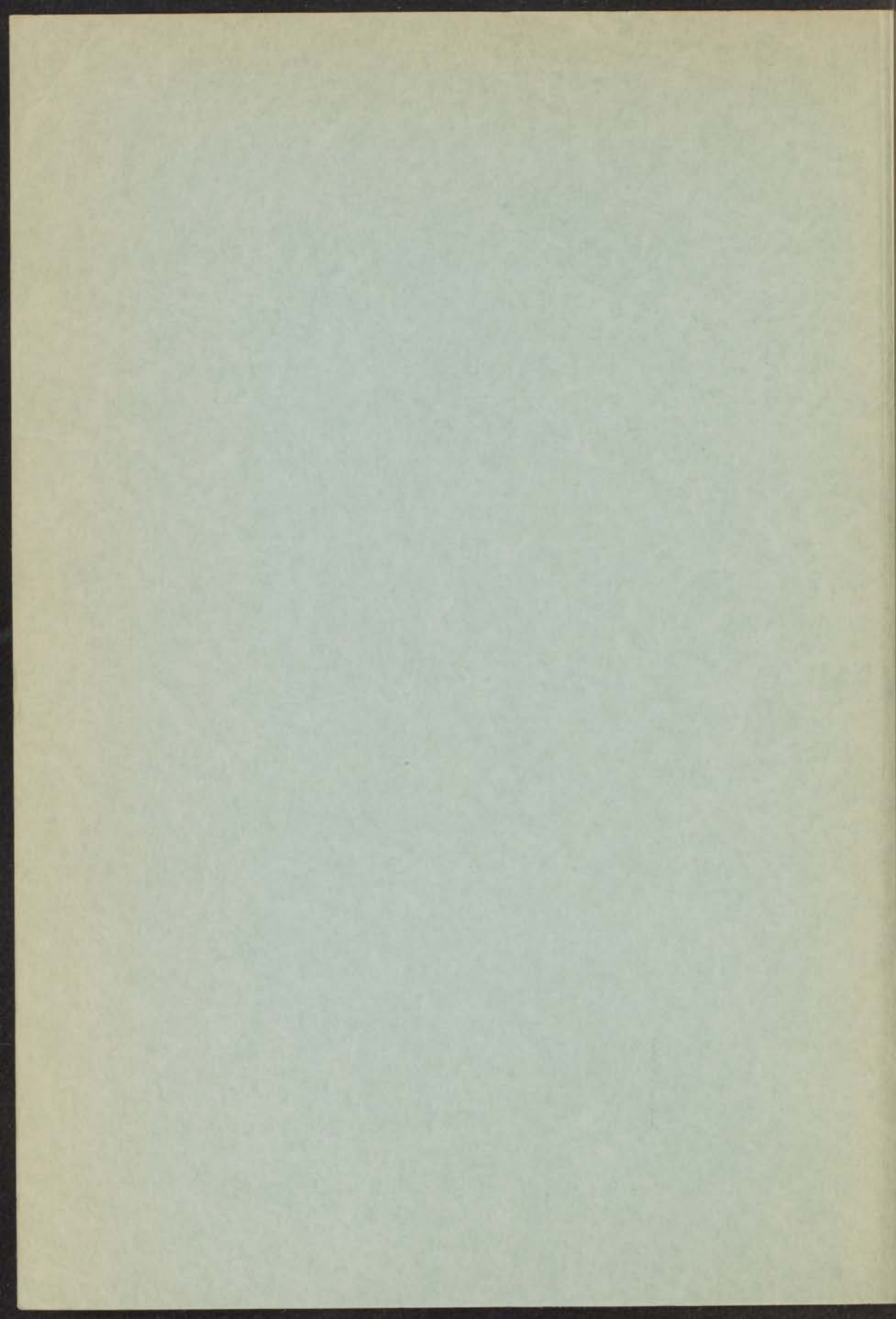


ON THE EXISTENCE
OF A
MOLECULAR OXYGEN DIMER

C.M. KNOBLER



STELLINGEN

1. De sterke afname in basiciteit van aniline ten gevolge van de invoering van ortho-alkylgroepen wordt hoofdzakelijk veroorzaakt door F-spanning.

B.M. Wepster
Progress in Stereochemistry II

2. Het is twijfelachtig of verbetering van de combinatieregels voor de wisselwerking tussen ongelijksoortige moleculen, zoals voorgesteld door Hudson en McCoubrey, zinvol is met het oog op de bestaande onzekerheid in de potentiaalparameters voor de zuivere componenten.

G.H. Hudson en J.C. McCoubrey
Trans. Faraday Soc. **56** 761 (1960)

3. De wijze waarop Roberts en Swartz de Redlich-Kister test op de metingen van Roberts en Sydoriak aan ^3He - ^4He mengsels toepassen is onjuist.

T.H. Roberts en B.K. Swartz
Proc. 2nd. Symp. on Liquid and
Solid ^3He

4. De vergelijkingen voor de transportverschijnselen in gasmengsels kunnen dikwijls sterk worden vereenvoudigd door gebruik te maken van het feit dat voor $T^* > 3$ geldt

$$[\Omega^{(i,j)*}(T_{12}^*)]^2 = [\Omega^{(i,j)*}(T_{11}^*)][\Omega^{(i,j)*}(T_{22}^*)].$$

J.O. Hirschfelder, C.F. Curtiss en
R.B. Bird
The Molecular Theory of Gases and Liquids

5. Het gebruik van $\epsilon(P)$ (extinctie per mol fosfor bij 259 $m\mu$) als enig criterium voor het al dan niet natief zijn van DNA is aan bedenkingen onderhevig.

D.O. Jordan
The Chemistry of Nucleic Acids

6. Het is mogelijk de B^E (exces tweede viriaalcoëfficiënt) voor ${}^3\text{He}$ - ${}^4\text{He}$ gasmengsels beneden het λ - punt van vloeibaar helium te bepalen met behulp van een superlek.

7. Wat betreft de twee gemeten afstanden tussen H_2O moleculen in water moet aan die van v. Panthaleon v. Eck e.a. de voorkeur gegeven worden boven die van Brady en Romanow.

C.L. v. Panthaleon v. Eck, H. Mendel
en J. Fahrenfort
Proc. Roy. Soc. (London) A **247** 472 (1958)

G.W. Brady en W.J. Romanow
J. Chem. Phys. **32** 306 (1960)

8. Keller en Hammel hebben de warmtegeleiding van He II in nauwe spleten gemeten. Tegen de wijze waarop zij de warmtestroomdichtheid in het helium berekenen zijn echter bedenkingen aan te voeren.

