strength. Ferromagnetism is instantly indicated by a susceptibility which changes as the field is varied. In the writer's experience [8] a very minute quantity of ferromagnetic impurity was detected in an organo-metallic compound as follows. The substance, hexaphenyldigermanium, gave evidence of having a susceptibility markedly dependent on field strength. The apparent susceptibility varied from $+ 1.45 \times 10^{-6}$ at 1000 oersteds to $- 0.10 \times 10^{-6}$ at 11,000 oersteds. Fig. 15 (p. 30) shows the apparent change in weight of the sample on the Gouy balance plotted against field strength. After recrystallization the sample gave a susceptibility independent of field strength. A small insoluble residue was found to contain a very few almost microscopic specks of some highly magnetic substance. Traces of iron may be introduced by the simple operation of scratching glass with a file.

A somewhat different method for detecting ferromagnetic impurities is that of Constant and Formwalt.[9] The specimen is placed in a field of several thousand oersteds, then removed and hung from a torsion fiber in the center of a pair of Helmholtz coils. A field of 40 oersteds or less is applied and the resulting rotation, due to residual magnetism, is observed with a mirror and scale. With this simple apparatus it is possible to detect a magnetic moment per cubic centimeter of 2×10^{-7}. This compares with a remanent moment of over 500 for pure iron. This method would appear to be convenient for the quick detection and estimation of ferromagnetic impurities. Sometimes it is possible to estimate the kind of impurity present.[10]

Studies of this kind have generally been made on the specimens as they are found in nature or otherwise made available. There seems no reason why they should not be extended to specimens which have under-

[8] P. W. Selwood, *J. Am. Chem. Soc.*, 61, 3168 (1939).
[9] F. W. Constant and J. M. Formwalt, *Phys. Rev.*, 53, 432 (1938); 56, 373 (1939).
[10] F. W. Constant and R. E. Faires, *Phys. Rev.*, 59, 938 (1941).

gone reduction in hydrogen, or possibly heat treatment, in order to bring out any latent ferromagnetism, as for instance the presence of a trace of paramagnetic ferric oxide.

3. Instruments Used in Metallurgical and Mineralogical Control

Considerable use is made in some industrial control laboratories of the permeability, coercive force, and Curie point of mineral and metal samples under investigation. Still other magnetic properties may be studied for special purposes. Most of such testing relates to the composition and structure of the specimen, although applications to the control, for instance, of metal fatigue have been reported.[11] Some of these tests are described under Standards of the American Society for Testing Materials but most have been developed for highly specialized analytical work and are not commonly found even in well-equipped analytical and testing laboratories. Among the results of such tests may be mentioned the development of magnetic separation methods for minerals,[12] and the possible relation between coercive force and geochemical history of lodestones.[13] Such studies may, of course, be carried on with instruments of the Gouy [14] or other types but the specialized instruments which have been developed are more convenient for the purpose.

The first instrument to be described is the "Coercimeter." [15–18] Its use depends on the fact that there is a linear relationship between coercive force and specific surface of ferromagnetic powders. The instrument may thus be used to determine grain size and to follow the progress and efficiency of grinding operations. The sample is magnetized first in a strong field, then removed to a controlled field the strength of which can be balanced against the residual magnetism of the sample. Exact balance is indicated by a movable secondary coil attached to a galvanometer. The primary current producing the controlled field is measured by an ammeter. A diagram of one type of the apparatus is shown in Fig. 55.

[11] S. Y. Sigolaev, *Zavodskaya Lab.*, 6, 1243 (1937).

[12] C. W. Davis, *U. S. Bur. Mines, Repts. Investigations Tech. Papers*, No. 3268, 91 (1935).

[13] D. J. Doan, *U. S. Bur. Mines Repts. Investigations Tech. Papers*, No. 3400, 65 (1938). This paper contains an excellent review of the magnetic properties of iron oxides, especially of magnetite.

[14] F. S. Wartman, *U. S. Bur. Mines, Repts. Investigations Tech. Papers*, No. 3400, 33 (1938).

[15] H. Neumann, *Archiv. techn. Messen*, 4, T64 (1933).

[16] V. H. Gottschalk, *U. S. Bur. Mines, Repts. Investigations Tech. Papers*, No. 3268, 83 (1935); 3400, 21 (1938); *Physics*, 6, 127 (1935).

[17] C. W. Davis and M. Hartenheim, *Rev. Sci. Instruments*, 7, 147 (1935).

[18] F. D. DeVaney and W. H. Coghill, *Am. Inst. Mining Met. Engrs., Tech. Pub.*, No. 862 (1938).

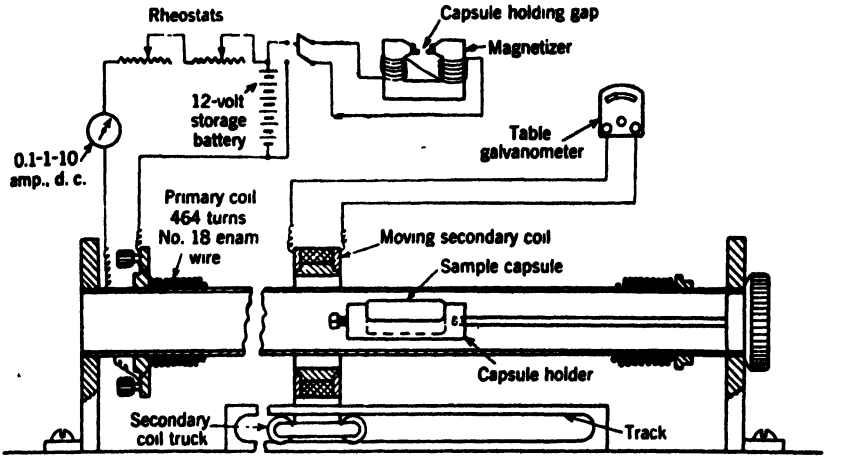


FIG. 55.—A form of coercimeter for determining the coercive force, principally of powdered specimens. (Reproduced from *U. S. Bur. Mines, Repts. Investigations* 3400.)

It should be pointed out that coercive force may be defined in two ways, either as the field of force necessary to reduce $\mathcal{J}$, the intensity of magnetization, to zero in an $\mathcal{J}$–H curve, or as the force necessary to reduce B to zero in a B–H curve. It is the former which is measured by the "Coercimeter" described. A curve showing the dependence of coercive force on grain size is shown in Fig. 56. Probably coercive force depends on other factors

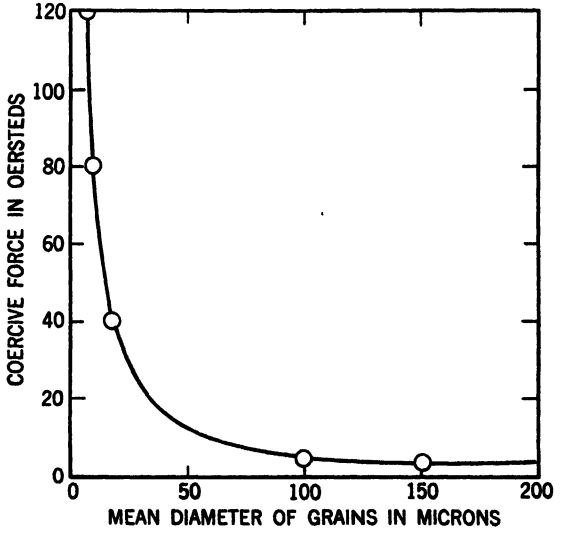


FIG. 56.—Relationship between coercive force and particle size.

as well as specific surface, and extension of the "Coercimeter's" applicability is to be expected to such properties as strains, lattice discontinuities, and carbon content.

The determination of carbon content in a steel is a common and important analytical problem. Many efforts have been made to solve it without recourse to chemical methods and, for specialized cases, some of these have been very successful. Properties such as magnetic saturation, permeability at low field strength, and coercive force have all been tried.[19,20] It is generally necessary to give the sample a careful heat treatment before measurement. Sometimes the kind of heat treatment necessary depends on the carbon content. A low frequency A. C. permeameter devised by Rogers, Wentzel, and Riott gives reasonably good results for routine work. A primary and a secondary coil are wound around a sample holder (Fig. 57). The primary is connected to a 5-cycle

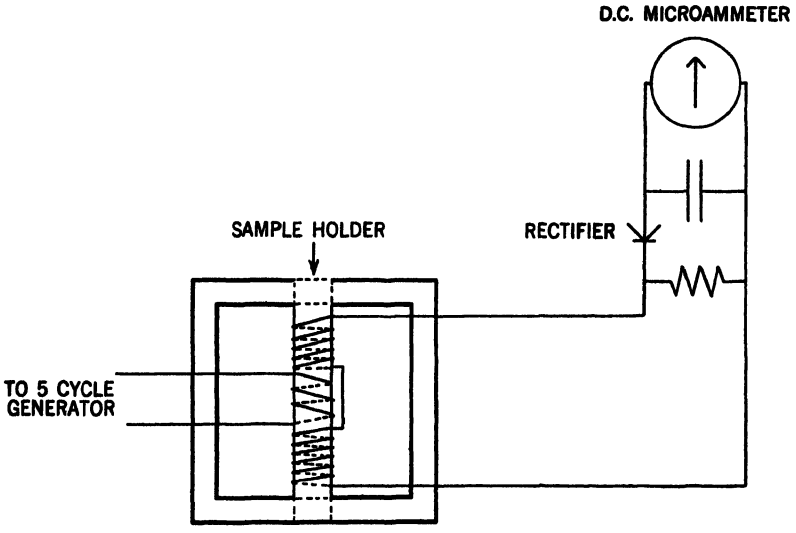


FIG. 57.—A low frequency AC permeameter. (After Rogers, Wentzel, and Riott, *Trans. Am. Soc. Metals*, 29, 969 (1941)).

generator, the secondary is connected through a copper-oxide rectifier and suitable resistances to a direct current microammeter. The carbon content of a specimen placed in the sample holder may be related by calibration curves to the readings of the microammeter.

[19] P. Klinger and H. Fucke, *Arch. Eisenhüttenw.*, 3, 347 (1929).

[20] B. A. Rogers, K. Wentzel, and J. P. Riott, *Trans. Am. Soc. Metals*, 29, 969 (1941).

The "Carbanalyzer," [21] a diagram of which is shown in Fig. 58, is a special form of permeameter. It measures the change in flux in a bar produced by a known change in magnetic force. The instrument requires a specially cast sample, but it is rugged, requires no elaborate training for its use, and gives the carbon content in a steel bath with great rapidity.

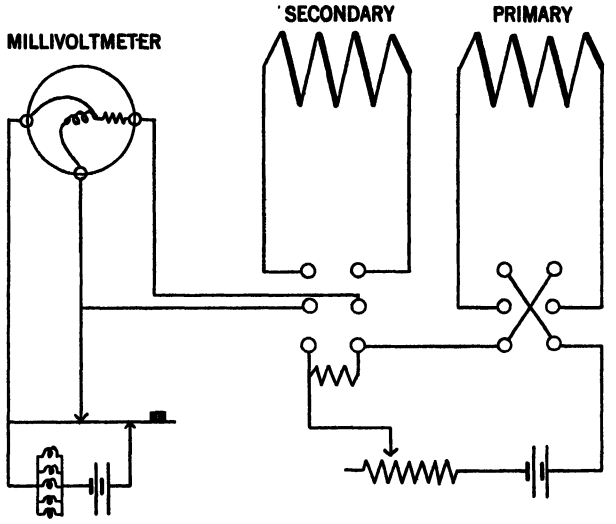


FIG. 58.—Electrical circuit of the "Carbanalyzer". (After Work and Clark, *Trans. Am. Inst. Min. Met. Engrs.*, 1940, 140. Iron and Steel Division, 475).

The "Carbometer" [22] is a related type of permeameter in which the sample is magnetized under certain standardized conditions. The intensity of magnetization is measured by induction in a coil attached to a ballistic galvanometer. The galvanometer reading is proportional to the difference in induction caused by two fields of different strength. As for the "Carbanalyzer" a specially designed test-bar is required, but under favorable conditions the carbon content of a steel may be given in units of 0.01 per cent in two minutes.

Another type of permeameter specially designed for saturation and coercive force measurements is shown in Fig. 59.[23] The sample is magnetized, then rapidly withdrawn from a secondary coil mounted as shown. Readings of the galvanometer attached to the secondary indicate the

[21] H. K. Work and H. T. Clark, *Am. Inst. Mining Met. Engrs., Tech. Pub.*, No. 1132 (1939).

[22] G. Soler, *Metal Progress*, 31, 159 (1937).

[23] A. Kussmann, *Z. Metallkunde*, 26, 25 (1934).

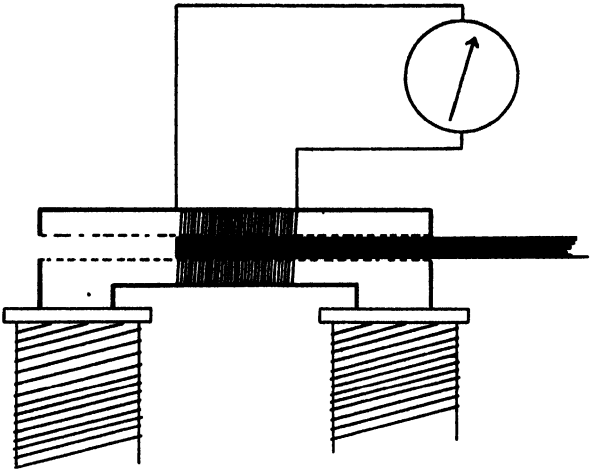


FIG. 59.—Isthmus permeameter.

magnetization of the sample. An example of the results obtained for the coercive force of an iron-nickel-copper alloy are shown in Fig. 60.

Still another isthmus permeameter of very flexible design is described by Gottschalk and Davis.[24] Various other instruments such as the

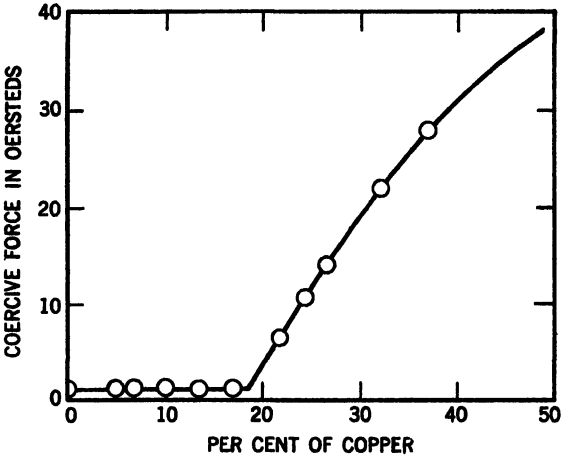


FIG. 60.—Coercive force for an alloy containing a 1 : 1 ratio of iron and nickel and a varying proportion of copper.

Siemens "Ferrometer" [25] (Fig. 61) of similar design and purpose are also in use. The applications of such instruments could probably be extended

[24] V. H. Gottschalk and C. W. Davis, *U. S. Bur. Mines, Repts. Investigations Tech Papers*, No. 3268, 51 (1935).

[25] W. Thal, *Z. tech. Physik*, 15, 469 (1934).

almost indefinitely. Their use has, for instance, been suggested in controlling the rate of formation of tin-iron alloy during hot dip tinning.[26]

Instruments based on the Curie point transition [27] are generally of rather different design. The principal structural difference is the presence of an oven so that the temperature may be raised above the Curie point of the substance under investigation. Fig. 62a and b shows a simple device made from a precision electric meter.[28] This instrument is designed for micro-determinations of cementite, Fe_3C, inclusions in steel. The sample holder is mounted in the variable field of an electromagnet and is

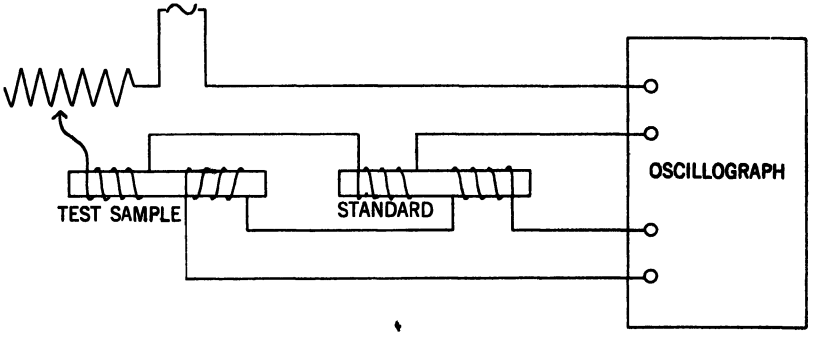


FIG. 61.—Siemens ferrometer.

surrounded by a small non-inductive electric oven. In order to measure the temperature accurately a platinum-rhodium thermocouple of very fine wire is mounted so that it is in contact with the bottom of the sample holder. The sample itself is distributed in an inert diluent such as very pure silica, thoroughly mixed and sealed off in a small glass bulb. By measuring the susceptibility above and below the Curie point it is possible to detect cementite and to estimate the amount present. The variation of the magnetization of cementite with temperature is shown in Fig. 63.

The magnetometer [29] has been used for similar work, and other balances such as the Gouy or Faraday types could be used for such determinations but they are much more cumbersome. The method could probably be extended to the detection of other kinds of ferromagnetic substances.

Measurements on cementite in steel such as those just described can

[26] A. U. Seybolt, *Trans. Am. Soc. Metals*, 29, 937 (1941).

[27] O. L. Bihet and F. Willems, *Arch. Eisenhüttenw.*, 11, 125 (1929).

[28] The writer is indebted to Mr. S. E. Q. Ashley of the General Electric Company, Pittsfield, Mass. for information and photographs of the Curie point magnetic balance. Acknowledgment is gratefully made to the General Electric Company for permission to reproduce the photographs shown.

