[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE MAGNETISM OF OXYGEN AND THE MOLECULE O_4

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One of the most characteristic properties of oxygen is its pronounced paramagnetism. This distinguishes molecular oxygen so sharply from other compounds in which oxygen is assumed to be tied by a double bond that I have recently concluded[1] that there is no double bond in the O_2 molecule. Rather I have assumed that the two electrons which have been supposed to constitute the second bond are actually separate so that each atom has an odd electron, according to the formula $:\overset{\cdot\cdot}{\underset{\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot}{O}}:$. Indeed, oxygen has the chemical properties of a molecule with odd electrons, for it has an appreciable color, and a much higher reactivity than has commonly been ascribed to it.

When we examine the magnetic susceptibility of oxygen at various temperatures we expect it (as a typical paramagnetic substance) to obey Curie's law, namely, $\chi = A/T$, where χ is the specific susceptibility, or susceptibility per gram, A is a constant, and T the absolute temperature. However, this law, which usually is fulfilled with much accuracy for the liquid and gaseous forms of a paramagnetic substance, fails entirely when we compare oxygen at different temperatures, and especially gaseous oxygen at room temperature with liquid oxygen at low temperature.

However, Perrier and Kamerlingh Onnes[2] in an extremely interesting investigation have shown that this anomaly is not due primarily to temperature; for, at a given temperature, if liquid oxygen is mixed with liquid nitrogen the susceptibility per gram of oxygen is not constant, but increases with dilution. At infinite dilution it reaches a value which is approximately that which would be calculated by Curie's law from the susceptibility of oxygen at room temperature.

These investigators mention the possibility that this phenomenon might be ascribed to some sort of polymerization, but they have preferred to adopt a theory that the magnetic field of one molecule influences other neighboring molecules (a sort of negative ferromagnetism), this influence becoming smaller as the oxygen molecules are more widely separated from one another. However, a tendency toward polymerization is so immediate a consequence of the views regarding molecular oxygen to which I have been led that it has seemed desirable to test more fully the theory of polymerization.

I shall therefore assume that the odd electrons in the oxygen molecule, while incapable of coupling with each other, are able to form bonding pairs

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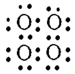
[1] Chemical Reviews, **1,** (3) (1924).

[2] Perrier and Kamerlingh Onnes, *Phys. Comm. Leiden,* **1914,** 139d.

with odd electrons from other molecules. In particular I shall assume that two molecules of the formula O_2 may combine to form the molecule O_4, which is chemically saturated, and also magnetically saturated in the sense that it is not paramagnetic. To this molecule we may assign the formula,



$$\begin{array}{c} :\ddot{O}:\ddot{O}: \\ :\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{O}}: \end{array}$$

Consequently we may assume that the paramagnetism of oxygen is due solely to the O_2 molecule, that the increase in susceptibility through dilution with nitrogen is due to the increase in the relative number of the O_2 molecules, and that the limiting susceptibility at infinite dilution gives the susceptibility of pure O_2. This limiting susceptibility, which we may denote by α, may be obtained by direct extrapolation at each temperature of the experimental values of Perrier and Kamerlingh Onnes. Their measurements were made at the three temperatures, 64.2° K., 70.9° K. and 77.4° K. My extrapolation (shown in Fig. 1) leads at each temperature to a slightly higher value of α than that obtained by the authors themselves. I find at 64.2°, $\alpha = 518 \times 10^{-6}$ (hereafter in giving susceptibilities the factor 10^{-6} will be understood), at 70.9° $\alpha = 469$, and at 77.4° $\alpha = 430$. These values are all consistent with Curie's law, which takes the form

$$\alpha = 33{,}250/T \tag{1}$$

This equation gives at 20°C., $\alpha = 113$. Now at this temperature, and with the small density of oxygen gas at atmospheric pressure, we shall see that the dissociation of the O_4 molecule is complete, and we may therefore write $\alpha = \chi$. The most recent determinations of the susceptibility of oxygen are those of Soné,[3] who obtained the value 104, Bauer, Weiss and Piccard[4] who found 108, and Wills and Hector[5] who found 109. The agreement between these values and the one calculated from the measurements of liquid oxygen, namely, 113, is probably within the limits of error of the various magnetic measurements.