W.E. Keller en E.F. Hammel
Annals of Physics **10** 202 (1960)

9. Het is oudere mensen op medische en fysieke gronden aan te bevelen van de gebruikelijke manier om schoenveters vast te maken af te wijken.

ON THE EXISTENCE
OF A
MOLECULAR OXYGEN DIMER

PROEFSCHRIFT TER VERKRIJGING VAN
DE GRAAD VAN DOCTOR IN DE WIS- EN
NATUURKUNDE AAN DE RIJSUNIVERSI-
TEIT TE LEIDEN, OP GEZAG VAN DE
RECTOR MAGNIFICUS

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HOGLERAAR IN DE FACULTEIT DER
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DEDIGEN OP WOENSDAG 22 MAART 1961
TE 15 UUR

DOOR

CHARLES MARTIN KNOBLER
GEBOREN TE NEWARK, N.J. (U.S.A.) IN 1934

DRUKKERIJ PASMANS - v. d. VENNESTRAAT 76 - 'S-GRAVENHAGE

Promotor: Prof. Dr K.W. Taconis
Dit proefschrift is bewerkt onder toezicht van Dr J.J.M. Beenakker

To Carolyn

'Pooh's found the North Pole,' said
Christopher Robin. 'Isn't that lovely?'
Pooh looked modestly down.
'Is that it?' said Eeyore.
'Yes,' said Christopher Robin.
'Is that what we were looking for?'
'Yes,' said Pooh.
'Oh!' said Eeyore. 'Well, anyhow—it
didn't rain,' he said.

— Winnie-the-Pooh

A. A. Milne

Published by the University of Chicago Press
Chicago, Illinois, U.S.A.

To the Editor

I have the honor to acknowledge the receipt of your letter of the 15th inst. in relation to the matter mentioned therein. I am sorry that I cannot give you a more definite answer at this time, but I am sure that you will understand my position.

Very truly yours,
[Signature]

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Chapter I
Introduction

Chapter II

Thermodynamic and the Second Virial Coefficients of Gases
Before 1957

Teneinde te voldoen aan het verzoek van de Faculteit der Wis- en Natuurkunde volgt hier een beknopt overzicht van mijn studie.

Nadat ik in 1951 mijn studie in de scheikunde aan de University College of Arts and Sciences of New York University was begonnen, werd mij in juni 1955 het baccalaureaat met hoofdvak scheikunde verleend. Aan de Pennsylvania State University vervolgde ik mijn studie in de fysische scheikunde en deed in juni 1956 mijn "admission to doctoral candidacy" en in juni 1958 het "comprehensive" examen. In 1957 verkreeg ik een "Union Carbide Fellowship". Inmiddels was ik sedert 1956 werkzaam op het cryogeen laboratorium onder leiding van Prof. Dr J. G. Aston, waar ik soortelijke warmte metingen aan organische stoffen verrichtte.

In 1958 stelde een "Fulbright Award" mij in staat om mijn studie verder voort te zetten aan het Kamerlingh Onnes Laboratorium, waar ik medewerker werd bij de werkgroep voor molecuul physica onder leiding van Prof. Dr A.F. van Itterbeek.

Sinds september 1959 ontving ik financiële steun van de F.O.M.

De metingen welke in dit proefschrift beschreven zijn werden verricht in samenwerking met de heer R. J. J. van Heijningen.

Chapter III
4. Chemical treatment

Chapter IV

Survey of Physical Properties and Coefficients

1. Introduction

2. Gases

3. Liquids and Solids

4. Corresponding states considerations

5. Jones-Danton formula

6. Excess properties of mixtures

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8. Properties of the solid

9. Conclusions

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CHAPTER I

INTRODUCTION

Of all the permanent gases, oxygen is unique for both its chemical and physical properties, but while the former characteristics have continually received considerable interest, many of the physical properties have not been carefully elucidated. Most characteristic of O_2 physically is its paramagnetism, for, although it has an even number of electrons, molecular oxygen has a triplet ground state; i.e. it has two unpaired electrons.

In 1913 Perrier and Onnes (Per 14) using mixtures of liquid oxygen and nitrogen performed a series of measurements aimed at demonstrating the effect of the distance between molecules involved in the paramagnetic exchange previously observed in pure liquid O_2 . By diluting the paramagnetic with a diamagnetic liquid they were able to secure large effective density changes at a constant temperature. They found that the susceptibility of liquid oxygen, which when pure is considerably less than that predicted by Curie's law, increases with increasing dilution, reaching a value at infinite dilution which is approximately that calculated for a free molecule. This behavior was attributed by them to a negative molecular field, but Lewis (Lew 24), on the basis of their data, showed that the increase in susceptibility could also be explained by assuming the existence of a diamagnetic dimeric form of oxygen, $(O_2)_2$.

He showed that an equilibrium of the form $O_4 \rightleftharpoons 2O_2$ described by the law of mass action in terms of the equilibrium constant $K_p = \rho_2^2/\rho_4$, where ρ_2 and ρ_4 are the densities of the monomer and the dimer, respectively, is consistent with the experimental data if the monomer is alone responsible for the paramagnetism and additivity of volumes is assumed, so that one may write

$$\rho_2/\rho = \rho_2/(\rho_2 + \rho_4) = \chi/\chi_1.$$

The total oxygen density is ρ ; χ is the measured susceptibility and χ_1 is the ideal susceptibility calculated from Curie's law. Further, he was able to evaluate K_p at the three temperatures of the measurements, namely 0.92 at 64.2, 1.01 at 70.9 and 1.10 at 77.4 °K, and from the linear relation between $\ln K_p$ and $1/T$ he found a heat of dissociation of 128 cal/mole O_4 .

This work seemed to be supported by spectral studies (Wul 28, Fin 32) and other magnetic and electrical measurements on both the liquid

(Gui 36a,36b, Lai 33) and the gaseous states (Wol 29, Wie 32, Ser 32). In the solid, evidence for the existence of pairs in the phase stable just below the melting point ($\gamma\text{-O}_2$) was also found by x-ray diffraction (Veg 35, Kee 36). None of these studies is clear-cut evidence for the dimer, however, and there is a noticeable discrepancy between the supposed concentration of pairs calculated on the basis of different experiments. The object of the present work is to try to clarify this situation.