[29] R. L. Sanford, *Bur. Standards J. Research*, 2, 659 (1929).

scarcely be made *in situ* because of the very large ferromagnetism of the iron and the relatively small proportion of cementite present. Smith [30] states that measurements with a magnetometer over low field strengths will detect cementite in steel even when the proportion of carbide is only a few tenths of a per cent. The Curie point of the cementite is indicated by a sharp peak rather than by a simple fall in the magnetization versus temperature curve. If this effect can be established it might be developed

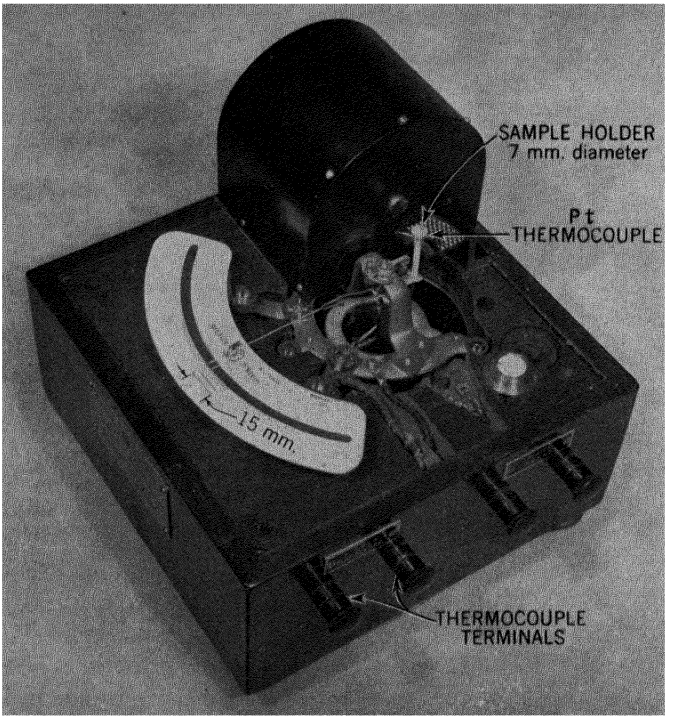


FIG. 62a. - General Electric magnetic balance for Curie point determinations.

into a very useful method for carbide determinations in steel. Efforts by the writer to detect the effect in a variety of commercial steels have not been successful. The possibilities of such a method are discussed by Vigoreux and Webb,[31] and by Spooner.[32]

[30] S. W. J. Smith, *Proc. Phys. Soc. London*, **25**, 77 (1912).

[31] P. Vigoreux and C. E. Webb, *Principles of Electric and Magnetic Testing*. Prentice-Hall, New York 1936.

[32] T. Spooner, *Properties and Testing of Magnetic Materials*. McGraw-Hill Book Co., New York 1927.

4. Structure of Alloys

Use of magnetic measurements to study the structure of alloys is relatively a new field. Many changes in the magnetic properties of alloys produced by heat treatment may be closely related to atomic rearrangements. Sometimes these changes are on such a small scale that magnetic measurements are more useful in their interpretation than microscopic or x-ray investigations.

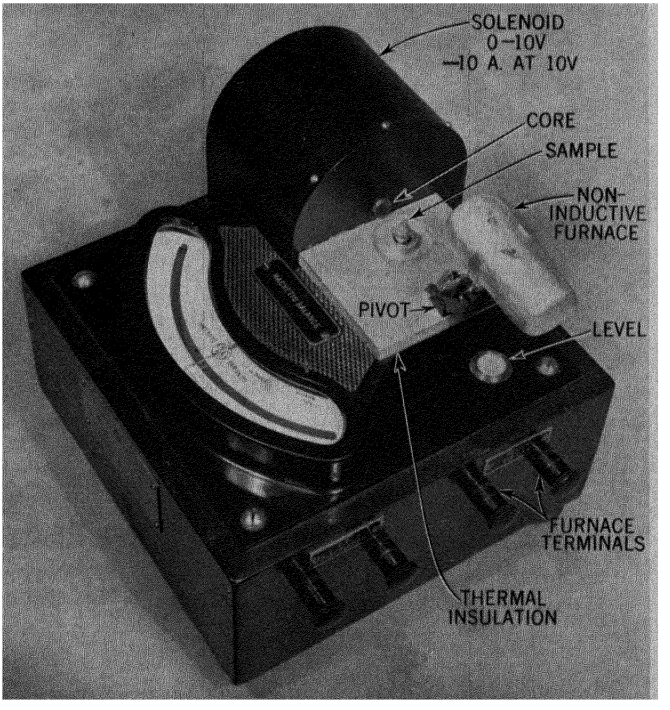


FIG. 62b.—General Electric magnetic balance for Curie point determinations.

One of the first studies in this field was that of Tammann and Oelsen [33–35] who determined the solubilities of the transition group metals in a large number of non-ferromagnetic metals. The apparatus used was a Faraday balance in which the force was exerted horizontally. The principle of

[33] G. Tammann and W. Oelsen, *Z. anorg. allgem. Chem.*, 186, 257 (1930).

[34] See also K. Honda and T. Murakami, *Science Repts. Tôhoku Imp. Univ., First Ser.*, 10, 79 (1921).

[35] K. Honda and H. Endo, *Science Repts. Tôhoku Imp. Univ., First Ser.*, 16, 627 (1927) for thermomagnetic studies of the iron-silicon and iron-carbon systems respectively.

the method is that for true solution ferromagnetism is a measure of the amount of nickel which has gone into solution. Sometimes the phase diagrams are complicated as, for example, in the cobalt-copper system shown in Fig. 64 in which the magnetization depends greatly on the temperature from which the alloy is quenched. In such cases interpretations of the magnetic data may be difficult. The subject is reviewed by Vogt.[36]

The form and arrangement of ferromagnetic precipitates have also been studied by use of the magnetic balance.[37] Bitter and his coworkers [38,39a] have used this method to study the precipitation of iron

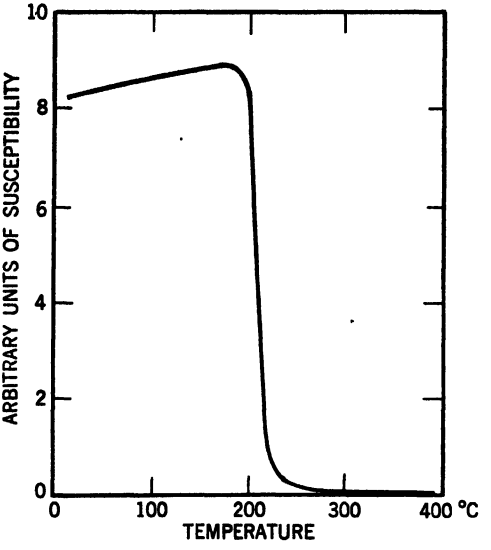


FIG. 63.—Curie point determination on cementite.

from copper. The reactions are complex. Alloys in which all the iron is in solid solution in electrolytic copper may be prepared by quenching from above the solubility limits. Below 0.7 per cent iron the quenched alloy is quite free from ferromagnetism indicating completely random uniform distribution of the iron atoms. At low temperatures such alloys obey the Weiss law, but with a varying effective Bohr magneton number for the iron. The magnetic method is obviously a powerful one for such studies but it is clear that much work remains to be done on it.

[36] E. Vogt, *Ann. Physik*, 29, 358 (1937); *Z. Elektrochem.*, 45, 597 (1939). This excellent review gives many experimental results and their interpretation. Also O. von Auwers, *Wiss. Veröffentl. Siemens-Werken*, 16, 92 (1937); 17, 74 (1938).

[37] E. Gerold, *Z. Metallkunde*, 24, 255 (1932).

[38] F. Bitter and A. R. Kaufmann, *Phys. Rev.*, 56, 1044 (1939).

[39a] F. Bitter, A. R. Kaufmann, C. Starr, and S. T. Pan, *Phys. Rev.*, 60, 134 (1941).

Magnetic studies on the precipitation of iron from α- and β-brass have been made by Smith.[39b] β-brass containing 0.3 per cent or more of iron is ferromagnetic when quenched from the solid solution range, and actually becomes less magnetic as iron precipitates during annealing at lower temperatures. β-brass with less than 0.2 per cent iron is not ferromagnetic when quenched from the solid solution range, but at low temperatures it readily precipitates iron in a ferromagnetic form.

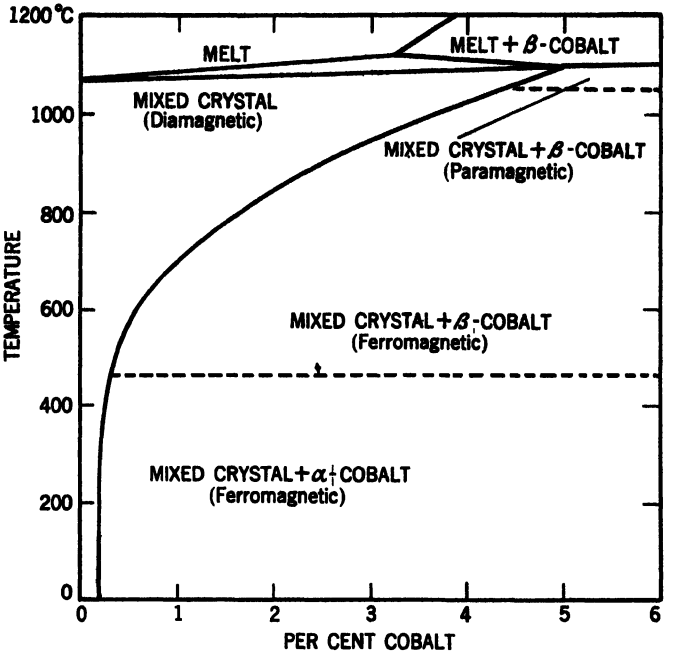


FIG. 64.—The cobalt-copper system.

Not only is it possible to examine the nature of ferromagnetic precipitates in alloys, but the kinetics of the precipitation process may be followed.[40] This method is not necessarily restricted to ferromagnetic metals. Fig. 65 shows the susceptibility plotted against temperature for aluminum and for a copper-aluminum alloy both in solid solution and in heterogeneous form. The nature of the reforming action, its velocity, and even its activation energy may be obtained by magnetic measurements. The magnetic method would seem to be a very generally useful

[39b] C. S. Smith, *Trans. Am. Inst. Mining Met. Engrs., Tech. Pub.*, No. 1394, 1941.
[40] H. Auer, *Z. Elektrochem.*, 45, 608 (1939).

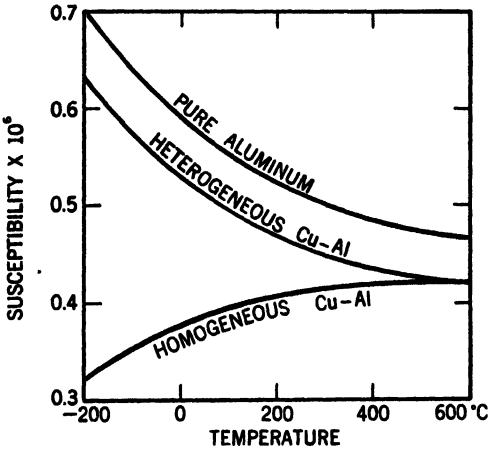


FIG. 65.—Aluminum-copper alloy before and after tempering.

one for following such precipitation and diffusion processes. Another example is the progress of austenite transformation in iron alloys.[41]

Use is also made of the Curie point in the study of alloys. There is the obvious application to detection of cementite inclusions by means

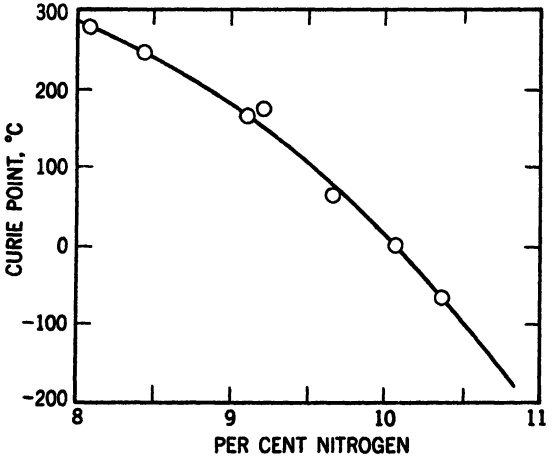


FIG. 66.—Variation of Curie point with composition in the ϵ-phase of the iron-nitrogen system.

suggested in the previous section. The ϵ-phase of the iron-nitrogen system shows an amazing dependence of Curie point on composition (Fig.

[41] H. Lange and K. Mathieu, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, 20, 125 (1938).

66).[42] This may be useful for quantitative estimation of nitrogen in steel. Forrer [43] has attempted a more fundamental study of alloy structure from the variation of Curie point with alloy composition. He finds that the Curie point is a function of the square root of the number of effective contacts per atom in the lattice. The method seems applicable to various structural problems of metals, alloys, ferrites, and other ferromagnetic substances, but it has not been developed.

5. Phase Ratios and Stoichiometry

Magnetic studies have been of considerable service in the study of phase ratios. Sometimes the phase diagrams are greatly clarified by thermomagnetic studies. Sometimes also, the magnetic measurements have revealed hitherto unsuspected phases in supposedly pure stoichiometric compounds. This type of work has not, however, been extended to a very large number of compounds.

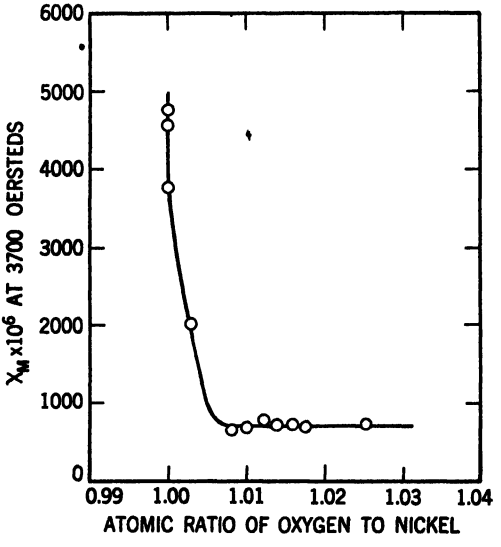


FIG. 67.—The nickel-oxygen system in the region of NiO.

Klemm and Hass [44] have made such a study of nickel oxide. Different samples of this substance have different susceptibilities, but all samples of stoichiometrically accurate NiO composition are ferromagnetic and contain metallic nickel as indicated by the coincidence of their Curie points with that of the metal. Fig. 67 shows the molar susceptibility plotted

[42] E. Lehrer, *Z. Elektrochem.*, 36, 460 (1930).
[43] R. Forrer, *J. phys. radium*, 4, 427, 501 (1933); *Compt. rend.*, 198, 1903 (1934).
[44] W. Klemm and K. Hass, *Z. anorg. allgem. Chem.*, 219, 82 (1934).

against composition for the range $NiO_{0.99}$ to $NiO_{1.04}$. According to these results the substance commonly called nickel oxide is actually a mixture and does not become stable until the nickel oxygen ratio exceeds about $NiO_{1.005}$. Further studies on this substance have been made by Bhatnagar and Bal.[45] These workers claim that NiO has a definite chemical existence and that when carefully prepared it is paramagnetic with $\chi = 9.56 \times 10^{-6}$.

Attempts have been made to use magnetic measurements for determination of the proportion of ferrous to ferric iron in complex systems. Gott

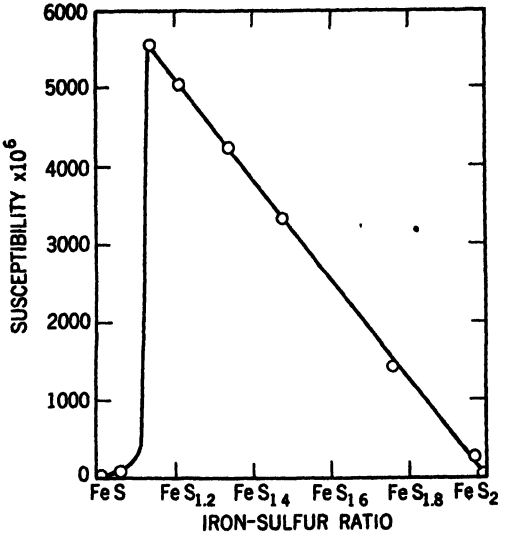


FIG. 68.—The iron-sulfur system.

and Krings [46] have made measurements on the systems FeO-Fe_2O_3-SiO_2, FeO-Fe_2O_3-P_2O_5, and on an iron-borax glass. Paramagnetism is dominant in the limiting system Fe_2O_3-SiO_2 but the susceptibilities do not follow the additive law for mixtures or solutions. There is an astonishing maximum in susceptibility at about 10 per cent SiO_2. Oxidation and reduction treatments lead to the appearance of ferromagnetism, hence the magnetic properties cannot readily be used as an index of the state of oxidation. On the other hand, for the phosphate system oxidation and reduction yield paramagnetic bodies although a definite relation between the degree of oxidation or reduction and the susceptibility has not been established.

[45] S. S. Bhatnagar and G. S. Bal, *J. Indian Chem. Soc.*, 11, 603 (1934).
[46] O. Gott-and W. Krings, *Z. anorg. allgem. Chem.*, 239, 345 (1938).

The iron-sulfur system has been investigated by Juza and Biltz,[47] and by Haraldsen.[48, 49] In several recent papers Haraldsen [50] has described what appears to be a very thorough study of the iron-sulfur system. Stoichiometric FeS is paramagnetic with a susceptibility which increases rapidly with temperature up to 138° C., less rapidly to 325°, and then decreases linearly. Up to the ratio $FeS_{1.09}$ the transitions are similar though less pronounced, and, in addition, the susceptibility has a sharp maximum at 210° C. Higher sulfur ratios than $FeS_{1.10}$ show increasing ferromagnetism, at first only between 190° and 270° C., then, at $FeS_{1.15}$

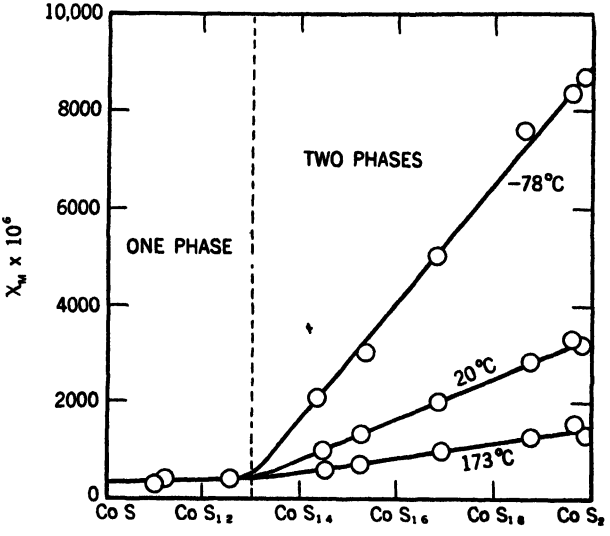


FIG. 69.—The cobalt-sulfur system.

ferromagnetism appears at room temperature. For still higher sulfur contents up to FeS_2 (see Fig. 68) the susceptibility drops linearly with concentration.