In describing the results of their experiments with liquid mixtures of oxygen and nitrogen, Perrier and Kamerlingh Onnes give the specific susceptibility, χ, at different values of ρ, the number of grams of oxygen per cubic centimeter. Adhering to their usage, we may write

$$\rho = \rho_2 + \rho_4 \tag{2}$$

where ρ_2 is the number of grams of O_2 and ρ_4 is the number of grams of O_4 per cubic centimeter. Representing the dissociation by the equation $O_4 = 2O_2$, we then have, by the mass law,

$$\frac{\rho_2^2}{\rho_4} = K_\rho \tag{3}$$

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[3] Soné, *Phil. Mag.*, **39,** 305 (1920).

[4] Bauer, Weiss and Piccard, *Compt. rend.*, **167,** 484 (1918).

[5] Wills and Hector, *Phys. Rev.*, **23,** 209 (1924).

where the equilibrium constant is represented by K_ρ as a reminder that we are using somewhat unconventional units of concentration. These equations should be completely valid in very dilute solutions in nitrogen, and in fact at all concentrations in which various constituents obey Raoult's law. On account of the close resemblance in physical properties between liquid oxygen and liquid nitrogen we may probably assume without great error that Raoult's law holds over the whole range, and that Equation 3 is therefore valid all the way from pure nitrogen to pure oxygen.

Since we are assuming that the O_2 molecule is alone responsible for the paramagnetism, we may take the fraction of the oxygen existing as O_2 as the ratio between the observed susceptibility and the limiting susceptibility at infinite dilution, that is

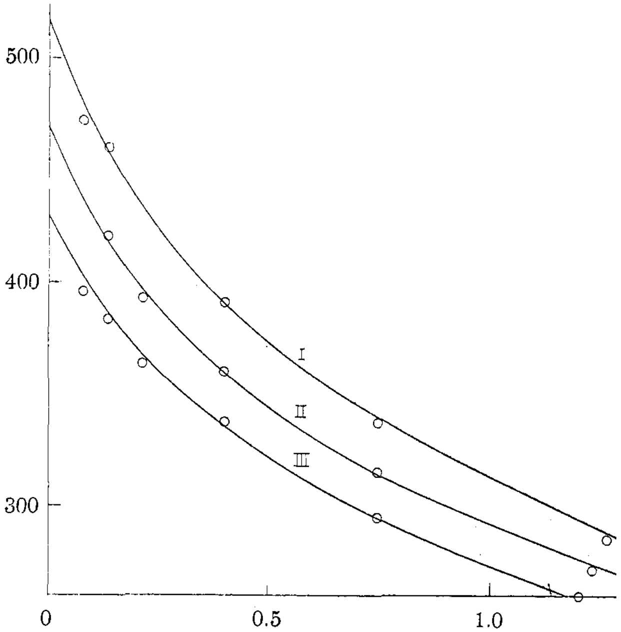

Fig. 1.—Ordinates, magnetic susceptibility per gram of oxygen (× 10^{-6}). Abscissas, grams of oxygen per cc. in liquid mixtures of oxygen and nitrogen. I, 64.2°K. II, 70.9°K. III, 77.4°K.

$$\frac{\rho_2}{\rho} = \frac{\chi}{\alpha} \tag{4}$$

By means of Equations 2, 3 and 4, I have evaluated K_ρ from each of the 16 actual measurements. Then taking the average value of K_ρ at the three temperatures, namely, 0.92 at 64.2°, 1.01 at 70.9°, and 1.10 at 77.4°, I have plotted $-R \ln K_\rho$ against reciprocal temperature. If we are not mistaken as to the interpretation of the data, thermodynamics demands that the points should lie on a straight line, and this proves to be the case. The equation for this line is

$$-R \ln K_p = \frac{128}{T} - 1.83 \qquad (5)$$

and since the value of R is taken in calories per degree, we find 128 calories as the heat of complete dissociation of one mol. of O_4.