After a survey of the literature and preliminary calculations, it was decided to examine the thermodynamic properties of liquid mixtures which were thought to be sensitive to association. In order to be able to evaluate these results it was necessary to know the equation of state of the gaseous mixture in equilibrium with the liquid, and an apparatus was constructed for measuring the departures from ideal mixing of gaseous mixtures at low temperatures. This work, which is discussed in chapter II, is moreover useful because it gives a direct measure of the difference between the interaction in binary collisions between a pure gas with itself and with other gases.

In chapter III the thermodynamic properties of $\text{O}_2\text{-N}_2$ and $\text{O}_2\text{-A}$ mixtures are considered. Measurements of the heat of mixing are presented and an evaluation of recent work on the corresponding vapor-liquid equilibria is given. The excess Gibbs functions and excess entropies are calculated as a function of the concentration of oxygen from the vapor-liquid and heat of mixing data, and the results are discussed. The application of modern theories of liquid mixtures to these systems and the basic assumptions of these theories are also considered.

Unfortunately, the original magnetic susceptibility measurements by Perrier and Onnes cannot be directly compared to the thermodynamic study, so a new series of relative measurements of the magnetic susceptibility was undertaken. Pure O_2 was studied between 65 and 90°K and the mixtures $\text{O}_2\text{-N}_2$ and $\text{O}_2\text{-A}$ were investigated between 65 and 90°K and at 90°K, respectively. The results are given in chapter IV. We also include a discussion of the results in terms of the physical picture of magnetic exchange, rather than the formation of dimers, and consider the consistence of this treatment with respect to the measurements.

The results of the thermodynamic study are compared to those from the susceptibility investigation as a part of chapter V, where the physical properties of oxygen and of its mixtures which are sensitive to association are reviewed and analyzed in an effort to evaluate them as evidence for the proposed dimerization.

CHAPTER II

MEASUREMENTS ON THE SECOND VIRIAL COEFFICIENTS
OF GASEOUS MIXTURES AT 90° K

1. INTRODUCTION

The calculation of the excess thermodynamic properties of liquid mixtures from the vapor-liquid equilibrium data requires the knowledge of the equation of state of the vapor mixture in equilibrium with the liquid. This PV relationship is also of theoretical importance, for it can give information concerning the intermolecular potential between unlike molecules. It has been often shown that the assumption that a vapor mixture is ideal can lead to totally erroneous results (see e.g. Din 59) and semi-empirical combination rules have been formulated (Hir 54) which attempt to describe the intermolecular interaction between unlike molecules in terms of combinations of the potential parameters of the pure components. The potential function thus derived can be used to calculate the second virial coefficient of the gas mixture. Unfortunately very little data exist concerning simple gases against which these formulae can be checked.

Absolute measurements of the second virial coefficient are laborious and until now thermal diffusion experiments have been the major source of data concerning the intermolecular potential in mixtures at low temperatures. A method of measuring the excess second virial coefficient of mixtures accurately and with considerable ease has been developed. Using this method the second virial coefficients of thirteen binary gas mixtures were measured at 90°K.

2. METHOD AND APPARATUS

Two bulbs maintained at a constant temperature are filled to the same pressure with different gases. They are connected and their contents mixed. The pressure after mixing is compared with that in another bulb held at the original pressure.

It is well known in the simple case $B_{12} = \frac{1}{2}(B_{11} + B_{22})$, where B_{11} and B_{22} are the second virial coefficients of the pure gases and B_{12} the virial coefficient representing the mixed interaction, that there is no pressure change on mixing. Hence, it is clear that a measured change in pressure is directly related to an excess quantity E , defined as $B_{12} - \frac{1}{2}(B_{11} + B_{22})$. To derive an expression for E in terms of the measured quantities we proceed as follows.

We may write the pressure of a gas, P , in terms of the second virial coefficient, B , the density, d , and a second constant, A :

$$P = Ad(1 + Bd).$$

Thus for the ratio of the final to the initial pressure we have:

$$\frac{P_f}{P_i} = \frac{A_f d_f (1 + B_f d_f)}{A_i d_i (1 + B_i d_i)} \quad \text{II.1}$$

where the subscripts f and i denote the final and initial states. If the temperature be held constant and the density be expressed in units of mole/cm³, the constants A_f and A_i are equal. Neglecting the effect of the pressure change on the density of that small part of the gas that is at room temperature we may substitute $(d_1 + d_2)/2$ for d_f , where d_1 and d_2 are the densities of the unmixed gases. As a consequence of the pressure equality in the bulbs before mixing we may write: $d_1(1 + B_{11}d_1) = d_2(1 + B_{22}d_2)$. Substituting the above relations into eqn. II.1 we find:

$$\frac{P_f}{P_i} = \frac{[(d_1 + d_2)/2] [1 + B_f(d_1 + d_2)/2]}{d_1 [1 + B_{11}d_1]} \quad \text{II.2}$$

It can be shown that the second virial coefficient of a binary mixture can be written in terms of the virial coefficients of the pure gases and of the virial coefficient representing the mixed interaction (Hir 54) as $x^2 B_{11} + 2x(1-x)B_{12} + (1-x)^2 B_{22}$.

Writing the mole fractions in terms of the densities and B_{12} in terms of E and the virial coefficients of the pure gases, we find under the assumption of equal volumes:

$$B_f = [d_1/(d_1 + d_2)] B_{11} + [d_2/(d_1 + d_2)] B_{22} + 2d_1 d_2 E / (d_1 + d_2)^2.$$

Using this result in eqn. II.2 leads to

$$\begin{aligned} \frac{P_f}{P_i} &= \frac{[(d_1 + d_2)/2] [\frac{1}{2}(1 + B_{11}d_1) + \frac{1}{2}(1 + B_{22}d_2) + d_1 d_2 E / (d_1 + d_2)]}{d_1 [1 + B_{11}d_1]} \\ &= \frac{1}{2} + \frac{d_2(1 + B_{11}d_1) + d_1(1 + B_{22}d_2)}{4d_1(1 + B_{11}d_1)} + \frac{d_1 d_2 E}{2d_1(1 + B_{11}d_1)}. \end{aligned}$$

Multiplying and dividing the second term by $d_1 d_2$ and then simplifying we write:

$$\frac{P_f}{P_i} = \frac{1}{2} + \frac{d_2^2 + d_1^2}{4d_1 d_2} + \frac{d_1 d_2 E}{2d_1(1 + B_{11}d_1)} = 1 + \frac{(d_2 - d_1)^2}{4d_1 d_2} + \frac{d_1 d_2 E}{2d_1(1 + B_{11}d_1)}$$

This then leads to the form

$$\frac{\Delta P}{P_i} = \frac{(P_f - P_i)}{P_i} = \frac{d_2 E}{2(1 + B_{11}d_1)} + \frac{(d_2 - d_1)^2}{4d_1 d_2} \quad \text{II.3}$$

from which E can be calculated. The second term on the right side of eqn. II.3 is small and in the following measurements was never more than 2–3% of the first term. A correction for the room temperature dead space volume (Kna 60) has not been applied as it is here of the order of 1%.