Similar types of measurements on the system cobalt-sulfur, from CoS to CoS_2, have been made by Haraldsen.[51] The data are summarized in Fig. 69.

[47] R. Juza and W. Biltz, *Z. anorg. allgem. Chem.*, 205, 273 (1932).

[48] H. Haraldsen, *Z. anorg. allgem. Chem.*, 231, 78 (1937); *Tids. Kjemi Bergvesen*, 19, 144 (1939).

[49] See also W. Klemm, *Magnetochemie*. Akademische Verlagsgesellschaft, Leipzig 1936, pp. 228, 237.

[50] H. Haraldsen, *Z. anorg. allgem. Chem.*, 246, 195, 169 (1941). These papers were unfortunately not available to the writer.

[51] H. Haraldsen, *Z. anorg. allgem. Chem.*, 224, 85 (1935).

Haraldsen [52–54] has also studied the systems chromium-sulfur, chromium-selenium, and chromium-tellurium. For the Cr-S system there is a very sharp maximum of susceptibility at $CrS_{1.175}$. Above 165° K. and below 310° K. the substance of this composition is ferromagnetic (see Figs. 70 and 71). The composition and temperature curves for the systems Cr-Se and Cr-Te are analogous.

Compounds of vanadium have already been discussed in Chap. IV. The substances from $VO_{1.5}$ to $VO_{2.5}$ have been studied by Klemm.[55,56]

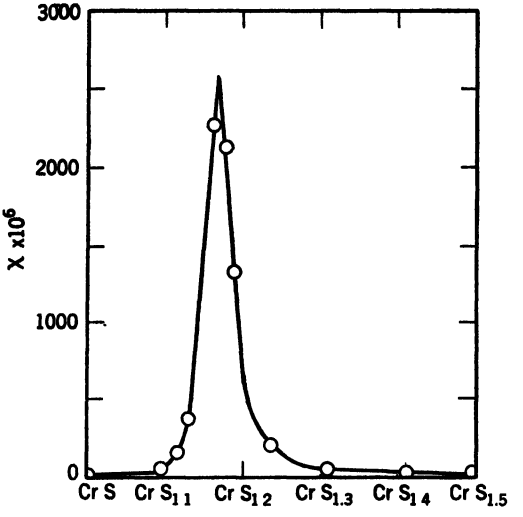


FIG. 70.—The chromium-sulfur system.

For $VO_{1.5}$ there is a discontinuous change of susceptibility at − 100° C. For the composition range $VO_{1.9}$ to $VO_{2.1}$ the change occurs at 68° C. and is very large, the susceptibility changes from 0.5×10^{-6} to 7.0×10^{-6}. This magnetic discontinuity does not correspond to a change of crystal lattice, but there is a thermal change amounting to about − 1 kcal. per mole.

The chalcogenides of vanadium have also been studied by Klemm.[57,58] The tellurides are not well defined but the sulfides and selenides show

[52] H. Haraldsen and E. Kowalski, *Z. anorg. allgem. Chem.*, 224, 329 (1935).

[53] H. Haraldsen and A. Neuber, *Naturwissenschaften*, 24, 280 (1936); *Z. anorg. allgem. Chem.*, 234, 337, 353, 372 (1937).

[54] H. Haraldsen and F. Mehmed, *Z. anorg. allgem. Chem.*, 239, 369 (1938).

[55] E. Hoschek and W. Klemm, *Z. anorg. allgem. Chem.*, 242, 63 (1939).

[56] W. Klemm and L. Grimm, *Naturwissenschaften*, 27, 787 (1939). H. Dressnandt and W. Schottky, *Naturwissenschaften*, 27, 840 (1939).

[57] E. Hoschek and W. Klemm, *Z. anorg. allgem. Chem.*, 242, 49 (1939).

[58] W. Klemm, *Atti X° congr. intern. chim.*, 2, 696 (1938).

some interesting anomalies. For instance, for the substance $VSe_{1.5}$ there is a very sharp peak of susceptibility. This is pronounced at − 183° C., but just perceptible at 20° C. (Fig. 72).

The system titanium-oxygen has been studied over the range $TiO_{2.00}$ to $TiO_{0.58}$ by Ehrlich.[59a, 59b] The susceptibility-concentration diagram is

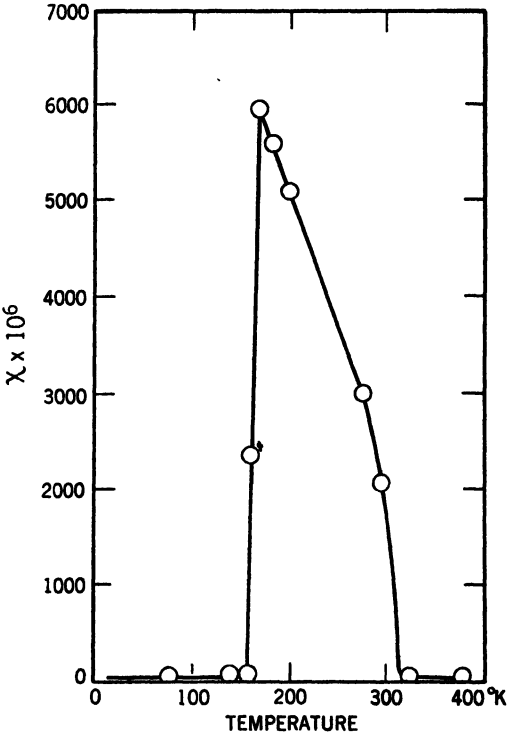


FIG. 71.—Susceptibility-temperature relationship for the atomic ratio $CrS_{1.17}$.

shown in Fig. 73. The results show that Ti^{+++} and Ti^{++} ions are present in atomic combination with one another, and that only for very high Ti^{++++} ion concentrations do the Ti^{+++} ions become independent.

Magnetic measurements on the system lead-oxygen have been made by Baroni.[60] The principal result of this work is that it discredits a supposed suboxide of lead reported by Pascal and Minne.[61] The same result had already been established by Welo and Petersen.[62]

[59a] P. Ehrlich, *Z. Elektrochem.*, 45, 362 (1939).
[59b] P. Ehrlich, *Z. anorg. allgem. Chem.*, 247, 53 (1941).
[60] A. Baroni, *Gazz. chim. ital.*, 68, 387 (1938).
[61] P. Pascal and P. Minne, *Compt. rend.*, 193, 1303 (1931).
[62] L. A. Welo and M. Petersen, *Phys. Rev.*, 49, 864 (1936).

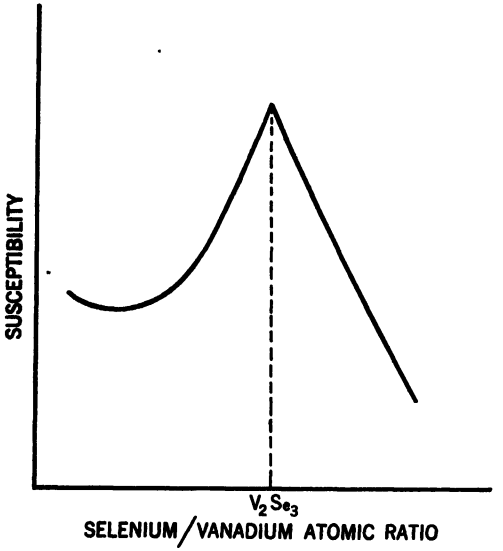


FIG. 72.—The selenium-vanadium system at −185° C.

A somewhat different, yet related, type of study is that of hydration. For instance, Bourion and Beau [63] show that the susceptibility of hydrated

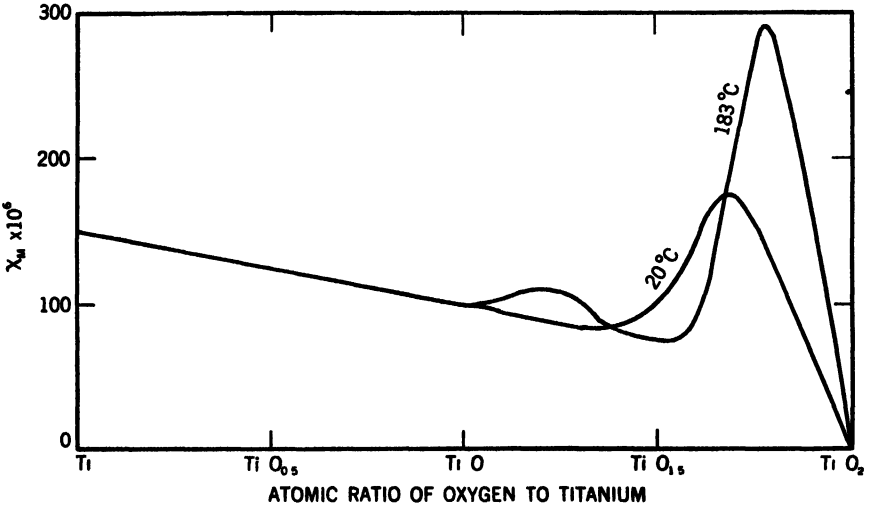


FIG. 73.—The titanium-oxygen system.

thoria varies linearly with the water content. This suggests that the water is merely bound mechanically rather than being chemically com-

[63] F. Bourion and D. Beau, *Compt. rend.*, 198, 916 (1934).

bined. A similar study on the oxides and hydroxides of aluminum has been made by Zimens.[64]

Hydrate binding on ions of the transition group elements may have a considerable effect. For instance, Joos [65] has found that the susceptibility of a cobalt alum increased over a two month period from 0.28×10^{-6} to 9.5×10^{-6}. This must have been due to a reorganization of the bonds involving the unpaired electrons of the cobalt ion.

6. Magnetism and Catalysis

A possible relationship between magnetism and catalysis has interested several workers. There can be no doubt that catalytic properties and noteworthy magnetic properties are often found together. This is not to say that catalytic activity is always due to high magnetic moment, any more than one can say that all catalytic activity is due to one mechanism. In certain instances such as the *ortho-para*hydrogen conversion there is a clear-cut relationship between the magnetic moment of the catalyst and its activity. In others, the magnetic properties of the catalyst are of use in determining its structure. In still other cases, some rather shadowy relationships have been found between catalytic activity and magnetic transformations.

The *ortho-para*hydrogen conversion and its catalysis by paramagnetic substances was mentioned in Chap. I, p. 24. This effect, discovered by Farkas and Sachsse,[66] makes it possible to determine magnetic moments by measurement of the velocity of the conversion $p\text{-}H_2 \rightarrow o\text{-}H_2$ or the reverse. The conversion may be either homogeneous, as in the presence of molecular oxygen, or heterogeneous as on a chromic oxide surface. Diamagnetic gases do not catalyze the reaction, but diamagnetic solids, such as charcoal, are often excellent catalysts. It is possible to make reasonably accurate susceptibility measurements from velocity measurements on the homogeneous catalyzed reaction. But the heterogeneous reaction has led so far only to qualitative results. A further complication is caused by the readily measurable conversion taking place in water. This seems to be due to the nuclear moment of the protons in the water molecules.

The theory of the paramagnetic conversion is given by Wigner [67] who shows that the velocity constant, k, should be proportional to the square of the Bohr magneton number. For several ions of the rare earths k/μ^2

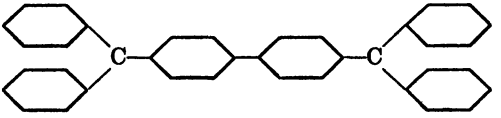
[64] K. E. Zimens, *Svensk Kem. Tid.*, 52, 205 (1940).

[65] G. Joos, *Ann. Physik*, 28, 54 (1937).

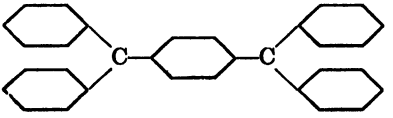
[66] A. Farkas and H. Sachsse, *Sitzber. preuss. Akad. Wiss. Physik. math. Klasse*, 1933, 268; *Z. physik. Chem.*, B23, 1, 19 (1933).

[67] E. Wigner, *Z. physik. Chem.*, B19, 203 (1932); B23, 28 (1933).

actually varies from 0.181 for Pr^{+++} to 0.502 for Yb^{+++}. This, however, can be explained because with increasing nuclear charge the collision diameter of these ions decreases. The collision efficiency of the process is very small, being only 10^{-12} to 10^{-14}. The magnetic moment of the ion, whether rare earth or of the iron group, determined by this method is independent of concentration.[68] The use of the method for establishing the diamagnetism of B_2H_6 has already been mentioned [69] (p. 138). One of the most recent applications of the method has been that of Schwab and Agliardi [70] to the configuration of the Chichibabin hydrocarbons. It will be recalled (p. 137) that the compound



has been shown by Müller to be diamagnetic and hence, probably existent in the quinoid form. An alternative suggestion is that the "odd" electrons on the methyl carbons are unpaired but that their spins are opposed so that the compound has the chemical and optical properties of a free radical, but not the magnetic properties. This compound catalyzes the *ortho-para*hydrogen conversion with a velocity corresponding to 9.7 per cent dissociation. The related compound



is apparently undissociated. Further applications of the method are discussed by Schwab and Schwab-Agallidis.[71] If this work is substantiated it will call for a revision of some of our ideas of free radicals. It will also show that the *ortho-para*hydrogen method is considerably more searching for certain types of problems than is the direct measurement of susceptibility.

The heterogeneous *ortho-para*hydrogen conversion on paramagnetic oxides has been studied by Taylor and Diamond.[72] The effect is marked. For instance, 6 hours contact with the diamagnetic lanthanum oxide produced only 17 per cent conversion, but less than 3 minutes contact with the strongly paramagnetic gadolinum oxide produced 100 per cent con-

[68] H. Sachsse, *Z. physik. Chem.*, **B24**, 429 (1934).
[69] H. Sachsse, *Z. Elektrochem.*, **40**, 531 (1934).
[70] G. M. Schwab and N. Agliardi, *Ber.*, **73B**, 95 (1940).
[71] G. M. Schwab and E. Schwab-Agallidis, *Z. physik. Chem.*, **B49**, 196 (1941).
[72] H. S. Taylor and H. Diamond, *J. Am. Chem. Soc.*, **55**, 2613 (1933); **57**, 1251 (1935).

version. This experiment is especially impressive because of the striking similarity in chemical and most physical properties of these oxides. Similar results are obtained with other paramagnetic oxides. The writer is not aware of any similar studies that have been made on substances such as α- and γ-ferric oxides. Such studies would show what, if any, relationship exists between velocity of *ortho-para* conversion and the ferromagnetic transition. Ferromagnetic metals catalyze the conversion, but so do other metals as well. The conversion is also catalyzed by diamagnetic substances such as charcoal. A possible explanation of this effect is the existence of a layer of paramagnetic atoms on the surface of

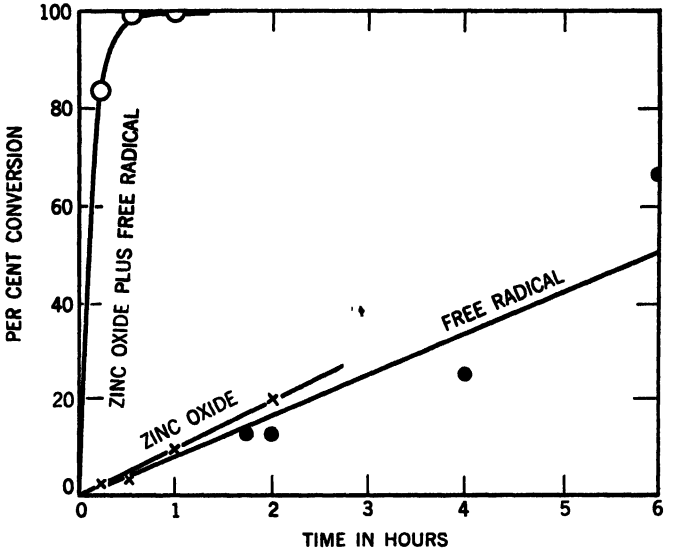


FIG. 74.—Catalytic *ortho-para*hydrogen conversion on a free radical, on zinc oxide, and on a mixture of the two.

the catalyst. The paramagnetic heterogeneous conversion and strong hydrogen adsorption apparently go together. Turkevich and Selwood [73] have shown that a solid free radical, α,α-diphenyl-β-picrylhydrazyl, does not appreciably catalyze the *ortho-para*hydrogen conversion although the radical is 100 per cent dissociated. Zinc oxide is also relatively inactive but it strongly adsorbs the hydrogen. When the free radical and the zinc oxide are mixed a very rapid conversion takes place (Fig. 74). This is interpreted to mean that two factors are necessary for the heterogeneous catalysis of *ortho* to *para* hydrogen at low temperatures, namely, the existence of an inhomogeneous field, produced in this case by the

[73] J. Turkevich and P. W. Selwood, *J. Am. Chem. Soc.*, 63, 1077 (1941).

free radical, and long contact of the hydrogen with the field, ensured by van der Waals' adsorption of hydrogen on the zinc oxide.