In order now to show the degree of agreement between these several thermodynamic consequences of our supposition and the experimental facts themselves, I have calculated a series of values of χ at each of the three temperatures from Equation 5, and have drawn in Fig. 1, the smooth curves which represent these equations. The circles show the experimental value of χ. The maximum discrepancy between the calculated and observed values of χ is less than 1%. This illustrates at the same time the accuracy of the experimental work of Perrier and Kamerlingh Onnes, and the success with which these data can be interpreted on the assumption of polymerization.

Indeed, the accuracy with which Equation 5 reproduces the experimental data seems alone sufficient to justify the assumption of the formation of the non-magnetic O_4 molecule. Nevertheless, recognizing the possibilities of deception inherent in such a calculation, I sought for some corroboration from independent evidence and recalled that when Professor Gibson and I were calculating the entropies of the elements we were struck by the fact that the specific heat of liquid oxygen diminishes with increasing temperature, whereas the specific heat of all ordinary liquids increases with the temperature. This effect, although small, is quite noticeable, as will be seen from Fig. 2, which reproduces the data of Eucken[6] for the molal heat capacity of carbon monoxide (I), nitrogen (II) and oxygen (III) as a function of the temperature.

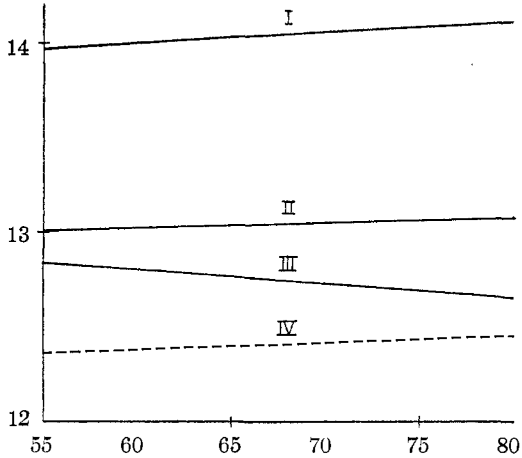

Fig. 2.—Ordinates, molal heat capacity. Abscissas, absolute temperature. I, Liquid CO. II, Liquid N_2. III, Liquid O_2. IV, Liquid O_2, corrected for dissociation.

Now if our suppositions are correct, a part of the heat capacity of oxygen must be due to the fact that as pure oxygen is heated a certain amount of O_4 is dissociated to form O_2, with an absorption of 128 calories per mol. of

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[6] Eucken, *Ber. deut. physik. Ges.*, **18**, 4 (1916).

O_4 dissociated. Thus from the experimental susceptibility of pure liquid oxygen we find χ/α to be 0.55 at 64.2°, 0.58 at 70.9° and 0.60 at 77.4°. These figures represent also the fraction by weight of the paramagnetic form O_2. Plotting these values against the temperature, we may find, from the slope of the curve, the rate of change of this fraction per degree, and thence we may calculate the amount of heat absorbed per degree as a consequence of the dissociation of O_4 molecules. We thus find, for example, that at 65° 0.33 calorie is absorbed per degree for each 32 g. of oxygen, and at 78° 0.20 calorie. If these figures are subtracted from the observed molal heat capacity we find the heat capacity which would be observed if there were no dissociation. In this way we obtain the dotted line (IV) of Fig. 2, which now has about the same slope as that exhibited by carbon monoxide and nitrogen.