The apparatus is shown schematically in fig. II.1. Three 100 cm³ glass bulbs R_1, R_2, R_3 are immersed in a refrigerant bath. They are connected to a filling system and an oil manometer by the long glass capillaries C_1, C_2, C_3 , which are 0.5 mm inside diameter. Stopcocks S_1, S_2 serve to isolate the bulbs from each other. The measuring procedure is as follows. With stopcock S_2 closed bulb R_2 is filled with gas. The other bulbs are filled to precisely the same pressure with the other gas, as can be observed on the oil manometer D. The absolute filling pressure can be measured with the mercury manometer M. After temperature equilibrium has been reached stopcock S_1 is closed and stopcock S_2 is opened. Part of the gas in bulbs R_2 and R_3 is withdrawn into the Toeppler pump T_o (volume 1000 cm³) and then recompressed. The procedure is repeated until the gases are thoroughly mixed. All of the gas is then returned to the bulbs and after temperature equilibrium is again reached the difference in pressure between the mixed gases and the pure reference gas is measured on the oil manometer using a cathetometer.

Three heavy-walled copper tubes, T , soldered together, surround the glass vessels, and they are covered by a common top and bottom, also of copper. This ensures an identical temperature environment for all the vessels. The temperature gradient along the capillaries is kept identical by strips of copper foil, W , which are interwoven between them and wrapped horizontally around them. The oxygen bath is stirred by a fine stream of oxygen gas which is first cooled in a copper coil and then bubbled through the liquid. With these precautions pressure fluctuations are reduced to 0.15 mm oil, corresponding to temperature differences between the bulbs of 0.001 degree. It should be remarked

that exact temperature equality between the bulbs is unnecessary. It is only required that the conditions before and after mixing be the same.

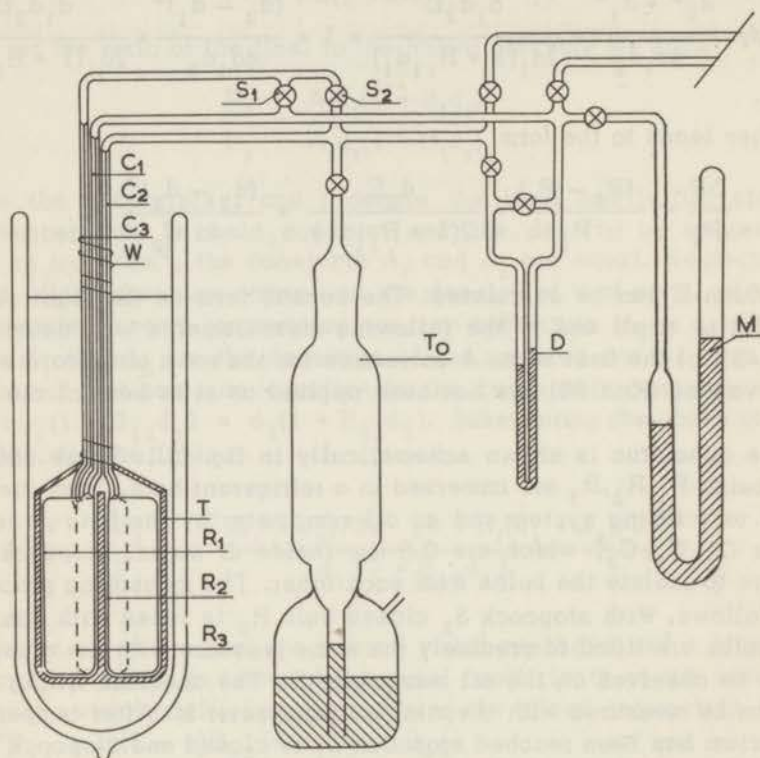


Fig. II.1 Apparatus for Measurement of E

In the mixing no gas may be lost. This was checked by running a blank with the same gas in both mixing vessels. Within the accuracy of the measurement no loss could be detected. Each experiment was repeated with the position of the gases reversed. This served as a check and the averaged value of the effect took into account any difference due to the unequal volume of the two measuring bulbs. After the series of measurements was completed the volumes were carefully determined and the difference between bulbs R_2 and R_3 was found to be of the order of 1%.

All the gases used were from laboratory stock and were better than 99% pure. Before use they were further purified by passing them through a copper spiral immersed in liquid oxygen.

3. CALCULATIONS AND RESULTS

The excess for each pair was calculated using eqn. II.3. The approximation $d = d_o (1 - Bd_o)$, where d_o is the ideal gas density, was used for all the densities. The second virial coefficients used are listed in table II.1.

TABLE II.1

Second Virial Coefficients at 90° K in cm ³ mole ⁻¹			
He	10.8 (a)	N ₂	-180 (d)
H ₂	-5.17 (b)	O ₂	-229 (d)
Ne	-2.08 (c)	A	-209 (d)

(a) Keesom, W.H., Helium (Elsevier, Amsterdam 1942) p.49.
 (b) Woolley, H.W., Scott, R.B. and Brickwedde, F.G., J. Research Nat. Bur. Standards **41** (1948) 379.
 (c) Crommelin, C.A., Palacios Martinez, J. and Kamerlingh Onnes, H., Leiden Comm.154a (1919).
 (d) Calculated.

Where no source is listed the value has been calculated from the Lennard-Jones (6-12) potential corrected for quantum effects and using the constants given in table II.2 which are taken from equation of state data. The observed pressure difference was corrected for the volume change caused by differences in the oil manometer level.

In table II.3 are the filling pressure in cm mercury, the observed effect in cm oil and E_m , the excess in cm³/mole obtained from the measurement.