Attention will now be turned to what may be called "active oxides." In Chap. VIII, p. 226, mention was made of the ferrites and other spinel structures, some of which are ferromagnetic. When ZnO and Fe_2O_3 are heated together they are gradually converted to zinc ferrite with an accompanying change in properties. Hüttig and his co-workers have published well over one hundred papers on the physical and chemical changes that occur during this, and other similar transformations. As a result of all this labor it has been shown that during the course of such transformations certain intermediate compounds must be formed and that these often exhibit pronounced catalytic and magnetic properties. In some cases it has been possible to obtain the intermediate "active oxides" in fairly pure form. In others the activity seems to be restricted to the surface of the original mixture. No useful purpose will be served by giving references to all this work, most of which has been published in the *Zeitschrift für anorganische und allgemeine Chemie* during the past ten years. A few examples will serve to illustrate the type of results obtained.[74–78] Zinc oxide heated with ferric oxide shows two peaks of catalytic activity, one after heating at 400° C., the other after heating at 600° C. The reactions used were $2N_2O \rightarrow 2N_2 + O_2$, and $2CO + O_2 \rightarrow 2CO_2$. Simultaneous measurements of magnetic susceptibility show a sharp rise after the heat treatment has reached 550° C., and incipient ferromagnetism at about 600° C. The surprising feature of these magnetic results is that x-ray diffraction studies show no trace of the zinc ferrite lattice before about 650° C. Many other physical properties point to the same conclusion, namely that active intermediates are formed during the course of the transformation of mixed oxides into spinels.

Somewhat similar results have been obtained for the oxides of beryllium and iron;[79] cadmium, copper, and lead, and iron;[80] magnesium and iron;[81] calcium and iron;[82] and sodium and iron.[83] Studies have also

[74] H. Kittel, G. Hüttig, and Z. Herrmann, *Z. anorg. allgem. Chem.*, **210**, 26 (1933).

[75] G. Hüttig, R. Geisler, J. Hampel, O. Hnevkovsky, F. Jeitner, H. Kittel, O. Kostelitz, F. Owesny, H. Schmeiser, O. Schneider, and W. Sedlatschek, *Z. anorg. allgem. Chem.*, **237**, 209 (1938).

[76] G. Hüttig, *Z. Elektrochem.*, **44**, 571 (1938).

[77] J. A. Hedvall, *Reactions in the Solid State.* J. A. Barth, Leipzig 1938, p. 152.

[78] G. Hüttig, *J. chim. phys.*, **36**, 84 (1939).

[79] G. Hüttig and H. Kittel, *Gazz. chim. ital.*, **63**, 833 (1933).

[80] H. Kittel, *Z. anorg. allgem. Chem.*, **221**, 49 (1934).

[81] G. Hüttig, W. Novák-Schreiber, and H. Kittel, *Z. physik. Chem.*, **A171**, 83 (1934).

[82] G. Hüttig, J. Funke, and H. Kittel, *J. Am. Chem. Soc.*, **57**, 2470 (1935).

[83] R. Knick and E. J. Kohlmeyer, *Z. anorg. allgem. Chem.*, **244**, 67 (1940).

been made on the oxides of beryllium, calcium, copper, cadmium, lead, and magnesium, mixed with chromic oxide.[84, 85] Very many other similar studies will be found in the literature.

Results such as those above and others raise the question as to whether or not the localized non-homogeneous magnetic field of an atom or ion may not be responsible for many types of catalytic action, in addition to the *ortho-para*hydrogen conversion already discussed. This possibility has been suggested by several workers,[86, 87] but as yet no definite answer can be given. Gilbert, Turkevich, and Wallis [88] tried to find a correlation between magnetic susceptibility and catalytic activity for the *cis-trans* isomerization of dimethyl maleate. It is quite true that some paramagnetic substances catalyze this reaction and that some diamagnetic substances do not. But tests with such diverse substances as Na, $AlCl_3$, $FeCl_3$, $ZnCl_2$, $CrCl_3$, Fe_3O_4, $NiCl_2$, $MgCl_2$, $HgCl_2$ Hg_2Cl_2, H_2O, and Fe_2O_3 failed to show any such relationship.

Possibly one of the most fruitful fields for magnetochemical investigation is that of structural determinations on catalytically active surfaces. Practically all the work already published in this field has appeared within the past two or three years, but as early as 1930 Merck and Wedekind [89a] used susceptibility measurements to study the structure of cobalt oxide used as a catalyst for the room temperature oxidation of carbon monoxide. Olmer [89b] failed to find any relationship between the catalytic activity of iron, nickel, and cobalt and their magnetic properties. The reaction studied was the catalytic decomposition of carbon monoxide. Bhatnagar and his co-workers [90, 91] have published a series of papers dealing with the magnetic properties of catalysts. A study of the thermal decomposition of potassium chlorate, with manganese dioxide as catalyst shows that an intermediate is formed having a smaller paramagnetism than MnO_2. The deviation from linearity is about 5 per cent. Conclusive evidence for an intermediate compound is also obtained when Co_3O_4 is the catalyst, but the results with Fe_2O_3 catalyst show no significant deviation between experimental and calculated values of the

[84] H. Kittel and G. Hüttig, *Z. anorg. allgem. Chem.*, 217, 193 (1934).

[85] H. Kittel, *Z. anorg. allgem. Chem.*, 222, 1 (1935).

[86] R. Kuhn in Freudenberg's *Stereochemie*. F. Deuticke, Leipzig 1933, p. 917.

[87] T. Kitagawa, *Rev. Phys. Chem. Japan*, 11, 71 (1937).

[88] W. I. Gilbert, J. Turkevich, and E. S. Wallis, *J. Org. Chem.*, 3, 611 (1939).

[89a] F. Merck and E. Wedekind, *Z. anorg. allgem. Chem.*, 186, 49 (1930).

[89b] F. Olmer, *Rev. mét.*, 38, 129 (1941); *J. Phys. Chem.*, 46, 405 (1942).

[90] S. S. Bhatnagar, B. Prakash, and J. Singh, *J. Indian Chem. Soc.*, 17, 125, 133 (1940).

[91] S. S. Bhatnagar, N. A. Yajnik, P. L. Kapur, and A. S. Bhatnagar, *J. Indian Chem. Soc.*, 18, 350, 371, 391 (1941).

susceptibility. Catalytic oxidation of potassium iodide by persulfate has also been studied. When ferrous sulfate is used as the catalyst the results indicate the formation of a relatively stable diamagnetic coordination compound of iron. Similarly an intermediate compound is indicated in the catalyzed reaction between ammonium oxalate and mercuric chloride. Gamma-ferric oxide is a better catalyst than α-Fe_2O_3 for the decomposition of $KClO_3$. Thus for α-Fe_2O_3 the temperature of spontaneous decomposition is 350° C., for γ-Fe_2O_3 it is 330° C.[92] This is in accord with the observation of Welo and Baudisch [93] who found γ-Fe_2O_3 to be a better catalyst than α-Fe_2O_3 for the oxidation of benzidine by hydrogen peroxide.

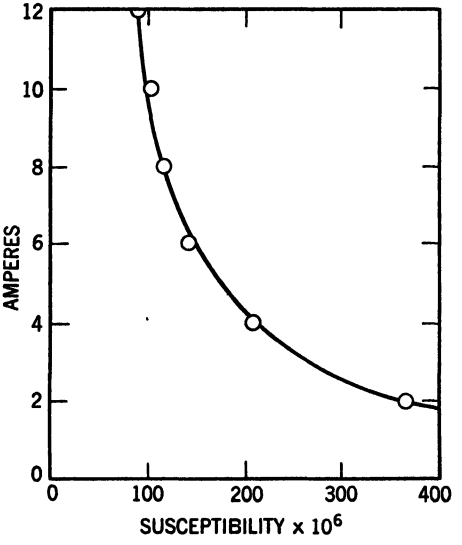


FIG. 75.—Susceptibility-field strength relation for a nickel-molybdena catalyst.

Woodman, Taylor, and Turkevich [94] have used magnetic measurements to study the structure of a nickel-molybdena hydrogenation catalyst. This catalyst was prepared by thermal decomposition of ammonium nickel molybdate in air, followed by reduction in hydrogen at moderately elevated temperatures. The catalyst was active for the hydrogenation of ethylene as low as − 80° C. On the assumption that the high activity was due to metallic nickel, susceptibility measurements were made over a range of field strength with the results shown in Fig. 75.

[92] S. S. Bhatnagar, P. L. Kapur, A. S. Bhatnagar, and M. A. Quayyum, *J. Indian Chem. Soc.*, 18, 391 (1941).

[93] L. A. Welo and O. Baudisch, *Chem. Ztg.*, 49, 961 (1925).

[94] J. F. Woodman, H. S. Taylor, and J. Turkevich, *J. Am. Chem. Soc.*, 62, 1397 (1940).

The catalyst is obviously ferromagnetic, and the magnetic data suggest that about 10 per cent of all the nickel in the catalyst is present as metallic nickel. This view is supported by poisoning experiments with hydrogen sulfide. It would be interesting, however, to have a Curie point determination on the same catalyst because this would definitely establish the presence or absence of metallic nickel.

A preliminary report on a somewhat similar type of investigation has been made by Morris.[95] Pure copper, containing less than one part per

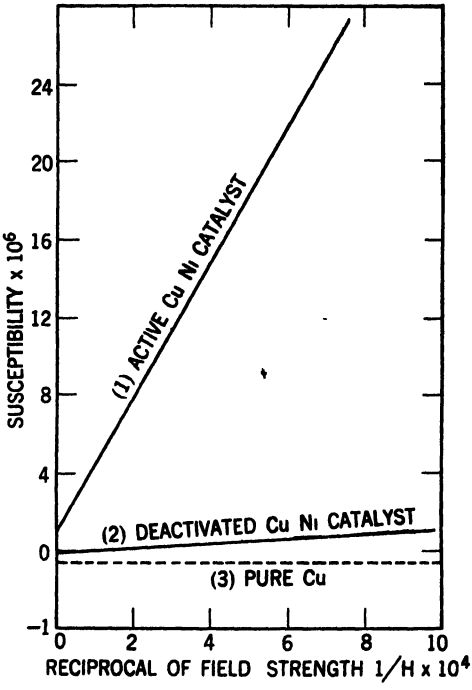


FIG. 76.—Field strength dependence of susceptibility for (1) an active catalyst consisting of 1 per cent nickel on copper, (2) the same catalyst after thermal inactivation, and (3) pure copper.

million of iron was prepared by electrolysis. This was inactive for the hydrogenation of benzene at 225° C. The copper was activated with 1 per cent nickel. It then became an active catalyst and at the same time became strongly ferromagnetic. It has been shown by Ross [96] that dilute solutions of nickel in copper are not ferromagnetic. It may therefore be concluded that the active nickel-copper surface is not a dilute solid

[95] H. Morris, *Trans. Illinois State Acad. Sci.*, **34**, No. 2, 122 (1941).

[96] W. H. Ross, *Phys. Rev.*, 46, 46 (1934).

solution, but consists rather of micro-crystals of pure nickel or of a nickel-rich alloy. Curie point measurements will throw more light on this problem. Thermal deactivation of the catalyst results in loss of ferromagnetism as shown in Fig. 76. It must therefore be a process of diffusion of the nickel into the copper.

Magnetic investigations on various iron and iron oxide catalysts have been made by Brunauer and Maxwell.[97] Replacement of Fe^{+++} by Al^{+++} in Fe_3O_4 causes a linear decrease in the intensity of magnetization but has no effect on the Curie point. Certain other promoters have a much

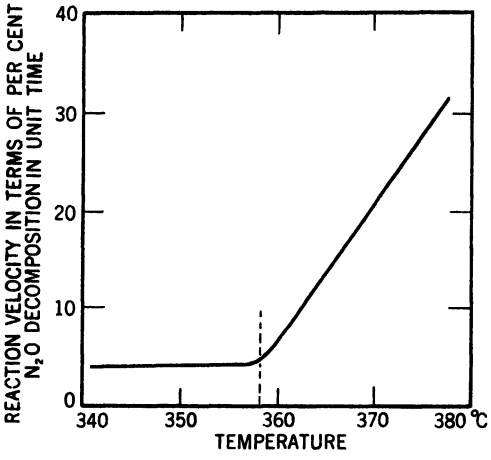


FIG. 77.—Catalytic decomposition of nitrous oxide in the neighborhood of the Curie point of nickel.

greater effect on the intensity of magnetization, but the constancy of the Curie point indicates that no chemical change takes place in the magnetite. On the other hand when B_2O_3 or Al_2O_3 are added together with an alkali or alkaline earth to Fe_3O_4, the effect on the intensity of magnetization is much greater than additive and the Curie point is also changed. In metallic iron, promoters have only a diluent effect, and the Curie point remains unchanged.

In addition to the above studies in which magnetic properties are used to determine the structure of catalysts, there have been some investigations, chiefly by Hedvall [98] (*op. cit.*, p. 164), to find the direct influence of magnetic state upon catalytic activity. As shown in Fig. 77 the velocity

[97] S. Brunauer and L. R. Maxwell, Abstracts of Papers presented at the Atlantic City meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, Sept. 8–12, 1941, p. 32.

[98] J. A. Hedvall, *Atti X° congr. intern. chim.*, 2, 255 (1938).

of the reaction $2N_2O \rightarrow 2N_2 + O_2$ changes its rate sharply over a nickel catalyst at the Curie point, about 359° C.[99,100] The effect is not accidental because with other catalysts or nickel alloys having different Curie points the catalytic inflection point is correspondingly altered. The sudden application of a magnetic field, either above or below the Curie point, produces no appreciable effect on the decomposition. This curious phenomenon is a general one. It has been demonstrated to occur with the reactions $2NH_3 \rightarrow N_2 + 3H_2$ on iron;[101] $2CO \rightarrow CO_2 + C$ on nickel;[102] the hydrogenation of carbon monoxide and of ethylene on Heusler alloys;[103] $2CO + O_2 \rightarrow 2CO_2$, $CO + H_2 \rightarrow C + H_2O$, and $CO + 3H_2 \rightarrow CH_4 + H_2O$ on synthetic magnesium ferrite, pig iron, and a tungsten-chromium steel;[104] the hydrogenation of castor oil and of cottonseed oil on nickel-copper and on palladium-cobalt alloys;[105] the hydrogenation of ethylene on nickel-copper alloy;[106] and the cleavage of formic acid on palladium-cobalt alloy.[107] The effect is a strange one. It may be related to the change of diffusion rate of hydrogen in nickel at the Curie point (p. 215).

The experiments described above raise the question as to whether there may not be a direct effect of a magnetic field on reaction velocity and chemical equilibrium. The problem lies outside the scope of this book. It is discussed by Bhatnagar and Mathur.[108] There seems little doubt that reactions involving the disappearance of a ferromagnetic substance, such as the solution of iron in hydrochloric acid, are retarded by a magnetic field.

Ogawa[109] claims that the *ortho-para*hydrogen conversion on a ferromagnetic catalyst is retarded by magnetization of the catalyst. This view is supported by measurements on the reaction between ethylene and hydrogen, in the presence of nickel or stainless steel. It is stated that formation of ferric chloride is promoted when solutions of ferric thiocyanate in ether and hydrochloric acid are placed in a magnetic field.

[99] J. A. Hedvall and E. Gustavson, *Svensk. Kem. Tid.*, **46**, 64 (1934).

[100] J. A. Hedvall, R. Hedin, and O. Persson, *Z. physik. Chem.*, **B27**, 196 (1934).

[101] K. Fischbeck, L. Neundeubel, and F. Salzer, *Z. Elektrochem.*, **40**, 517 (1934).

[102] J. A. Hedvall and F. Sanford, *Z. physik. Chem.*, **B29**, 455 (1935).

[103] J. A. Hedvall and R. Hedin, *Z. physik. Chem.*, **B30**, 280 (1935).

[104] J. A. Hedvall and A. Berg, *Z. physik. Chem.*, **B41**, 388 (1938).

[105] J. A. Hedvall and H. Byström, *Z. physik. Chem.*, **B41**, 163 (1938).

[106] S. Aoyama, J. Matsuzawa, and T. Takahashi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **34**, 957 (1938).

[107] G. Cohn, Svensk., *Kem. Tid.*, **52**, 49 (1940).

[108] S. S. Bhatnagar and K. N. Mathur, *Physical Principles and Applications of Magnetochemistry*. MacMillan and Co., Ltd., London 1935, p. 326.

[109] E. Ogawa, *Tech. Repts. Kyusha Imp. Univ.*, **14**, 243 (1939).

In addition to the work cited above there have been some suggestions of a possible relationship between magnetic susceptibility and enzymatic action.[110,111] Mention has already been made (p. 172) of the use of magnetic measurements to determine the configuration of the iron complex in the enzyme catalase.

7. Magnetism and Adsorption

Very few studies have been made of the magnetic properties of adsorbed substances. This is, however, a field of particular interest, especially in connection with the activation and poisoning of catalytic surfaces.

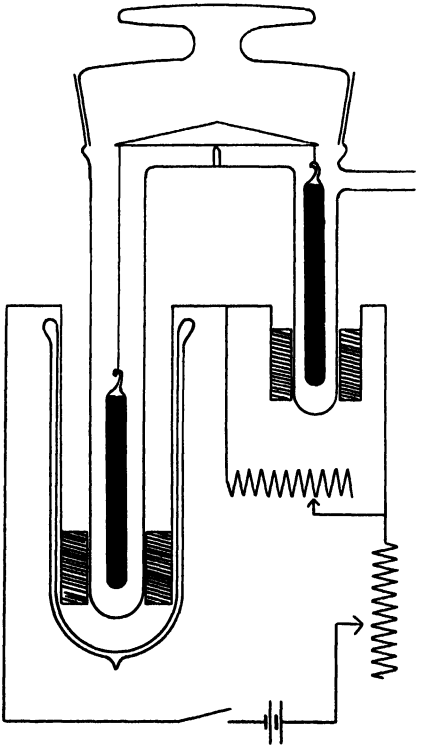


FIG. 78.—Magnetic balance for the study of adsorbed gases.

The first work in this field appears to be that of Bhatnagar, Mathur, and Kapur [112] who examined the adsorption of iron, nickel, cobalt, and

[110] R. Willstätter, *Naturwissenschaften*, 588 (1927).

[111] E. Wedekind, *Naturwissenschaften*, 21, 24 (1933) (wood ash). V. Jessen and E. Wedekind, *Forstl. Wochschra. Silva*, 22, 193 (1934).