We may next inquire whether gaseous oxygen at room temperature still contains an appreciable amount of O_4. Equation 5 is valid only for such a small range of temperature that the heat of dissociation may be regarded as constant. As a matter of fact, the heat capacity of two moles of gaseous O_2 is undoubtedly larger than that of one mol. of O_4, and therefore ΔH, the heat of dissociation, increases with increasing temperature. The actual dissociation will therefore increase more rapidly than would be predicted from Equation 5. The specific heat of O_4 is, of course, unknown but from an examination of the data for other polyatomic gases we may estimate that the heat capacity of 2 O_2 exceeds that of O_4 by 2 calories per degree. Making this assumption, and using the same data as before, we find in place of equation 5

$$—R\,ln\,K_p = -\frac{12}{T} - 2\,ln\,T + 8.67 \qquad (6)$$

Hence we find at 20°C., $K_p = 4$, which is only four times as great as at the temperature of liquid air. But when we introduce into our equations the small density of oxygen at atmospheric pressure, namely, 0.0013, we find $\chi/\alpha = 0.9997$, that is, the equation shows that only 0.03% is undissociated, and we may conclude that it would take a pressure of about 30 atmospheres to produce a change in the magnetic susceptibility of 1%.

Professor Hildebrand has kindly called my attention to a paper by Dolezalek[7] in which the latter, from a study of the partial pressures of oxygen and nitrogen from their liquid mixtures, has concluded that oxygen associates to form the molecule O_4, and calculated the percentage of O_2 and O_4 molecules. His method is open to serious question, and the fact that he likewise finds some association in the case of argon[8] has made it hard for the majority of chemists to accept his conclusions. Nevertheless, it is interesting to find that his values for the degree of association of

[7] Dolezalek, *Z. physik. Chem.*, **71**, 191 (1910).

[8] Dolezalek, *ibid.*, **93**, 585 (1919).

oxygen at liquid-air temperature are of the same order of magnitude as those which we have here obtained, although he deduced a much more rapid change of the dissociation constant with the temperature.

Summary

The magnetic properties of oxygen show that it is a mixture of O_2 and O_4. The molecule of O_2 is paramagnetic, that of O_4 is not. The paramagnetism of unassociated O_2 obeys Curie's law. At the temperature of liquid air about one-half (by weight) is in the associated form. The thermodynamic consequences of this theory with respect to the influence of temperature and of concentration are in accord with the experiments of Perrier and Kamerlingh Onnes. The heat of dissociation is about 128 calories per mole of O_4. This heat of dissociation is responsible for the diminution in the specific heat of liquid oxygen with rise of temperature. Gaseous oxygen, at room temperature and atmospheric pressure, is associated to the extent of only a few hundredths of a per cent.

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OPTICALLY ACTIVE DYES

II. ADSORPTION, ABSORPTION SPECTRA AND ROTATION

BY WALLACE R. BRODE[1] WITH ROGER ADAMS

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In a previous article by Ingersoll with Adams[2] a very convenient method was described for the preparation of pairs of enantiomorphic dyes. The research had as its ultimate object the determination of whether the mechanism of dyeing of fibers was a physical process, a chemical process, or both. With the pure *d* and *l* forms of a dye, a comparison of the two equivalent solutions as regards adsorption by the fiber could be made. By means of a colorimeter or, perhaps, polarimeter, the concentration of the partially exhausted *d* and *l* solutions could be compared with each other and with the original solutions. The assumption was that compounds that are mirror images would have the same dyeing properties provided the adsorption by the fiber was a purely physical process. On the other hand, if a chemical reaction of any sort took place when the dye was adsorbed, the degrees or rates of adsorption of the *d* and *l* forms might be different on account of the optical activity of the substance of which the fiber was composed.

In order to be sure that, if such results as have been mentioned were

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[1] This communication is an abstract of a portion of a thesis submitted by Wallace R. Brode in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Ingersoll with Adams, THIS JOURNAL, **44**, 2930 (1922).