A glance at the table shows the good reproducibility of the experimental method. The main source of error is the slight instability in the pressure difference of 0.15 mm oil mentioned earlier. Taking this into account we estimate the accuracy of the measurement to be about 2-3% for the larger effects and 2-3 cm³/mole for the smaller ones.

To compare our data with the theoretical predictions we have also tabulated the excesses, E_c , calculated on the basis of the Lennard-Jones potential using the constants in table II.2 and the combination rules $\sigma_{12} = 1/2(\sigma_{11} + \sigma_{22})$ and $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$. This was done as follows. First a $T_{12}^* = kT/\epsilon_{12}$ was calculated for each mixture. B_{12} was then obtained using the equation (Hir 54)

$$B^* = B_{c1}^* + \Lambda^{*2}B_I^* + \Lambda^{*4}B_{II}^* + \Lambda^{*6}B_{III}^* + \dots$$

TABLE II.2

Potential Parameters From Hirschfelder, Curtiss and Bird, Molecular Theory of Gases and Liquids, pp.110-11.				
	ϵ/k °K	σ Å	T^*_{90} °K	Λ^*
He	10.2	2.56	8.82	2.68
H ₂	37.0	2.93	2.44	1.73
Ne	34.9	2.78	2.58	0.592
N ₂	95.9	3.71	0.940	0.227
O ₂	118	3.58	0.767	0.200
A	122	3.40	0.740	0.185
He-H ₂	19.4	2.74	4.64	2.22
-Ne	19.1	2.65	4.72	1.47
-N ₂	31.3	3.13	2.87	0.922
-O ₂	34.7	3.07	2.60	0.885
-A	61.2	2.98	2.55	0.889
Ne-H ₂	36.3	2.84	2.49	1.30
-N ₂	58.4	3.23	1.54	0.366
-O ₂	64.7	3.16	1.39	0.314
-A	65.9	3.08	1.37	0.299
N ₂ -O ₂	106	3.64	0.851	0.253
-A	108	3.56	0.837	0.242
A-H ₂	67.2	3.16	1.34	0.835
-O ₂	120	3.49	0.752	0.224

giving the second virial coefficient in terms of a power series in the reduced de Broglie wave length $\Lambda^* = h/[\sigma(2\mu\epsilon)^{1/2}]$. Here h is the Planck constant and μ the reduced mass. The values of B_{c1}^* , B_I^* , B_{II}^* and B_{III}^* were obtained from the tables listed by Kihara (Kih 55). Terms higher than Λ^{*2} were not significant. $(B_{11} + B_{22})/2$ was calculated from the measured values for the pure gases, or in the case of A, O₂ and N₂ from the B's calculated in a procedure identical to that described above for B₁₂. The excess is then the difference between the average of the virial coefficients of the pure gases and the B₁₂. Finally, the value of the B₁₂ derived from the measurements is also listed in table II.3.

TABLE II.3

Mixture	Filling pressure cm Hg	Effect cm oil	E_m cm ³ /mole	E_c cm ³ /mole	B_{12} cm ³ /mole
He-H ₂	75.8	0.569	9.0	6.0	12.8
	70.1	0.654	11.0		
-Ne	74.2	0.156	2.6	1.2	7.4
	76.2	0.079	1.4		
-N ₂	76.2	5.684	99.5	80.0	12.4
	78.7	6.748	94.4		
-O ₂	65.9	5.530	106.9	101.3	-4.4
	63.3	4.952	102.6		
-A	76.3	7.224	106.3	91.4	6.6
	76.2	6.646	105.2		
Ne-H ₂	79.1	0.183	2.7	-1.8	-1.9
	75.6	0.047	0.7		
-N ₂	76.4	4.164	60.8	44.5	-31.0
	72.3	3.634	59.2		
-O ₂	65.1	3.897	77.8	62.5	-40.2
	64.2	3.627	73.1		
-A	68.3	4.020	71.5	55.4	-35.3
	72.8	4.401	69.1		
N ₂ -O ₂	64.9	-0.141	-3.5	2.6	-209.
	63.1	-0.212	-4.4		
-A	76.9	0.000	0.0	1.6	-195.
	78.6	0.004	0.0		
A -H ₂	77.0	3.850	54.9	53.2	-52.1
	77.7	3.945	55.3		
-O ₂	64.8	0.066	1.3	0.0	-217.
	64.8	0.146	2.9		

4. CONCLUSIONS

Comparing the measured and the calculated data we have to be mindful of the fact that in the case of A, N₂ and O₂ no direct experimental measurements of the second virial coefficients of the pure gases are available. We used, as mentioned, calculated values that can only be regarded as reasonable extrapolations of higher temperature data. Thus in mixtures of these gases there exists an added uncertainty in the calculations. However, the calculated excess values for the three mixtures of these gases with each other agree rather well with the experimentally determined values, as one should expect, and this gives

the impression that the uncertainty is not more than a few cm^3/mole . Thus, in the calculation of the thermodynamic properties of the $\text{O}_2\text{-A}$ and $\text{O}_2\text{-N}_2$ systems the use of the combination rules for the calculation of B_{12} can be regarded as a very satisfactory procedure.

It appears that the only large discrepancies between observed and calculated values are found in the mixtures He-N_2 , He-A , Ne-N_2 , Ne-O_2 and Ne-A . The deviations in all of the other cases fall within the expected accuracy. It is difficult to ascribe the source of these discrepancies to any particular failure of the Lennard-Jones model or of the combination rules. For the Ne mixtures it must be mentioned that there is a rather large uncertainty in the potential parameters and one can remark that in the case of the He mixtures there is a large difference both in the polarizability and in the diameter between the components. Modified forms of the combination rules may be used to take this into account (Sri 53, Mat 53). Application of these corrections does indeed alter the excess value in the right direction but it is felt that the lack of sufficient data prohibits a more quantitative study of these considerations. Only after data for a great number of gas mixtures over a large range of T^* are reported will systematic deviations from the combination rules be evident.