[112] S. S. Bhatnagar, K. N. Mathur, and P. L. Kapur, *Indian J. Phys.*, 3, 53 (1928).

manganese salts by charcoal and by silica. With silica the susceptibilities are not far from additive, but with charcoal the metal ions lose their paramagnetism and become diamagnetic. This suggests a type of binding similar to that found in the diamagnetic cyanide and carbonyl complexes of iron.

Oxygen adsorbed on chabasite and on charcoal has been studied by Aharoni and Simon,[113] and Juza and Langheim [114,115] have studied the absorption of oxygen on charcoal very thoroughly. A simplified diagram of the apparatus used is shown in Fig. 78. In this apparatus the force of attraction on the sample is balanced by the field applied to a counter-poise

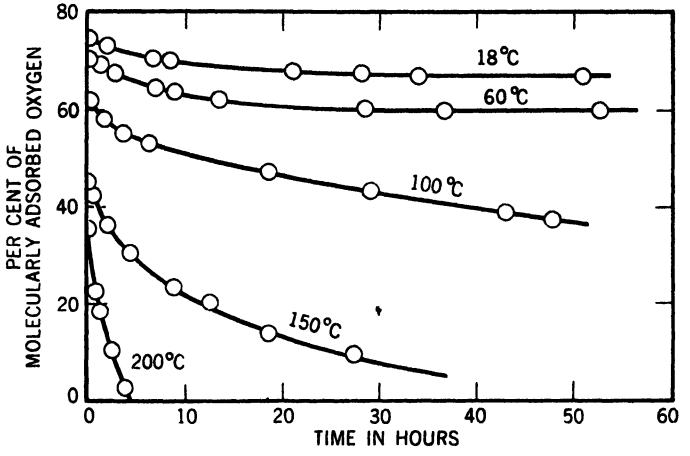


FIG. 79.—Change of molecularly adsorbed oxygen with time, determined from susceptibility measurements of oxygen adsorbed on charcoal.

roughly similar in form to the sample itself. The fields are applied momentarily. The method is the Gouy balance specially adapted to the problem of adsorption.

Results obtained clearly indicate that the susceptibilities are not additive. This is to be expected if chemical adsorption takes place, because although molecular oxygen is paramagnetic, combined oxygen is diamagnetic. The measurements therefore afford a means of finding relative proportions of molecularly adsorbed and of combined oxygen. The results show that at room temperature the proportion of molecularly adsorbed oxygen decreases with increasing temperature and time. Fig. 79 shows the per cent of molecularly bound oxygen in dependence on time

[113] J. Aharoni and F. Simon, *Z. physik. Chem.*, **B4**, 175 (1929).

[114] R. Juza and R. Langheim, *Naturwissenschaften*, **25**, 522 (1937); *Z. Elektrochem.*, **45**, 689 (1939).

[115] R. Juza, R. Langheim, and H. Hahn, *Angew. Chem.*, **51**, 354 (1938).

and temperature. From the temperature coefficient of reaction velocity it is found that the activation energy of surface oxide formation is about 5 kcals. per mole. At − 183° C. the susceptibility of adsorbed oxygen is more complicated, and depends on the density of the oxygen layer. In connection with the paramagnetic catalysis of the *ortho-para*hydrogen conversion it would be interesting to have reaction rates as a function of time, over charcoal on which oxygen was adsorbed. Magnetic measurements have also been made on bromine adsorbed on charcoal and on silica. The use of paramagnetic gases and vapors naturally yields more striking results.

8. Miscellaneous Measurements

In addition to the large number of studies already described, there are a few which are not readily classified in any of the preceding sections. One of these is the study of sols and gels. Several references have already been made to studies of matter in the colloidal state, as this topic is of interest in connection with the theory of elementary ferromagnetic domains. There have not been many studies of sols and gels *per se*, but that of Prakash [116] may be mentioned. He has determined the susceptibilities of $Fe_2(HAsO_4)_3$, $Fe_2(HPO_4)_3$, $FeBO_3$, $Fe_2(WO_4)_3$, $Fe_2(MoO_4)_3$, $Cr_2(HPO_4)_3$, and $Cr_2(HAsO_4)_3$ all in the colloidal state. These substances have susceptibilities slightly higher than the corresponding powders. Aluminum and zirconium hydroxides show an increase of diamagnetism on aging.

The magnetic susceptibility of potassium bromide crystals with color centers has been studied by Jensen.[117] He concludes that there is an increase of volume susceptibility at room temperature amounting to $2.6 \times 10^{-27} N$ where N is the number of color centers per cubic centimeter. The molar susceptibility of the color centers is 1.58×10^{-3} and the effective Bohr magneton number of a color center is 1.93.

The paramagnetic anisotropy and pleochroism of biotite mica have been studied by Nilakantan.[118] The anisotropy increases with increasing concentration of ferrous iron.

Reference [119] has already been made to the possible use of magnetic methods in the detection of ferric oxide in glass sands. A study of the state of metallic ions in borax and phosphate glasses has been made by

[116] S. Prakash, *Indian J. Phys.*, **8**, 243 (1933).

[117] P. Jensen, *Ann. Physik*, **34**, 161 (1939).

[118] P. Nilakantan, *Proc. Indian Acad. Sci.*, **8A**, 39 (1938).

[119] G. Charlesworth and F. A. Long, *Proc. Leeds Phil. Lit. Soc., Sci. Sect.*, **3**, 515 (1939).

Bhatnagar.[120,121] The color of the glass is sometimes related to the valence state of the metallic ions as determined by susceptibility measurements. For instance, manganese in reduced colorless glasses is in the bivalent state. The pink-violet color of some manganese glasses is caused by Mn^{+++} ions. The blue color of cobalt glasses is caused by bivalent Co^{++} ions, and the yellow color of nickel glasses by Ni^{++} ions. The aging of vitreous substances such as various glasses has been studied by Hüttig and Strotzer.[122] Commercial colorless glasses are diamagnetic, but if a paramagnetic oxide such as CoO is added, the susceptibility first decreases, then rises to a maximum, and finally slowly decreases to a constant value.

The magnetic properties of luminous sulfides have been studied by Rupp,[123] and by Sibaiya and Venkataramiah.[124] The susceptibility changes during the period of phosphorescent decay. For instance, for a CaS-Bi phosphor the susceptibility ($\times 10^6$) varied from -0.268 at 0 minutes, to -0.250 at 3 minutes, and to -0.247 at 12 minutes. This change is parallel to the light output, and presumably, to the photoconductivity. A change in susceptibility is not unexpected if the luminescence of such substances involves a falling of electrons out of the conductivity bands. It is a little surprising that the effect is so large.

A group of studies somewhat foreign to the purpose of this book have been made on what is called the "photomagnetic effect." Bose and Raha [125] state that, on exposure to light, the magnetic susceptibility of certain paramagnetic salts in solution is changed. Originally this was reported as a decrease, but later as an increase of susceptibility. Later studies have failed to establish the reality of this effect.[126-128] In any event the change observed is very small.

There have been a number of attempts to relate magnetic properties to the geochemical history of minerals.[129-137] Possible applications to the

[120] S. S. Bhatnagar, *Nature*, **143**, 599 (1939).

[121] S. S. Bhatnagar, B. D. Khosla, and R. Chand, *J. Indian Chem. Soc.*, **17**, 515 (1940).

[122] G. F. Hüttig and E. Strotzer, *Z. anorg. allgem. Chem.*, **236**, 107 (1938).

[123] E. Rupp, *Ann. Physik*, **78**, 505 (1925).

[124] L. Sibaiya and H. S. Venkataramiah, *Current Sci.*, **9**, 224 (1940).

[125] D. M. Bose and P. K. Raha, *Nature*, **127**, 520 (1931); **130**, 544 (1932); *Z. Physik*, **80**, 361 (1933).

[126] O. Specchia, *Nature*, **130**, 697 (1932); *Nuovo cimento*, **8**, 291 (1931).

[127] C. J. Gorter, *Nature*, **130**, 60 (1932).

[128] P. W. Selwood, *Nature*, **131**, 761 (1933).

[129] J. G. Koenigsberger, *Beitr. angew. Geophys.*, **4**, 385 (1934); E. Thellier, *Compt. rend.*, **204**, 876 (1937).

[130] K. G. Bronshtein, *J. Geol., Ukrain. Acad. Sci.*, **7**, Nos. 1–2, 167, 178, (1940).

[131] R. Chevallier and J. Pierre, *Ann. Phys.*, **18**, 385 (1932).

history of such minerals as magnetite are obvious. Magnetic prospecting methods are in use to correlate strata information obtained from wells

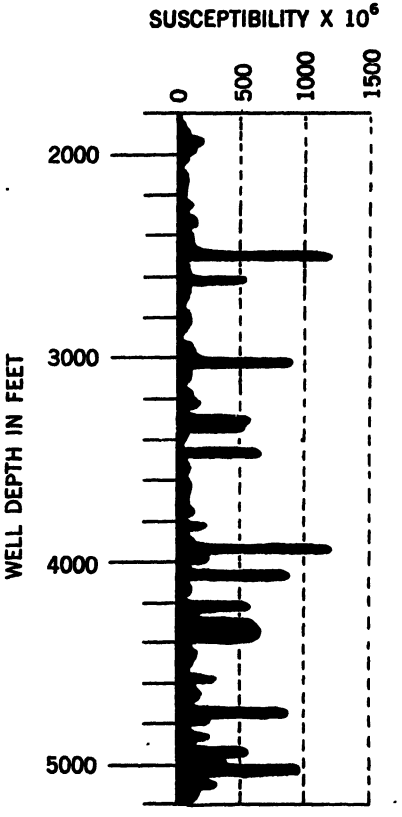


FIG. 80.—Susceptibility plotted against well-depth.

situated at various distances from each other.[138] An application of such methods is given in patents issued to Herrick.[139,140] A torsion type astatic

[133] H. Reich, *Beitr. angew. Geophys.*, 9, 40 (1941).

[134] K. Puzicha, *Beitr. angew. Geophys.*, 9, 158 (1941).

[135] F. Kutscher, *Beitr. angew. Geophys.*, 9, 187 (1941).

[136] B. Marsch and H. J. Schoene, *Beitr. angew. Geophys.*, 8, 195 (1939).

[137] H. Reich, *Z. deut. geol. Ges.*, 93, 443 (1941).

[138] O. N. Al'Thauzen, *Compt. rend. acad. sci. URSS*, 31, 661 (1941).

[138] "A Method for Determining Magnetic Susceptibility of Core Samples" in the publication *Geophysical Prospecting* published by the American Institute of Mining and Metallurgical Engineers, 1932.

[139] H. N. Herrick, (to Standard Oil Co. of Calif.) U. S. Patent 2, 104, 743.

[140] E. D. Lynton and H. N. Herrick (to Standard Oil Co. of Calif.) U. S. Patent 2, 104, 752.

magnetometer is used to measure the susceptibilities of core samples from different well depths. The kind of data obtained is indicated in Fig. 80 which shows susceptibility plotted against well depth. The sequence of susceptibilities in the different strata is related to similar sequences obtained from other wells in the vicinity. In this way it may be possible to locate tectonic structures favorable to the accumulation of valuable mineral deposits. Other properties such as radioactivity, fossil content, and heavy mineral content, are used for the same purpose.

Blood and its components have been studied by Kudo.[141] Human and animal bloods are diamagnetic with a susceptibility only slightly different than that for water. The diamagnetism is said to fall in fever, starvation, and in menstruation. The most important work on blood components is, of course, that of Pauling and of Coryell and others on hemoglobin and related compounds described in Chap. VI.

The anisotropy of naturally occurring substances has been studied by Nilakantan.[142] He derives, for instance, the crystalline character and probable crystal orientations of molluscan shells from magnetic measurements. Finally there must be mentioned the work of Nicholas Perakis [143] who conducted a magnetochemical analysis of sea-urchin eggs (Echinus melo). He analyzed the egg and the sperm. Virgin eggs in sea water have a susceptibility of -0.71×10^{-6}, a value which is not changed by fertilization. Sperm is also diamagnetic, $\chi = -0.69 \times 10^{-6}$.

[141] H. Kudo, *Acta Med. Scand.*, 81, 511 (1934).
[142] P. Nilakantan, *Proc. Indian Acad. Sci.*, 4A, 542 (1936).
[143] N. Perakis, *Compt. rend.*, 208, 1534 (1939).

AUTHOR INDEX

A

Abonnenc, L., 14, 34, 83
Adams, S. C., 174, 178, 182
Ady, P., 62
Agallidis, E., 128
Agliardi, N., 252
Aharoni, J., 120, 261
Aikawa, H., 221
Akulov, N. S., 212
Albertson, W., 83
d'Albon, G., 212
Albrecht, W. H., 105, 108, 158, 161, 225
Allard, S., 135
Allen, M. B., 171
Alphen, P. M. van, 22, 94, 186
Al'Thauzen, O. H., 222, 264
Amiel, J., 100, 101
Anderson, J. S., 149, 153
Angus, W. R., 33, 45, 54, 55, 64, 65
Anwar-ul-Haq, M., 186
Aoyama, S., 259
Aravamuthachari, S., 65, 188, 193
Arreghini, E., 157, 175
Arstadt, O., 229
Asmussen, R. W., 121, 122, 139, 152, 161, 182, 184
Athenasiadis, G., 14
Auer, H., 45, 46, 112, 191, 193, 243
Auméras, M., 111
Auwers, O. von, 206, 210, 211, 229, 242

B

Baker, C. J. W., 14, 193, 218, 220
Bakken, R., 106
Bal, G. S., 246
Bale, W. F., 171
Banerjee, S., 15, 16, 41, 69, 70, 107–109, 111
Baqi, A., 202, 229
Barkworth, E. D. P., 174
Bartlett, B. W., 102, 112
Baroni, A., 249
Basileiados, K., 83, 175
Bates, L. F., 14, 109, 190, 193, 202–204, 206–208, 214, 217, 218, 220, 229
Baudisch, O., 142, 221–226, 256
Bauer, E., 7, 29, 66, 118, 120
Beau, D., 250
Becker, G., 216, 229
Becker, R., 212
Becquerel, J., 92
Bedel, C., 213
Beeson, C. M., 122
Bégui, Z. E., 225
Beischer, D., 209
Bell, F., 139
Berg, A., 259
Bergmann, L., 21
Berkman, S., 146, 158 (ref. 18), 159, 176
Berthier, P., 163
Bhagavantam, S., 66
Bhar, H., 153
Bhar, H. J., 184
Bhargava, L. N., 224
Bhatnagar, A. S., 255, 256
Bhatnagar, S. S., 2, 10, 33, 38, 39, 48, 54, 60, 61, 65, 66, 101, 105, 107–109, 113, 114, 139, 147, 148, 152, 154, 183, 186, 190, 229, 231, 246, 255, 256, 259, 260, 263
Bhattacharjya, J., 70
Bhattacharya, A. K., 156
Bihet, O. L., 239
Biltz, W., 146, 150, 153, 155 (ref. 56), 161 (ref. 56), 181, 184, 247
Bittel, H., 18, 21, 206, 215, 231
Bitter, F., 7, 13, 18, 21, 27, 103, 107, 110, 114, 120, 206, 208, 210 (ref. 32), 212, 214, 242
Bizette, H., 104, 107, 108, 110, 111, 120
Blackman, M., 94
Blair, C. M., 37
Bleaney, B., 4
Bockemühl, K., 226
Böhm, B., 187, 188

Boeker, G. F., 13, 46–48, 130
Bommer, H., 106, 153, 173, 194, 195, 202
Bonhoeffer, K. F., 24
Bonneviale, R., 225
Bos, J. G., 179
Bose, A., 50, 90, 102, 104, 107, 111, 112
Bose, A. K., 229
Bose, D. M., 142, 146, 147, 148 (ref. 23), 149, 150, 154 (ref. 23), 158, 174, 177, 181, 184, 263
Bourion, F., 250
Bourland, L. T., 9, 204
Boutaric, A., 225
Bouwkamp, C. J., 93
Bozorth, R. M., 19, 212
Bradley, A. J., 187
Bragg, W. L., 187
Brant, L., 29
Breit, G., 92
Breuel, W., 183
Brindley, G. W., 35, 36, 38
Broniewski, W., 21, 191, 216
Brons, F., 23, 24, 93
Bronshtein, K. G., 263
Brooks, H., 67
Brown, W. F., 212
Browne, S. H., 201
Bruins, E. D., 29
Brukhatov, N. L., 215
Brunauer, S., 258
Brunetti, R., 83
Bryant, J. M., 21
Buckingham, R. A., 44
Bunge, W., 122, 124, 129
Burton, E. F., 22, 92
Byerly, W., 54, 128
Byström, H., 259

C

Cabrera, B., 2, 10, 29, 46–50, 55, 81–83, 100, 114, 152
Cabrera, N., 82
Cagnasso, A., 152, 158, 161, 166, 177, 178
Cambi, L., 121, 122, 152, 153, 158, 161, 166, 171, 175, 177, 178, 184
Cameron, A., 105, 108
Capatos, L., 102, 109, 182, 204
Capel, W. H., 82, 120
Carapella, L. A., 229
Casimir, H. B. G., 111
Cavell, H. J., 178
Chéneveau, C., 10
Chakravorty, N. C., 107
Chand, R., 263
Charlesworth, G., 226, 262
Chaudhury, P. C. R., 147, 148
Chaudron, G., 224, 227
Chaumeton, L., 101
Chevallier, R., 225, 226, 263
Chevenard, P., 212
Christiansen, J. A., 184
Christy, A., 120
Clark, H. T., 19, 237
Clews, C. J. B., 70
Clow, A., 62–64
Cockcroft, J. D., 28
Coffin, C. C., 200
Coghill, W. H., 234
Cohen, E., 192
Cohn, G., 259
Collet, P., 154, 204
Colsen, H., 55
Constant, F. W., 220, 231
Coppoolse, C. W., 117, 118
Corson, A. J., 214
Coryell, C. D., 122, 131, 152, 163–165, 167–170, 174, 178, 265
Cotton, A., 27
Coulsen, C. A., 44
Courty, C., 66, 102
Craig, D. P., 177, 180, 182
Cruickshank, J. H., 47, 55, 62, 63
Curie, P., 8, 73, 118
Cutforth, H., 232
Cuy, E. J., 159