Mixture	B_{12} (observed)	B_{12} (calculated)	Deviation
$\text{O}_2\text{-A}$	107.2	107.2	0
$\text{O}_2\text{-N}_2$	107.2	107.2	0
He-N_2	107.2	107.2	0
He-A	107.2	107.2	0
Ne-N_2	107.2	107.2	0
Ne-O_2	107.2	107.2	0
Ne-A	107.2	107.2	0

CHAPTER III

EXCESS THERMODYNAMIC PROPERTIES OF THE LIQUID
SYSTEMS O₂-A AND O₂-N₂

1. INTRODUCTION

An excess property of a mixture is defined as

$$A^E = A^M - \sum x_i A^i$$

where A^E is the excess property, A^M that property for the mixture and A^i the property for pure component i . The mole fraction of component i is x_i and the summation is over all the components. In order to obtain a complete knowledge of the excess thermodynamic properties of a liquid mixture at any one temperature, two quantities must be known, the excess Gibbs function G^E and the excess enthalpy or heat of mixing H^E . Theoretically H^E can be calculated from the temperature derivative of the excess Gibbs function by means of the relation

$$G^E = H^E - TS^E = H^E + T (\delta G^E / \delta T)_p. \quad \text{III.1}$$

In practice, however, the limit in the accuracy to which G^E can be measured and the restricted range of temperatures over which experiments can be easily carried out make such a procedure highly inaccurate, so that two independent measurements are usually necessary. Although neither of these measurements is easily accomplished at low temperatures it is only in this region that theoretically tractable systems can be studied.

The excess Gibbs function is normally derived from vapor-liquid equilibrium studies. In general, the total pressure of the system and the composition of the liquid and of the vapor phase are measured at constant temperature for different mixtures. Inherent difficulties in such experiments are the establishment of a true equilibrium between the phases (e.g. no entrainment of liquid droplets in the vapor), representative sampling and accurate analysis, especially at low concentrations.

The heat of mixing is measured directly, generally isothermally. Two pure liquids are mixed and, as the mixture generally cools, the heat effect is compensated with a measured amount of energy so that the temperature of the system remains constant. The vapor pressures of the pure components are not usually equal and often there is an appreciable change in the total volume on mixing. If there is any vapor

space in the calorimeter, evaporation of liquid or condensation of vapor will occur. Thus, there is a possibility that the heat associated with these effects could cause a serious error in the measured heat of mixing. It is also obvious that there must be some reliable method for thoroughly stirring the contents of the calorimeter once the components have been brought together.

The construction of only two low-temperature heat of mixing calorimeters has been reported (Poo 57, Jee 57) but because of undesirable features associated with these devices, a new type of calorimeter was designed for the present experiments.

2. EXPERIMENTAL DETERMINATION OF H^E

The calorimeter is pictured in fig. III.1. It consists of an upper and

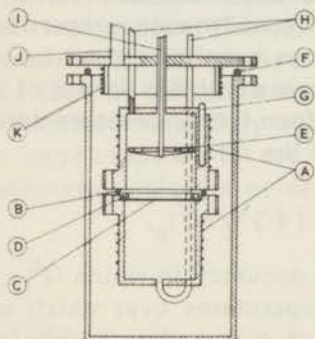


Fig. III.1 Heat of Mixing Calorimeter

a lower brass vessel joined in a vacuum-tight seal by an indium 'o'-ring B (1.2 mm circular cross-section) compressed by the action of six brass bolts. The two chambers are separated by a diaphragm C made of household aluminum foil (20μ). The diaphragm is held in position in a recess in the lower vessel by ring D, the top of which projects 0.1 mm above the surface of the bottom calorimeter section. Thus, when the two halves are bolted together the foil is clamped securely in place, forming a tight seal. In the early experiments a thin layer of silicone grease aided the closure but in later work a very thin indium ring (0.4 mm) placed under the foil proved to be more reliable.

The foil can be punctured by a point at the end of the stirrer E, a thin perforated copper disk which is soldered to a 0.8 mm stainless steel capillary. The capillary fits closely inside another capillary I, which passes through the top of the vacuum can, goes through the bath and ends in a packing box at room temperature. The stirrer capillary is brought out of the vacuum system there through a teflon packing. Two filling capillaries H, also of stainless steel, are led out through the bath to a gas handling system. A 100 Ω constantan heater A is non-

inductively wound around both calorimeter sections, and a small platinum thermometer G of the glass enclosed type manufactured by Degussa is secured in a well in the wall of the upper chamber with Wood's metal. All wires are lacquered to a brass ring K which is at bath temperature and then exit through the vacuum can pumping tube J. The 'o'-ring used for the calorimeter and a similar one, F, used for the vacuum can closure, allow rapid replacement of the punctured foil. In order to make measurements over the entire concentration range various size lower sections were made and these can be changed by soldering one joint and splicing two heater wires. For the N_2-O_2 measurements a 10 cm^3 upper vessel was employed while for the $A-O_2$ series the upper vessel had a volume of 5 cm^3 .

The vapor space problem is eliminated by overfilling the calorimeter so that the liquid level stands high in the capillaries outside the vacuum can. On mixing, any pressure change results in condensation or evaporation at the surface of the liquid in the capillary. Since the thermal conductivity of the liquid is poor and the resistance to flow in the capillaries is high, the calorimeter remains thermally isolated and unaffected by these secondary effects.

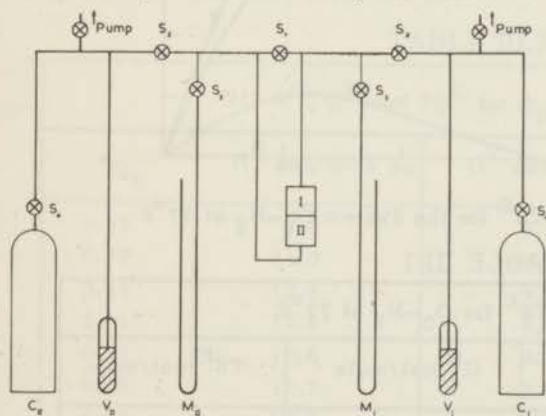


Fig. III.2
Calorimeter Filling System

The calorimeter is filled with the aid of the gas handling system shown in fig. III.2. Gas from a cylinder C enters the system through stopcock S_4 and is maintained at a pressure of about 80 cm by the mercury safety V. The mercury manometer M registers the filling pressure, and on it can be observed the rapid rise in the pressure caused by the thermal gradient along the filling lines in the bath, when the calorimeter capillaries are full. The lines between the stopcocks S_2 and S_3 are constructed of narrow capillary so that the gas volumes are kept small. The stopcock S_1 facilitates pumping the calorimeter when the foil is in place prior to filling. The use of the mercury safeties reduces

the danger of accidental rupture of the diaphragm during the filling process. However, the aluminum foil proved to be amazingly strong and did not leak even under a pressure difference of one atmosphere. The measurements were performed using the standard compensation heating technique. For details see, for example (Waa 50). The resistance of the thermometer was determined with a compensation bridge, the heating current and voltage were measured with accurate meters and the timing of the heating periods (2 minutes) was with a stop watch. All gases were from laboratory stock and were at least 99% pure.

The experimentally measured heats of mixing for the O_2-N_2 system at $77^\circ K$ are given in table III.1 and fig. III.3 and the results for the $A-O_2$ system at $86^\circ K$ are found in table III.2 and in fig. III.4.

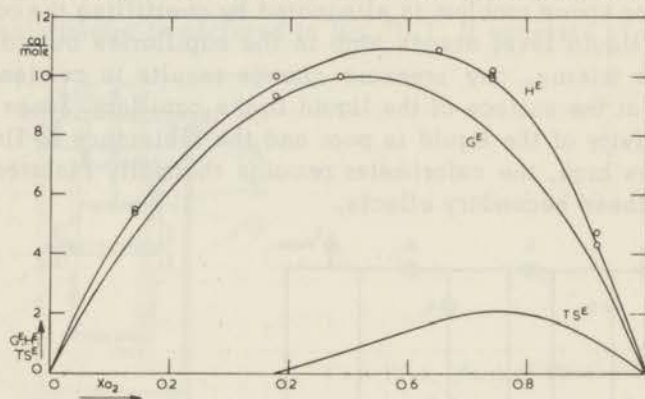


Fig. III.3 H^E , G^E and TS^E for the System O_2-N_2 at $77^\circ K$

TABLE III.1

H^E , G^E and TS^E for O_2-N_2 at $77^\circ K$			
x_{O_2}	H^E cal/mole	G^E cal/mole	TS^E cal/mole
0.14	5.4	4.6	0.8
0.14	5.5	4.6	0.9
0.38	10.0	9.3	0.7
0.38	9.3	9.3	0.0
0.49	10.0	9.9	0.1
0.65	10.9	9.3	1.6
0.74	10.2	8.1	2.1
0.74	10.0	8.1	1.9
0.74	9.9	8.1	1.8
0.92	4.7	3.4	1.3
0.92	4.4	3.4	0.6

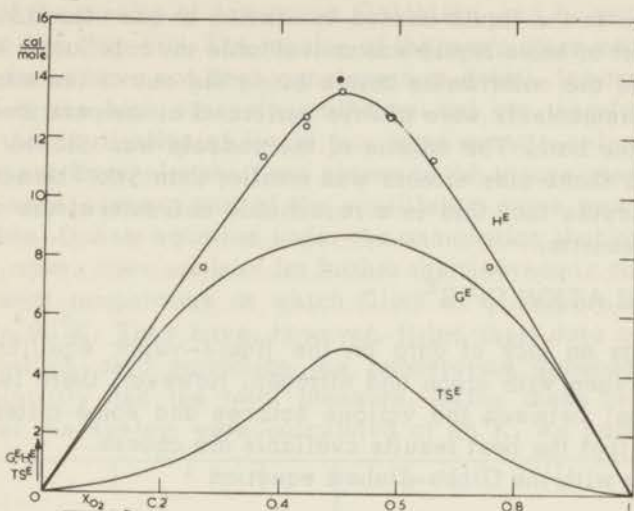


Fig. III.4 H^E , G^E and TS^E for the System O_2 -A at $86^\circ K$

The blackened circle is the one point reported by Pool and Staveley.

TABLE III.2

H^E , G^E and TS^E for O_2 -A at $86^\circ K$			
x_{O_2}	H^E cal/mole	G^E cal/mole	TS^E cal/mole
0.27	7.6	7.4	0.2
0.37	11.0	8.7	2.3
0.44	12.4	9.2	3.2
0.44	12.6	9.2	3.4
0.51	13.6	9.3	4.3
0.58	12.7	8.9	3.8
0.58	13.0	8.9	4.1
0.66	10.5	8.1	2.4
0.76	7.5	6.5	2.0

The errors associated with the measurement lie mainly in the definition of the liquid volumes and in the energy input due to effects associated with the mixing process. Upon mixing two things occur simultaneously: the pressure and the volume change, causing liquid to be transported from the filling capillaries to the calorimeter or vice-versa, depending on the sign of the changes. In order to minimize this effect the diameter of the filling lines was kept small, which not only reduced the volume of the "dead space liquid" but helped to damp any

oscillations in the liquid caused by stirring or gas vibrations. Because the transport of some liquid was unavoidable the capillaries were coiled once around the calorimeter before being led out of the vacuum space and the measurements were always performed at temperatures very near to that of the bath. The volume of the vessels was chosen so that the error due to these side effects was smaller than 5%. The scatter of the points indicates that this is a reasonable estimate of the accuracy of the measurements.

3. CALCULATION OF G^E

There is no lack of data on the liquid-vapor equilibria for mixtures of oxygen with argon and nitrogen. However, there is noticeable disagreement between the various sources and some criteria must be applied so that the best results available are chosen.

Starting with the Gibbs-Duhem equation

$$\sum_{\alpha} m_{\alpha} d\mu_{\alpha} = 0$$

various tests of the thermodynamic consistency of vapor-liquid equilibrium measurements may be derived. Following Rowlinson (Row 59), we may write

$$\begin{aligned} \mu_2^E - \mu_1^E &= RT \ln \frac{\gamma_2}{\gamma_1} = \left(\frac{\delta G^E}{\delta x_2} \right)_T \\ &= RT \ln \left(\frac{\alpha p_1^{\circ}}{p_2^{\circ}} \right) + (p - p_1^{\circ})(v_1^{\circ} - B_{11}) - (p - p_2^{\circ})(v_2^{\circ} - B_{22}) + 2pE(y_1^2 - y_2^2) \end{aligned}$$

III.2

where μ is the chemical potential, γ the activity coefficient, p the total pressure of the system, p° the vapor pressure of a pure component, v° the molar volume of a pure component, B_{ii} the second virial coefficient of the pure vapor, E the excess second virial coefficient as defined in chapter II and B_{12} the second virial coefficient for the mixed interaction. The relative volatility α is defined as $y_2 x_1 / y_1 x_2$ where y and x represent the concentration in the vapor and in the liquid phases, respectively, and the subscripts 1 and 2 refer to the two components. For thermodynamic consistency it is necessary because of the Gibbs-Duhem relation that this equation, when integrated between the limits $x_2 = 0$ and $x_2 = 1$, be equal to 0. Thus, if the right side of eqn. III.2 be plotted against x_2 , the areas under the curve above and below the x axis must be equal.