D

Dänzer, H., 93
Dammerau, I., 135
Danz, W., 205
Dakers, J., 148
Datar, D. S., 147, 148
Datt, T. R., 66
Datta, S., 112
David, A. W., 196
Davidson, D., 156
Davis, C. W., 221, 222, 234, 238
Dean, R. S., 222
Debye, P., 92, 93
Decker, H., 13, 27, 81

Dehlinger, U., 210
DeVaney, F. D., 234
Devaud, A., 45
Dharmatti, S. S., 65, 202, 203
Diamond, H., 25, 252
Dietz, F. C., 126
Dijkstra, L. J., 93
Doan, D. J., 221, 234
Dodson, R. W., 165
Döll, W., 95
Döring, W., 206, 212
Doescher, R. N., 133
Dorfman, J., 216
Dorfman, Y. G., 21, 217
Drabkin, D. L., 163
Dressnandt, H., 101, 248
Duchemin, E., 39
Dunn, C. L., 182
Duperier, A., 114
Dupouy, G., 81
Dutt, N. K., 174
Dwyer, F. P., 179
Dyjkema, K. M., 179

E

Ehrlich, P., 249
Eley, D. D., 172
Elliott, N., 139, 152, 157, 175, 182
Ellis, C. D., 28
Elmen, G. W., 214
Elmore, W. C., 18, 208, 222, 225
Emeléus, H. J., 149, 153
Enderlin, L., 135
Endo, H., 218, 241
Espurz, A., 81
Ewens, R. V. G., 158

F

Fahlenbrach, H., 46–50, 114
Faires, R. E., 233
Fallot, M., 109, 184, 214
Faraday, M., 8, 163
Farcas, T., 220
Farkas, A., 24, 251
Farkas, L., 24, 25, 138
Farquharson, J., 11, 44, 54, 58–62, 64, 65, 123, 140
Fehrenbach, C., 83, 113
Fereday, R. A., 90, 112
Fierz, M., 93
Fink, D. G., 28
Firgau, V., 208
Fischbeck, K., 259
Fitzwilliam, J., 198
Flordal, M., 38
Fobes, M. A., 178
Focke, A. B., 201
Förster, F., 19
Foëx, G., 9, 71, 72, 83, 95, 100, 108, 112, 113, 202, 204
Fonseca, A., 191, 217
Forestier, H., 227
Formwalt, J. M., 233
Forrest, J., 111
Forrer, R., 9, 207, 222, 224, 228, 245
Foster, A., 218
Franczak, S., 21, 191
Franke, W., 136, 188
Frantz, S. G., 20
Fraser, R. G. J., 77
Frazer, J. H., 13, 175
Freed, S., 39, 42, 84, 103, 153, 188, 192
French, H. S., 180, 181
Freundlich, H., 159
Friederick, E., 230
Frischmuth, G., 154
Fritsch, H., 85, 86
Frivold, O. E., 37, 38, 84
Fucke, H., 236
Funke, J., 254

G

Gaines, A., Jr., 159, 161
Galavics, F., 122
Gallais, F., 183
Gallissot, M., 205, 224, 225
Gamgee, A., 163
Ganguli, N., 68, 69, 197, 198
Gans, R., 191, 212, 217
Garssen, J. E., 55
Gaubatz, H., 191
Geisler, R., 254
Gerlach, W., 18, 21, 34, 76, 206, 207, 215, 217, 231
Gerloff, G., 215
Gerold, E., 242
Gheorghiu, D., 56
Giauque, W. F., 23
Gibbs, R. E., 204
Gilbert, W. I., 255

Ginsberg, E., 126
Girard, A., 223
Glaser, A., 13
Glemser, O., 224
Gleu, K., 183
Goetz, A., 201
Goldacre, R. J., 173
Goldenberg, N., 151–154
Goldschmidt, V. M., 229
Goldstein, L., 117
Goodeve, C. F., 123
Gorter, C. J., 22–24, 80, 83, 85, 92, 93, 100, 104, 105, 263
Gott, O., 246
Gottschalk, V. H., 19, 234, 238
Gouy, L. G., 2
Govindarajan, S. R., 41, 66, 203
Grabbe, E. M., 214
Graf, L., 214
Graff, M., 108, 202
Graham, T., 205
Granick, S., 131, 159, 161, 166, 172
Gray, F. W., 11, 47, 54, 55, 62, 63, 148
Grew, K. E., 191, 217
Grimm, L., 248
Groendijk, H., 93
Grube, G., 19, 203, 205, 218, 220
Gruner, E., 102
Gucker, F. T., 140
Guha, B. C., 15, 41, 69, 196
Gustafsson, G., 204, 217
Gustavson, E., 259
Guthrie, A. N., 9, 204
Guzman, J., 29
Gwinner, E., 224

H

Haas, W. J. de, 22–24, 82, 83, 85, 92–94, 100, 101, 104–106, 111, 114, 120, 153, 186
Haenny, C., 81
Hafsted, L. R., 115
Hahn, H., 261
Hahn, P. F., 171
Haller, R. L., 24
Ham, W. R., 215, 216
Hamid, A., 105, 147, 148
Hammett, L. P., 159, 161
Hampel, J., 254
Handel, J. van den, 22, 83, 90, 92, 103–105
Haraldsen, H., 101, 106–108, 202, 228, 231, 247, 248
Harbard, E. H., 105, 108
Hart, H. M., 201
Harteck, P., 24
Hartenheim, M., 234
Hartree, D. R., 33, 34
Hashmi, M. S., 65
Hass, K., 245
Haul, R., 209, 223
Haurowitz, F., 163, 178
Hauschulz, B., 187, 188
Havens, G. G., 33, 34, 43, 47, 121
Hayes, E. T., 221, 225
Hebb, M. H., 91, 92
Hector, L. G., 7, 33, 34, 118
Hedin, R., 259
Hedvall, J. A., 39, 254, 258, 259
Hein, F., 149
Heisenberg, W., 87, 208
Helms, A., 123
Hendricks, S. B., 42
Henkel, P., 45, 101, 113
Herrick, H. N., 264
Herrmann, Z., 254
Herroun, E. F., 104, 107, 110, 112
Hettig, R. A., 171
Heydenburg, N. P., 115
Heymann, E., 140
Hieber, W., 158
Hildebrand, E., 191
Hill, W. K., 64
Hilpert, R. S., 224, 227
Hilpert, S., 227
Himel, C. M., 125–127
Hirone, T., 208, 212, 215, 216
Hnevkovsky, O., 254
Hoard, J. L., 172
Hoare, F. E., 35, 36, 38, 47
Hocart, R., 36, 109
Hoffmann, A., 224, 227
Hoge, H. J., 200
Hollens, W. R. A., 140
Hommel, F., 102
Honda, K., 186, 192, 195, 212, 220, 241
Horst, C., 154
Hoschek, E., 103, 248
Howard, J. B., 156
Hubard, S. S., 124
Hückel, E., 67, 137

Hüttig, G. F., 24, 226, 254, 255, 263
Huggett, J., 223
Huggins, M. L., 143
Hughes, G., 85, 95, 96
Hull, R. A., 4
Hultgren, R., 229
Hume, D. N., 145
Hund, F., 78, 79
Hupse, J. C., 90
Huster, E., 188

I

Ikenmeyer, K., 35
Illsley, P. F., 214
Inglis, D. R., 208, 228
Ireland, A. W., 190
Ishiwara, T., 229
Isihara, S., 227
Iskenderian, H. P., 12

J

Jacini, G., 158
Jackson, L. C., 15, 29, 82, 90, 91, 104, 107, 111, 142, 146, 153, 156
Jacobi, H., 148, 150, 158, 159, 178, 184
James, C., 81
Janes, R. B., 112, 114, 184
Janke, W., 134
Jatkar, S. K. K., 147, 148
Jeitner, F., 254
Jensen, K. A., 108, 138, 154
Jensen, P., 262
Jessen, V., 260
Jogelkar, M. S., 110
Johansson, C. H., 191
John, W. J., 201
Johner, W., 46, 48
Johnson, C. H., 153
Jones, H., 187
Joos, G., 35, 251
Jordahl, O., 86
Juza, R., 119, 261, 247

K

Kalckar, F., 24
Kamen, M. D., 171
Kanzler, M., 118
Kapitza, P., 27
Kaplan, J. F., 126, 127
Kapur, P. L., 39, 61, 65, 105, 108, 113, 190, 255, 256, 260
Karantassis, T., 83, 109, 175
Kasper, C., 153
Kassatochkin, W., 123
Kato, Y., 221
Katsurai, T., 226
Katz, H., 121, 122, 129, 132, 133, 136, 188
Kaufmann, A. R., 21, 103, 107, 110, 114, 187, 191, 194, 198, 214, 242
Kaur, Gurbaksh, 61
Kawai, N., 221
Kaya, S., 212, 215, 216, 220
Kenyon, J., 122
Kershaw, H., 28
Khanna, M. L., 48, 101, 114
Khosla, B. D., 61, 263
Kido, K., 35
King, A., 105, 108
Kinoshita, S., 40
Kirenskii, L. V., 215
Kirton, H. M., 64
Kitagawa, T., 255
Kittel, H., 163, 254, 255
Klemm, L., 138, 139, 162, 193, 198, 200
Klemm, W., 2, 34, 36, 37, 45, 83, 95, 96, 101–109, 113, 123, 124, 138, 141, 148–152, 154, 158, 159, 162, 163, 178, 184, 187, 188, 193, 194, 199, 210, 228, 231, 245, 247, 248
Koolhaus, J., 101, 105, 107, 114
Klerk, D. de, 111
Klinger, P., 236
Knaggs, I. E., 70
Knappworst, A., 30, 191
Knauer, H., 156, 161
Knick, R., 254
Kobell, F. von, 225
König, H., 68
Koenigsberger, J. G., 223, 263
Kohlmeyer, E. J., 254
Kostelitz, O., 254
Kotow, W., 123
Kowalski, E., 106
Kracek, F. C., 42
Kraeber, L., 221
Kramers, H. A., 23, 83, 85
Krause, A., 223
Krings, W., 246
Krishnan, K. S., 15–17, 40, 41, 67–69, 90, 91, 101, 102, 104, 107–109, 111, 112, 176, 196–198

Kronig, R. de L., 93
Kruck, W., 126
Krueger, H., 191, 217
Kuck, J. A., 131
Kudo, H., 163, 265
Kürti, N., 23, 82, 110
Kuhn, R., 132, 136, 255
Kussmann, A., 21, 206, 213, 214, 216, 218, 227, 229–231, 237
Kutscher, F., 264
Kowalski, E., 248
Kynch, G. J., 91

L

Lainé, P., 110, 119
Lakra, C. L., 66
Lallemand, A., 111, 159, 160
Landau, L., 185
Lane, C. T., 191, 192, 201
Lange, H., 20, 244
Langevin, P., 31, 73
Langheim, R., 119, 261
Langmesser, P., 124
Larmor, J., 31
Laurent, P., 114
Lawrence, R. W., 106
Lazarev, B. G., 83, 194
Lecuir, L., 182
Lehrer, E., 118, 245
Leiterer, L., 147
Leitgebel, W., 226
Lessheim, H., 101
Levinson-Lessing, F. Y., 222
Lewis, G. N., 116, 118
Lifschitz, I., 179
Lille, R., 224, 227
Linde, J. O., 191
Lips, E., 104, 121
Liquier-Milward, J., 81
Lockwood, W. H., 180, 184 (ref. 163)
London, F., 67
Long, F. A., 226, 262
Long, N. O., 13, 175
Lonsdale, K., 15, 64, 67, 68, 70
Lunde, L., 84
Luyken, W., 221
Lynton, E. D., 264

M

Macdougall, D. P., 23
Magee, M. Z., 180, 181
Maheshwari, J. C., 109, 152, 154
Maier, K.-H., 224, 227
Malatesta, L., 102, 146, 147, 150, 161, 178, 179, 181, 182, 184
Malmstrom, H. E., 215
Manders, C., 217
Mann, K. E., 34
Margolin, J. M., 213
Marian, V., 216
Marsch, B., 264
Marvel, C. S., 7, 124–127
Massey, H. S. W., 44
Masing, G., 199
Masumoto, H., 220
Mathieu, K., 20, 244
Mathieu, S., 225, 226
Mathur, K. N., 2, 54, 139, 183, 259, 260
Mathur, R. N., 10, 39, 46, 48, 60
Matsuzawa, J., 259
Mauguin, C., 71
Maxwell, L. R., 258
McKeehan, L. W., 2, 206, 208, 212, 222
McLennan, J. C., 192
Meakin, R., 14
Mehmed, F., 108, 248
Meisel, K., 95
Mella, A. A., 178, 182
Mellor, D. P., 145, 152, 173, 174, 177, 179–182, 184 (ref. 163)
Menéndez, N., 81
Mercier, R., 111, 112
Merck, F., 255
Messkin, W., 213, 229
Metcalf, R. P., 42
Meyer, S., 94, 95
Michaelis, L., 129–131, 133, 159, 161, 166, 172
Michel, A., 205, 223–228
Mills, J. E., 179
Milward, J. L., 175
Milyutin, G. A., 110, 114
Minne, P., 249
Mitra, N. G., 54
Mittal, G. L., 190
Miyahara, S., 228
Moles, E., 29
Montgomery, C. G., 191
Monti, F., 181
Mookherji, A., 90, 101, 102, 104, 111, 112, 176

Morgenstern, G., 158, 161
Morris, H., 128, 257
Mounic, M., 111
Müller, E., 122, 124–126, 129, 134–138, 252
Mueller, M. B., 126, 127
Müller-Rodloff, I., 122, 124, 129, 134–136
Mulliken, R. S., 145
Munch, R. H., 140
Mundle, N. K., 57
Murakami, T., 241

N

Nahinsky, P., 171
Narayanaswamy, A. S., 57, 195
Nast, R., 158
Naudé, S. M., 120
Nayar, M. R., 57
Néel, L., 89, 120, 195, 215, 216
Nettleton, H. R., 29
Neuber, A., 149, 248
Neugebauer, Th., 67
Neuhoff, H., 137
Neuman, E. W., 123
Neumann, H., 18, 234
Neundeubel, L., 259
Nevgi, M. B., 33, 38, 39, 48, 54, 60, 65, 76, 107, 114, 195
Nicolau, A., 106, 110, 112
Niessen, K. F., 216
Nilakantan, P., 42, 70, 262, 265
Nishina, T., 212
Nitka, H., 218, 227
Novák-Schreiber, W., 254
Nowotny, H., 191, 229
Noyes, A. A., 182
Nygaard, E., 202

O

Ochsenfeld, R., 204, 229
Oelsen, W., 241
Ogawa, E., 259
Ohri, G. L., 65
Olmer, F., 255
Olsen, N. G., 37
Onnes, H. K., 22, 23, 81, 92, 118
Oosterhuis, E., 118
Ostinelli, P., 153
Owen, M., 42, 186, 187, 195
Owesny, F., 254
Oxley, A. E., 11, 49, 50, 178

P

Pan, S. T., 214, 242
Pantulu, D. V. R., 203, 204
Paramasivan, S., 68
Pascal, P., 50, 51, 53–55, 59, 64, 125, 129, 135, 249
Pauli, W., 185
Pauling, L., 33, 34, 63, 67, 118, 124, 130–132, 143, 145, 159, 163–165, 167, 168, 172, 174, 178, 185, 265
Pearce, D. W., 85, 94–96
Pearce, R. R., 10, 20, 207
Peierls, R., 94, 185
Penney, W. G., 86, 91, 104, 107, 111, 145
Perakis, N., 83, 102, 109, 175, 182, 204, 265
Perrier, A., 22, 118
Persson, E., 229
Persson, O., 259
Petersen, M., 249
Peype, W. F. van, 67
Pfanz, H., 138
Phipps, T. E., 120
Piccard, A., 7, 29, 45, 118, 120
Piekara, A., 70
Pierre, J., 263
Pietrek, W., 216
Piloty, O., 136
Pitzer, K. S., 182
Posnjak, E., 42
Post, C. B., 215, 216
Potter, H. H., 229
Powell, H. M., 145, 158
Prasad, M., 66, 70, 202, 203
Prakash, B., 105, 108, 109, 147, 148, 152, 154, 229, 255
Prakash, S., 224, 262
Pré, F. K. du, 24, 93
Preckel, R. F., 127, 128, 140
Prentice, J. H., 217
Procopiu, S., 212
Puzicha, K., 264

Q

Quartaroli, A., 160, 226
Qayyum, M. A., 229, 256
Quincke, G., 6
Qureshi, M., 37, 57

R

Rabi, I. I., 16
Raha, P. K., 263

Raman, C. V., 40, 41, 67
Ramiah, H. S. V., 193
Ranganadham, S. P., 37, 57
Rankine, A. O., 12
Rao, S. R., 38, 41, 55–57, 65, 66, 187, 188, 190, 192, 193, 195, 200, 203, 215
Raskin, A., 66
Rautenfeld, F. v., 55
Rawlinson, W. A., 28, 150, 166, 167 (ref. 103), 168, 169
Rây, P., 153, 173, 175
Raychaudhuri, D. P., 19, 154, 227, 229
Reber, R. K., 13. 130, 131, 212
Redslob, F., 227
Reekie, J., 100
Reich, H., 264
Rice, O. K., 120, 143
Richardson, J., 152, 157, 175
Richardson, F. D., 123
Riedl, E., 191
Rieger, W. H., 126
Rienäcker, G., 191
Riott, J. P., 236
Robertson, J. M., 70
Rocard, Y., 117
Rockstroh, J., 96
Rodden, C. J., 82
Rogers, B. A., 20, 236
Rollier, M. A., 157, 175
Rosenbohm, E., 146, 155 (ref. 16), 176, 181
Ross, J. F., 171
Ross, W. H., 191, 217, 257
Roy, B. P., 196
Roy, M. F., 124
Ruben, S., 171
Ruedy, R., 192
Rummel, K. W., 24
Rumpf, P., 132, 133
Rupp, E., 263
Russell, C. D., 167
Ruttewit, K., 199

S

Sachsse, H., 25, 138, 222, 251, 252
Sadron, C., 216
Salceanu, C., 13, 56, 70
Salzer, F., 259
Sampson, J. B., 188
Sandler, L., 24
Sanford, F., 259
Sanford, R. L., 239
Sastri, M. V. C., 54, 61, 64
Savithri, K., 192
Schackleton, J. W., 126
Scharnov, B., 227, 229
Scherrer, P., 120
Schlapp, R., 86, 104, 145
Schlechtweg, H., 212
Schmeiser, H., 254
Schneider, O., 254
Schnurmann, R., 77, 117
Schön, K., 132
Schoene, H. J., 264
Schoon, T., 209, 223
Schottky, W., 248
Schramm, J., 217
Schubert, M. P., 131
Schüth, W., 83, 96, 109, 113, 114
Schultz, B. H., 84, 101, 105, 107, 114, 153
Schulze, A., 21, 227
Schulze, G. E. R., 42
Schwab, G. M., 24, 25, 128, 252
Schwab-Agallidis, E., 25, 252
Scott, A. F., 37
Sedlatschek, W., 254
Seely, S., 46, 47, 56
Seemann, H. J., 191
Seitz, F., 185, 187
Selwood, P. W., 13, 24, 54, 81, 84, 85, 88 (refs. 13, 48a), 94, 95, 96 (ref. 44), 127–129, 140, 231, 233, 253, 263
Sen, D. C., 173, 175
Senff, H., 96, 152, 162, 163, 178 (ref. 93)
Sengupta, P. N., 154
Serres, A., 112, 203
Seybolt, A. U., 239
Shalyt, S. S., 104, 110, 114
Shanker, J., 70
Sharma, R. L., 38, 107
Shaw, E. J., 120
Sheffield, E., 180, 181
Sherman, A., 24
Shih, J. W., 191, 216
Shimizu, Y., 51, 186, 191, 200, 203
Shoenberg, D., 22, 94, 191, 201
Shubnikov, L. V., 83, 194
Shur, J., 50
Sibaiya, L., 47, 263
Sibata, N., 191
Sidgwick, N. V., 63, 145

Sidorov, S., 21, 217
Siegert, A., 103, 111
Sieverts, A., 205
Sigolaev, S. Y., 234
Simon, A., 156, 158, 161
Simon, F., 23, 110, 261
Singh, A., 66
Singh, J., 108, 255
Singh, M., 66
Slater, J. C., 33–35, 88, 208
Smith, C. S., 243
Smith, H. G., 22, 92
Smith, S. W. J., 240
Snoek, J. L., 211, 227
Sodomann, H., 123, 124
Sogn, H., 38
Soler, G., 19, 237
Soné, T., 116, 118, 120, 229
Specchia, O., 263
Spedding, F. H., 84, 86
Spence, R., 24
Spencer, J. F., 47, 49, 56, 140, 196
Spooner, T., 240
Squire, C. F., 68, 108, 198, 199
Sriraman, S., 57, 187, 192
Stackelberg, M. von, 83
Stamm, K. O., 20
Stansfield, R. G., 28
Starr, C., 93, 103, 107, 110, 114, 187, 191, 194, 242
Steinberg, H., 106, 149, 150, 151, 154
Steller, J. S., 153, 161, 174, 178, 182
Stern, O., 77
Steurer, E., 55
Stierstadt, O., 201
Stitt, F., 165, 167, 168
Stöhr, H., 199, 200
Stössel, R., 117, 120
Stone, H. W., 145
Stoner, E. C., 1, 3, 14, 29, 31, 33, 44, 55, 80, 100, 110, 116, 117, 187, 189, 207, 208, 215, 220, 221, 228
Strock, L. W., 176
Strotzer, E., 263
Sturdivant, J. H., 132
Subramaniam, K. C., 50, 195, 200
Sucksmith, W., 9, 10, 20, 82, 85, 106, 207
Sugarman, N., 42, 188
Sugden, S., 29, 102, 122, 133, 139, 174, 178
Svensson, B., 191, 205
Sykes, C., 187
Szegö, L., 153, 161, 171, 177

T

Tai, L. C., 202, 203
Takagi, Y., 208
Takahashi, T., 259
Takai, T., 221, 227
Takatori, N., 51, 204
Tammann, G., 47, 241
Tarasov, L. P., 213
Taylor, D. S., 169–171
Taylor, G. G., 229
Taylor, H. S., 24, 25, 252, 256
Taylor, N. W., 116
Teller, E., 24
Teschner, F., 134
Teunissen, P., 93
Thal, W., 238
Thellier, E., 263
Thielmann, K., 229
Thode, H. G., 39, 188
Thompson, J. M. C., 64
Thompson, N., 216
Theorell, H., 171
Theron, R., 205
Tibbs, S. R., 44
Tietz, E., 137, 138
Tilk, W., 105, 141, 148, 150, 158, 159, 178, 184
Tin, M. T., 102
Tjabbes, B. T., 148–150
Tobusch, H., 19
Tremolada, E., 177
Trew, V. C. G., 34, 36, 37, 47, 49, 56
Trombe, F., 132, 133, 194, 195
Tsaï, B., 104, 107, 108, 110, 111, 120
Turkevich, J., 24, 129, 253, 255, 256
Turtsev, A. A., 109
Tuve, M. A., 115
Tyler, R. W., 107
Tyson, Jr., G. N., 153, 161, 174, 178, 182

U

Ubbelohde, A. R., 67
Uddin, M. Z., 22, 94, 201
Urbain, G., 194

V

Vaidyanathan, V. I., 11, 50
Valentiner, S., 216, 229

Vallesi, E., 226
VanVleck, J. H., 32, 33, 38, 39, 43, 54, 55, 74, 76, 78–80, 83–85, 87–89, 91–93, 98, 100, 103, 104, 107, 111, 114, 117, 120, 145, 208
Varadachari, P. S., 38, 55
Veiel, U., 37
Velayos, S., 82, 215
Venkataraman, S., 57
Venkataramiah, H. S., 64, 263
Vereshchagin, L. F., 83, 194
Verma, M. R., 186
Vigoreux, P., 240
Vinti, J. P., 66
Vivian, R. E., 182
Vogel, H. V. v., 95
Vogel, W., 136
Vogt, E., 187, 188, 191, 193, 204, 206, 213, 217, 242
Voigt, W., 40

W

Walden, G. H., Jr., 159, 161
Wallis, E. S., 255
Wardlaw, W., 175
Wartman, F. S., 6, 234
Way, W. J. R., 175
Webb, C. E., 240
Webb, J. S., 21
Wedekind, E., 105, 154, 225, 255, 260
Weil, L., 204
Weiss, P., 9, 25, 29, 35, 85, 193, 194, 208, 211, 222, 228
Welo, L. A., 142, 146, 147, 155, 156, 221–226. 249, 256
Wentzel, K., 236
Werth, H., 148
Wheeler, M. A., 203, 204
Wheland, G. W., 133
Whipple, G. H., 171
Whitmore, B. G., 229
Whitson, J., 126
Wiersma, E. C., 22, 23, 82, 84, 90, 100, 117, 118, 120
Wiesemann, W., 134, 136
Wigner, E., 24, 251
Wiley, J. W., 153, 161, 174, 178, 182
Wilhelm, J. O., 22, 92
Wille, A., 227
Willems, F., 239
Williams, C., 216
Williams, E. H., 82, 191, 217
Williams, H. J., 213
Williams, S. R., 208
Wills, A. P., 7, 33, 34, 46, 47, 118, 130
Willstätter, R., 260
Wilson, A. H., 185
Wilson, E., 11
Wilson, E. B., Jr., 122
Winkel, A., 209
Winkler, O., 19, 203, 205, 218, 220
Witkowski, R., 21, 191
Woltjer, H. R., 22, 23, 81, 92, 117, 118
Witmer, E. E., 43, 44
Woodbridge, D. B., 7, 54, 130
Woodward, I., 70, 162, 163
Woodman, J. F., 256
Work, H. K., 19, 237
Wulf, O. R., 118

Y

Yajnik, N. A., 255
Yamasaki, K., 226
Yanus, R. I., 50, 194
Yasuda, T., 227
Yensen, T. D., 210, 211, 213, 215

Z

Zernike, J., 81
Zimens, K. E., 39, 251
Zocher, H., 146, 158 (ref. 18), 159, 176

SUBJECT INDEX

A

Absorption, measurements, 23, 260
Acetone, 60
Acetylacetonate, nickel, 177
Acetylcyanide, 60
Acid, cinnamylidenemalonic, 65
  cyclopropanecarboxylic, 64
  cyclohexanecarboxylic, 64
  hyposulfurous, 139
  hydrochloric, 37
  iodic, 57
  nitric, 57
  sulfuric, 38
Acids, organic, 54
"Active" oxides, 254
Additivity of susceptibilities, deviations, 56
Adiabatic demagnetization, 23
Adsorbed gases, 261
Adsorption and magnetism, 260
Alkali metals, 187
  amalgams, 188
  in liquid ammonia, 188
  mixtures, 188
  polyoxides, 123
  selenides, 124
  sulfides, 124
  tellurides, 124
  vapors, 76
Alkaline earths, halides in solution, 37
  metals, 191
  metals, solutions in liquid ammonia, 192
Alloys, (see under constituent metals)
  Heusler, 229
  structure, 241
Alcohols, aliphatic, 48
Alkyl acetates, 51
Alkyl iodides, 48
Alum, 39
Aluminum, hydroxide, 262
  metal, 193
Amalgams, alkali metal, 188
  chromium, 202
  copper, 190
  nickel, 218
Aminothiazine, semiquinone ions, 133
Ammonia, solutions of alkali metals, 188
  solutions of alkaline earth metals, 192
Ammonium, hexabromohypoantimonate, 139
  ion, diamagnetism of, 36
  nitrate, anisotropy, 41
Analysis, of rare earth mixtures, 231
Anisaldazine, 72
Anisotropy, ammonium nitrate, 41
  benzene, 67
  carbonates, 41
  chlorates, 41
  compounds, 69
  diamagnetic ionic crystals, 40
  diphenyldiacetylene, 68
  ferromagnetic crystals, 212
  graphite, 196
  hexamethylbenzene, 68
  liquid crystals, 71
  from magneto-optical data, 70
  measurements, 15
  mica, 262
  molecular crystals, 66
  natural substances, 265
  nitrates, 41
  rare earth compounds, 89
Anisotropy, salts (see under metallic element)
  sodium nitrate, 40
  sulfates, 41
  tellurium, 41
  temperature dependence, 70
  temperature dependence in diamagnetic solids, 41
Anthracene, 60, 135
Antimony, 200
  chlorides, 139
Argentic ion, 102
Argon, 34
  temperature dependence, 47

Arsenic, 200
Aryl iodides, 48
Apparatus, for adsorbed gases, 261
Atomic crystals, diamagnetism, 42
Atomic, diamagnetism, 31
  orbitals, 143
  paramagnetism, 73
Azoxyanisole, 71
Azoxyanisolephenetol, 72

B

Barium, metal, 191
Benzaldehyde, 60
Benzene, 48, 135
  anisotropy, 67
  mixtures, 56
  vapor, 50
Benzoin, 60
Benzophenone, 50
  potassium, 133
Benzylbenzoate, 60
Beryllium, basic acetate, 65
  acetylacetonate, 65
  metal, 191
Biotite mica, 262
Biphenylphenylketone potassium, 133
Bismuth, 200
  anomalous field strength dependence, 93
  dioxide, 139
Biradicals, 122, 134
  nitrogen, 136
Blood, 163, 265
Bohr magneton, 74
Boron, 193
  hydride, 138
Borax glasses, 262
Brass, structure, 243
Bromate ion, diamagnetism, 36
Bromide ion, diamagnetism, 36

C

Cadmium, metal, 192
  univalent, 140
Calcium, metal, 191
Calibration of magnetic balances, 28
Calomel, 140
Capillary rise method, 6
"Carbanalyzer," 237
"Carbometer," 237
Carbonate ion, diamagnetism, 36
Carbon disulfide, vapor, 50
Carbon in steel, 236
Carbonmonoxyhemoglobin, 165
Carbon tetrachloride, 48
  mixtures, 56
Carbonyl, chromium, 148
  iron, 158
  molybdenum, 150
  nickel, 178
Catalase, 172
Catalysis and magnetism, 251
Catalysts, structure, 255
Catalytic activity, at the Curie point, 258
Ceric, oxide, 94
  sulfate, 95
Cerous, orthophosphate, 82
  chloride, 83
  fluoride, 83
Cerium, metal, 193
  salts, 81
Cementite, 228
  determination, 239
Cesium, ionic diamagnetism, 36
  metal, 187
  tetraiodide, 124
  tetroxide (dioxide), 123
Chabasite, as adsorbent, 261
Charcoal, as adsorbent, 261
Chichibabin hydrocarbons, 136, 252
Chlorate ion, diamagnetism, 36
Chloride, antimony, 139
  ionic diamagnetism, 36
Chlorine, dioxide, 116
  oxides, 123
  trioxide (hexoxide), 123
Chromic, anhydride, 148
  arsenate, 262
  phosphate, 262
Chromium, 202
  carbonyl, 148
  chromates, 148
  complex compounds, 145
  compounds, 104
  dioxide, 147
  polyphenyl, 149
Chromium compounds, ferromagnetic, 229
Chromium-selenium system, 248
Chromium-sulfur system, 248
Chromium-tellurium system, 248
Cinnamylidenemalonic acid, 65

Cobalt, 220
above the Curie point, 207
alum, hydrate binding, 251
complex compounds, 172
compounds, 112
as catalyst, 255
compounds, adsorbed, 260
oxide, as catalyst, 255
oxides, 229
sulfide, 228
Cobalt-copper system, structure, 242
Cobalt-sulfur system, 247
Cobaltous oxide, 228
"Coercimeter," 234
Coercive force, and particle size, 234
definition, 18
Colloids, copper, 190
iron and chromium salts, 262
magnetite, 222
nickel, 215
tin, 200
Color, and complex configuration, 179
Color centers, in potassium bromide, 262
Columbium, 200
compounds, 104
Complex compounds, 142
prediction of configuration, 179
Complex configuration and color, 179
Complexes, polynuclear, 147
Compounds, complex, 142
Concentration, effect on diamagnetism of solutions, 37
Conjugated systems, 134
Constants, Pascal's, 51
Constitutive correction, 51
Copper, alloys, 190, 191
Copper-aluminum alloy, structure, 243
Copper, amalgams, 190
colloidal, 190
complex compounds, 181
compounds, 100
metal, 189
phosphides, 101
sulfate, anisotropy, 101
trivalent, 102
Copper-nickel catalyst, 257
Correction, constitutive, 51
for ferromagnetism, 186
Cresol, 48
Crystal form, effect on diamagnetism, 39
Crystallization, effect on molecular diamagnetism, 49
Crystals, ionic diamagnetic, 38
liquid, 71
Cupric, compounds, 100
ion, 100
fluoride, 101
hydroxide, 101
Cuprous ion, 102
Curie-Chéneveau method, 10
Curie law, 73
Curie point, and alloy composition, 245
and catalysis, 258
definition, 18
determination, 21, 239
of the ferromagnetic metals, 207
of the rare earths, 89
Cyanate ion, diamagnetism, 36
Cyanide ion, diamagnetism, 36
Cyanogen chloride, 59
Cycloheptanone, 64
Cyclohexane, 64
Cyclohexanecarboxylic acid, 64
Cyclohexanol, 64
Cyclohexanone, 64
Cyclopropanecarboxylic acid, 64
Cytochrome, 171

D

Decahydronaphthalene, 54
Decalin, 54
De Haas-van Alphen effect, 93
Demagnetization, adiabatic, 23
Deuterium, dissolved in palladium, 205
molecular, 44
oxide, 47
Diamagnetism, atomic, 31
of atomic crystals, 42
classical theory, 31
definition, 1
effect of particle size, 51
effect of crystalline form, 39
effect of temperature, 38
effect of vaporization, 50
and electric polarizability, 66
of ions, 34
of ions, table, 36
of living cells, 66
metallic, 185
modern theory, 32

Diamagnetism (contd.)
of molecular mixtures, 55
of molecules, 43
of molecules, effect of physical state, 48
of molecules, temperature dependence, 47
near the melting point, 49
in non-aqueous solvents, 38
Diacetone alcohol, 60
Diacetylcyanide, 60
Diamond, 42
Dianthracene, 60
Diaryl nitric oxides, 121
Dibenzanthracene, 135
Dibenzoxanthone potassium, 134
Diborane potassium, 138
Dihydropyocyaninium perchlorate, 132
Dimethylbutadiene, 62
polymerization, 58
Dioxydiborane potassium, 138
Di-*p*-anisyl nitric oxide, 122
Di-*p*-nitrophenylene nitric oxide, 122
Diphenyl nitric oxide, 121
Diphenyldiacetylene, anisotropy, 68
Diphenyldiazomethane, 135
Dispersion, measurements, 23
Divalent rare earths, 96
Duroquinone, 131
Dysprosium, Curie point, 195
metal, 193
oxide, 80, 82, 232
sulfate octahydrate, 82

E

Effective atomic number, 142
Effective magneton number, 79
Eggs, sea-urchin, 265
Ethylazoxybenzoate, 72
Electron isomers, 83
Electron precession, 31
Elements, transition group, 97
Enzymatic action and susceptibility, 260
Erbium, Curie point, 195
metal, 193
oxide, 82, 232
sulfate octahydrate, 82
Esters of hypophosphoric acid, 139
Europium, chloride solutions, 81
compounds, temperature coefficient, 83
divalent, 95
metal, 193
oxide, 82, 232
sulfate octahydrate, molecular field, 89
Europous compounds, 95, 96
Exchange interaction, 86
Experimental methods, 1
Explosive antimony, 200

F

Faraday method, 8
Ferric, arsenate, 262
borate, 262
chloride vapor, 159
ferrocyanide, 156
hydroxide, 226
molybdate, 262
oxide, α, 222
oxide, γ, 222
oxide, as catalyst, 255, 256
oxide hydrate, 224
oxide in glass sands, 262
phosphate, 262
tungstate, 262
Ferricyanides, 154
Ferriheme, chloride, 164
hydroxide, 165
Ferrihemoglobin, cyanide, 167
derivatives, 167
hydrosulfide, 167
Ferrites, 226, 254
Ferritin, 166
Ferrocyanides, 155
Ferroheme, 165
Ferrohemoglobin, 165
derivatives, 168
Ferromagnetic, Curie point, 207
gels, 226
impurities, 29, 233
precipitates in alloys, 242
Ferromagnetism, 206
corrections for, 186
definition, 1
ultimate particle, 208
"Ferrometer," 238
Ferrous alloys, 212
Ferrous, ammonium sulfate, as a calibration agent, 29
kojate, 161
oxide hydrate, 226
sulfide, 228
Field intensity, measurements, 28

control, 27
non-homogeneous, 8, 77
Fluoride ion, diamagnetism, 36
Fluorides, liquid, 45
Free radical, as catalyst, 253
definition, 122
degree of dissociation, 125
disproportionation, 126
hexaarylethanes, 124
ions, 131
in polymerization reactions, 61
o-p-hydrogen method, 128, 252
organo-metallic, 128
Fremy's salt, 121
Furfural, 60
Furoin, 60

G

Gadolinium, chloride solutions, 81
Curie point, 195
ferromagnetism, 194
metal, 193
molecular field in compounds, 88
oxide, 82, 232
oxide as catalyst, 252
sulfate octahydrate, 81, 82
Gallium, dichloride, 141
metal, 193
Gases, adsorbed, 261
inert, 33, 34
measurements, 7
monatomic paramagnetic, 76
Gauss, definition, 1
Gels, 262
Geochemistry of minerals, 263
Germanium, 197, 199
alloys, 199
triphenyl, 128
Glasses, 262, 263
Goethite, 224
Gold, alloys, 191
divalent, 103, 182
metal, 189
Gouy method, 2
Graphite, 196
Guanidine hypophosphate, 139

H

Hafnium compounds, 103
Heavy water, 47
Helium, 34
temperature dependence, 47
Hematin, 165
Hematite, 222
Hemin, 164
temperature coefficient, 171
Hemochromogens, 168
Hemoglobin, from different animals, 169
magnetic determination, 170
nomenclature, 163, 164
Heusler alloys, 229
Hexaarylethanes, 124
Hexamethylbenzene, anisotropy, 68
Hexane, 64
Hexaphenylethane, 124
High frequency measurements, 21
Holmium, Curie point, 195
metal, 193
oxide, 80, 232
sulfate octahydrate, 82
Homologous series, 54
Hydration, effect on susceptibility, 38, 250, 251
Hydrazyls, 129
Hydrocarbons, 54
Chichibabin, 136
Hydrochloric acid, 37
Hydro-*p*-naphthophenazinium perchlorate, 132
Hydrogen bonding, 64
Hydrogen chloride, in solution, 37
Hydrogen, dissolved in iron, 212
dissolved in manganese, 204
dissolved in nickel, 212
dissolved in palladium, 205
dissolved in titanium and zirconium, 198
molecular, 43
temperature dependence, 47
Hypoantimonate, ammonium hexabromo-, 139
Hypophosphates, 139
Hypophosphoric acid, esters, 139
Hyposulfurous acid, 139
Hysteresis loop, determination, 19

I

Ice, 47
Imidazole ferrihemoglobin, 168
Impurities, ferromagnetic, 29, 186, 233
paramagnetic, 30

"Inactive" iron, in blood, 170
Indium, dichloride, 141
  metal, 193
Induction methods, 18
Inert gases, 33, 34
  temperature dependence, 47
Instruments, used in metallurgical and mineralogical control, 234
Intensity of magnetization, 2, 17
Iodate ion, diamagnetism, 36
Iodic acid, 57
Iodides, alkyl, 48
  aryl, 48
Iodide ion, diamagnetism, 36
Iodine, solutions, 66
Ionic crystals, diamagnetic, 38
  diamagnetic anisotropy, 40
Ionic diamagnetism, 34
  table, 36
Iridium, 204
  complex compounds, 184
  compounds, 114
Iron, 210
  above the Curie point, 207
  adsorbed compounds, 260
  alloys, 212
  boride, 228
  carbide, 228, 239
  carbonyl, 158
  as catalyst, 255, 258
  complex compounds, 154
  compounds, 109
  dipyridyl complexes, 161
  exchange in complex compounds, 171
  hydroxides, 220
  "inactive" in blood, 170
  nitride, 228
  oxide catalysts, 258
  oxides, 220
  phenanthrolene complexes, 161
  polynuclear complexes, 154
  sulfide, 228
  thin layers, 212
  trichloride vapor, 159
Iron-borax glass, 246
Iron-nitrogen system, 244
Iron-oxygen-phosphorus, system, 246
Iron-oxygen-silicon system, 246
Iron-sulfur system, 246, 247
Isomerism, photochemical, 65
Isomers, organic, 54
Isomorphous systems, diamagnetic, 39
Isthmus permeameter, 238

K

Kaolin, 39
Ketyls, metal, 133
Krypton, 34

L

Lanthanum, compounds, 80
  metal, 193
  oxide, 232
  oxide as catalyst, 252
Lead, 197
  tricyclohexyl, 128
  triphenyl, 128
Lead-oxygen system, 249
Lepidocrocite, 224
Light, effect on susceptibility, 263
Liquid crystals, 71
Liquids, measurements, 4, 6, 11
Lithium, chloride solution, 37
  hydride, 39
  ion diamagnetism, 36
  metal, 187
Living cells, diamagnetism, 66
Low temperature measurements, 21
Luminous sulfides, 263
Lutecium, compounds, 80
  oxide, 232

M

Magnesium metal, 191
Magnetic anisotropy, measurements, 15
Magnetic balance, calibration, 28
  Curie-Chéneveau, 10
  Faraday, 8
  Gouy, 2
  induction, 18
  magnetometer, 18
  miscellaneous, 12
  Quincke, 6
  Rankine, 11
  Sucksmith modification, 8
Magnetic dilution, 80
Magnetic dispersion, measurements, 23
Magnetic field, 1
  and catalytic activity, 255
  control, 25, 27

and reaction velocity, 259
production, 25
Magnetic measurements, 1
o-p-hydrogen method, 24
Magnetic state and catalytic activity, 258
Magnetic susceptibility, definition, 2
Magnetic titration, 165
Magnetic viscosity, 227
Magnetism, and adsorption, 260
and catalysis, 251
nuclear, 115
Magnetite, 221
Magnets, 25
coreless, 27
permanent, 28
Magnetometer, 239
methods, 18
Magneton, Bohr, 74
Weiss, 80
Magneton numbers, for transition elements, 99
Manganates, 154
Manganese, 203
complex compounds, 151
compounds, 107
compounds adsorbed, 261
dioxide as catalyst, 255
ferromagnetic compounds, 229
sulfide, 228
Mechanical mixtures, 39
Mercuriiodide ion, 183
Mercurous chloride, 140
Mercury alkyls, 183
compounds, 65
metal, 192
vapor, 33
Mesomorphic state, 71
Metal ketyls, 133
Metals, magnetic properties, 185
rare earths, 193
theories, 185
Metallic magnetism, dependence on particle size, 186
Metallurgical instruments, 234
Methane, 44
Methyl viologen, 133
Methylene group, 54
Michler's ketone potassium, 134
Mineralogical instruments, 234
Minerals, geochemical history, 263
Mixtures, diamagnetic solids, 39
diamagnetism of molecular, 55
Mohr's salt, as a calibration agent, 29
Molecular diamagnetism, 43
effect of physical state, 48
temperature dependence, 47
Molecular field, 85
of oxygen, 118, 119
in solid solutions, 89
Molecular hydrogen, 43
Molecular mixtures, diamagnetism, 55
Molecular paramagnetism, 116
Molecules, polynuclear, 44
Molluscan shells, 265
Molybdates, 150
Molybdenum, 202
carbonyl, 150
complex compounds, 149
compounds, 106
hexafluoride, 45
Molybdic anhydride, 150
Multiplet intervals, 75
Myoglobin, 170

N

Naphthacene, 135
Naphthalene, 135
Naphthylxanthyl, 135
Natural substances, anisotropy, 265
Nematic state, 71
Neodymium, chloride solutions, 81
metal, 193
molecular field in compounds, 88
nitrate, 81
oxide, 80, 82, 232
oxide, solutions in lanthanum oxide, 89
sulfate octahydrate, 82
Neon, 34
temperature dependence, 47
Nickel, 215
above the Curie point, 207
alloys, 216
bis-acetylacetone, 177
carbonyl, 178
as catalyst, 255
chloride, as a calibration agent, 29
complex compounds, 176
compounds, 112
compounds, adsorbed, 260
cyanide, 177

Nickel (contd.)
glyoxime, 178
oxide, 245
sulfide, 228
Nickel-copper catalyst, 257
Nickel-molybdena catalyst, 256
Nitrate ion, diamagnetism, 36
Nitric acid, 57
Nitric oxide, 120
derivatives, 120
di-*p*-anisyl, 122
diphenyl, 121
di-*p*-nitrophenylene, 122
Nitrobenzene, 48
mixtures, 56
Nitrogen compounds, as biradicals, 136
Nitrogen in iron, 244
Nitrogen oxides, 120
Nitrosobenzene, 59
Nitrosodimethylaniline, 122
Nitrosyl chloride, 22
addition compounds, 122
Nitrosyl potassium sulfite, 121
Nitrotoluene, 50
Non-aqueous solvents, effect on diamagnetism, 38
Non-homogeneous systems, measurements, 14
Non-trivalent rare earths, 94
Nuclear magnetism, 115

O

"Odd" molecules, 116
Oersted, definition, 1
Orbital contribution, 74
Organic compounds, anisotropy, 69
Organic isomers, 54
Organo-metallic free radicals, 128
*Ortho-para*hydrogen, conversion, 251
experimental methods, 24
method applied to free radicals, 128, 252
method for boron hydride, 138
method for porphyrins, 172
theory of conversion, 251
Osmium, 204
complex compounds, 184
compounds, 114
Oxides of chlorine, 123
of nitrogen, 120
Oxonine, semiquinone ions, 133
Oxygen, adsorbed, 261
as a calibration agent, 29
liquid, 118
molecular, 116
O_4, 118
solid, 118
temperature coefficient, 117
Oxyhemoglobin, 165
Ozone, 119

P

Palladium, 204
complex compounds, 184
compounds, 114
Paramagnetic absorption measurements, 23
Paramagnetic impurities, 30
Paramagnetism. definition, 1
of atoms, 73
metallic, 185
of molecules, 116
monatomic gases, 76
orbital, 74
spin, 74
surface, 51
temperature independent, 39, 45
theories, 73
Pascal's constants, 51
table, 52
Particle size, and coercive force, 234
and ferromagnetism, 208
and metallic magnetism, 186
Pentaphenylcyclopentadienyl, 134
Perchlorate ion, diamagnetism, 36
Perchromates, 148
Permanent magnets, 28
Permanganate, 154
Permeability, definition, 17
measurements, 17
Permeameters, 236, 237, 238
Phase ratios, 245
Phenanthrenequinone-3-sulfonate, 130
Phenylchromiums, 149
Phosphate glasses, 262
Phosphorus, 65
Photomagnetic effect, 263
Phototropy, 65
Phthalocyanine complexes, 162
Physical state, effect on diamagnetism, 38

Platinum, 204
complex compounds, 184
compounds, 114
Polyatomic molecules, theory, 43
Polychromates, 148
Polymerization, 58, 59, 60, 61
Polynuclear complexes, 147
Polynuclear molecules, 44
Polyoxides, of alkali metals, 123
Polyoxymethylene, 59
Porphyrin, 163
Porphyrindine, 136
Porphyrins, *o-p*-hydrogen method, 172
Potassium, berlinate, 156
bromide, with color centers, 262
diborane, 138
dioxydiborane, 138
ion, diamagnetism, 36
metal, 187
nitrate in solution, 37
permanganate, 154
tetrasulfide, K_2S_4, 124
tetroxide (dioxide), 123
vapor, 74
Praseodymium, chloride solutions, 81
dioxide, 95
metal, 193
oxide, 82, 232
Precession of electrons, 31
Prospecting, magnetic, 264
Protoactinium compounds, 104
Prussian Blue, 155
Pyrrhotite, 228

Q

Quincke method, 6
Quinhydrone, 131
Quinodimethane, derivatives, 135

R

Rankine method, 11
Rare earths, 78
analysis, 231
borides, 83
chlorides, anisotropy, 91
cobalticyanides, 83
Curie temperatures, 89
compounds, anisotropy, 89
divalent, 96
ethylsulfates, anisotropy, 90
metals, 193
metals, Curie points, 195
nitrates, 81
in non-aqueous solvents, 81
non-trivalent, 94
oxides, 82
oxides, table, 232
quadrivalent, 96
solutions, 80, 81
sulfate octahydrates, 81, 82
sulfate octahydrates, anisotropy, 90
Reaction velocity in magnetic field, 259
Relaxation effects, 92
Remanence, definition, 18
Rhenium, 204
complex compounds, 154
compounds, 107
Rhodium, 204
complex compounds, 184
compounds, 114
Ring closure, 64
Rubidium ion, diamagnetism, 36
metal, 187
tetroxide (dioxide), 123
Ruthenium, 204
complex compounds, 183
compounds, 114
Rutile, 39

S

Samarium, chloride solutions, 81
compounds, temperature coefficient, 83
metal, 193
oxide, 82, 232
Samarous ion, 96
Saturation effects, 23, 92
Scandium, metal, 193
Sea-urchin eggs, 265
Selenium, 39, 202
compounds, 65
hexafluoride, 45
Semiquinone, 129
Semiquinone ions, from dipyridyl bases, 133
Shells, molluscan, 265
Siderac, 225
Silica, as adsorbent, 261
Silver, alloys, 191
chromate, 148
compounds, paramagnetic, 182

Silver (contd.)
divalent, 102, 182
hypophosphate, 139
metal, 189
permanganate, 154
subfluoride, 42
trivalent, 102
Size of grains, and coercive force, 234
Smectic state, 72
Sodium, carbonate, 39
hypophosphate, 139
ion, diamagnetism, 36
metal, 187
nitrate, anisotropy, 40
nitrate, in solution, 37
Solid solutions, diamagnetic, 39
Solids, measurements on, 4, 8, 10, 12
Sols, 262
Solutions, effect of concentration, 37
measurements, 4, 6, 11
Solvents, effect on diamagnetism, 38
Sommerfeld-Kossel rule, 94
Specific magnetization, 18
Sperm, 265
Spin contribution, 74
Spin moments, table, 144
"Spin only" formula, 98
Stannic ion, effect of temperature, 38
Stern-Gerlach experiment, 76
Stoichiometry, 245
Strontium, metal, 191
Structure of alloys, 241
Styrene, polymerization, 61
Sucksmith method, 9
Sulfate ion, diamagnetism, 36
Sulfides, luminous, 263
Sulfur, compounds, 65
hexafluoride, 45
vapor, 120
Sulfuric acid, 38
Superoxides, of alkali metals, 124
Surface, specific, of ferromagnetic powders, 234
"Surface" paramagnetism, 253
Susceptibility, definition, 2
and magneto-optical rotation, 91
molar, 2

T

Tantalum, 200
compounds, 104
Tellurium, 202
anisotropy, 41
compounds, 65
hexafluoride, 45
Temperature, control, 5
effect on diamagnetism, 38
measurements at low, 21
Temperature independent paramagnetism, 39
Terbium, Curie point, 195
dioxide, 95
metal, 193
sulfate octahydrate, 82
Tetrabenzmonazaporphin, anisotropy, 163
Tetraiodide, cesium, 124
Tetramethyl-*p*-phenylene-diaminium perchlorate, 131
Tetraphenylnaphthacene, 135
Tetraphenylrubrene, 135
Tetra-*p*-tolylhydrazinium perchlorate, 132
Tetroxides, of alkali metals, 123
Thallium, alloys, 196
metal, 193
vapor, 76
Thallous ion, diamagnetism, 36
Theories of diamagnetism, 31, 32
Thiazine, semiquinone ions, 133
Thiocyanate ion, diamagnetism, 36
Thiocyanogen, 60
Thiomagnetite, 227
Thionine, semiquinone ion, 133
Thiophosgene, 65
Thoria, effect of hydration, 250
Thorium, 197
compounds, 103
Thulium, Curie point, 195
metal, 193
sulfate octahydrate, 82
Tin, 197, 200
trimethyl, 128
tri-*o*-tolyl, 128
Titanium, 197, 198
compounds, 103
dioxide, 39
effect of dissolved hydrogen, 198
Titanium-oxygen system, 249
Titration, magnetic, 165
Toluene, 48
Transition group elements, 97
magneton numbers, 99

Triphenylmethyl, 124
Tri-*p*-tolylaminium perchlorate, 133
Tungsten, 202
  bronze, 151
  complex compounds, 150
  hexafluoride, 45
Turnbull's Blue, 156

U

Uranium, 202
  compounds, 106
  hexafluoride, 45
Urea, 63

V

Vanadium, 200
  compounds, 103
Vanadium-oxygen system, 248
Vanadium-selenium system, 248
Vanadium-sulfur system, 248
Vanadium-tellurium system, 248
Vaporization, effect on diamagnetism, 50
Verdet constant, 91

W

Water, as calibration agent, 28
  frozen, 47
  heavy, 47
  susceptibility, 45, 46
  temperature coefficient, 46
Weiss law, 85
Weiss magneton, 80
Wiedemann law, 231
Wurster's salts, 131

X

Xenon, 34

Y

Ytterbium, metal, 193
  oxide, 82, 232
Ytterbous, ion, 96
  compounds, 96
Yttrium, metal, 193
  oxide, 232

Z

Zirconium, 197, 198
  compounds, 103
  effect of dissolved hydrogen, 198
  hydroxide, 262
Zinc, metal, 192
  sulfide, 39