Making use of this criterion the results of Clark, Din and Robb (Cla 54) and those of Wang (Wan 57) for the A-O₂ system have been analyzed for reliability. In the case of the N₂-O₂ system a similar study has

been made of the results of Armstrong, Goldstein and Roberts (Arm 55) and those of Din (Din 60). The results of the many other measurements on these systems have not been considered in detail, for many of them are limited to the high pressure isotherms and are therefore of more interest in the distillation of liquid air, some contain only incomplete data and others have already been shown to be inconsistent by other authors. In some cases a part of the equilibrium curve was calculated from the Gibbs-Duhem equation under the assumption that the vapor is ideal, which makes them useless for further thermodynamic calculations.

The lowest temperature at which Clark et al. report an isotherm for A-O₂ is 90°K. They have, however, fitted their data to empirical equations which also reproduce the temperature dependence of the relative volatility and the total pressure. Using these relations the properties of the system were calculated at 86°K. As pointed out by

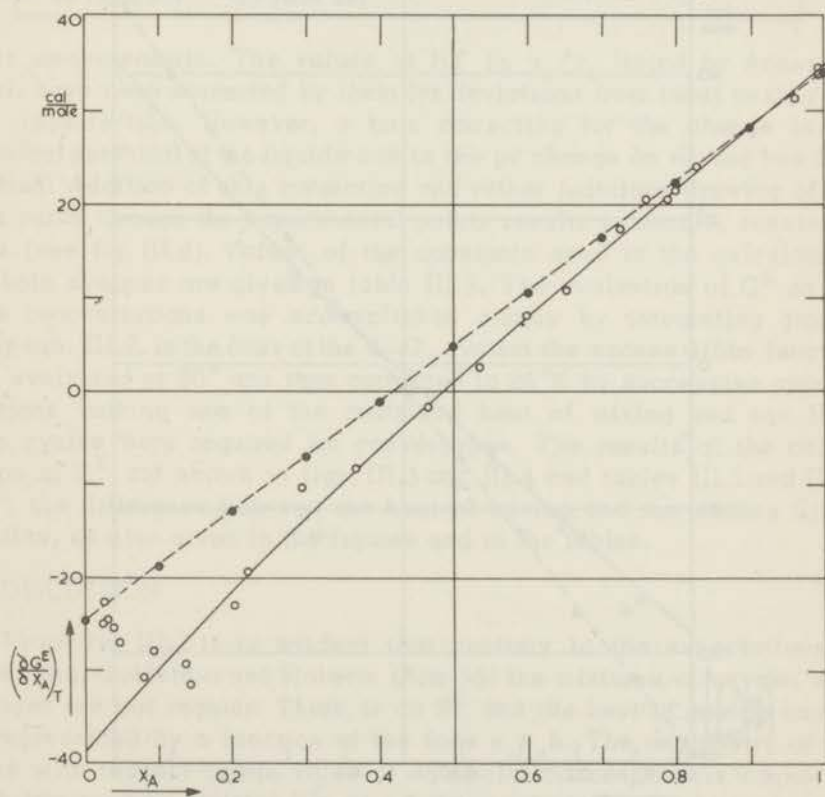


Fig. III.5 Test of the Thermodynamic Consistency for O₂-A Vapor-Liquid Equilibrium Data

● - - - - - Clark, et al. 86°K ○ - - - - - Wang 90°K

the authors, even within the temperature range of the measurements their results are not entirely consistent and extrapolation to the lower temperature results in greater inconsistency. Wang's measurements at 90°K appear to be more reliable.* However, there is some uncertainty in the results at high oxygen concentrations and, as may be seen in fig. III.5, there is considerable latitude in the choice of the best curve through the measured points. We have chosen that curve which best satisfies the thermodynamic consistency criterion. For a comparison, the results of Clark et al. are also included in the figure.

Extrapolation to 77°K of the smoothed values reported by Din for the mixtures of oxygen with nitrogen results in a curve which is considerably less consistent than the results in the temperature range of

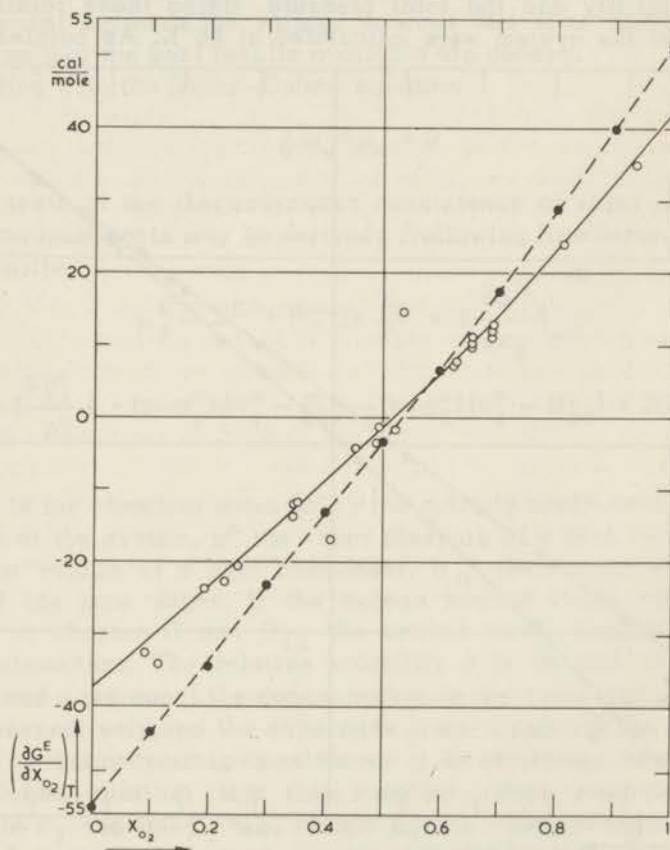


Fig. III.6 Test of the Thermodynamic Consistency for O_2-N_2 Vapor-Liquid Equilibrium Data at 77°K

● - - - - - Din ○ - - - - - Armstrong, et al.

* In order to reduce the vapor pressure data given by Wang to 90°K, the dp/dT as a function of concentration given by Clark, et al. (Cla 54) have been used.

TABLE III.3

Values of Constants Used in Calculation of G^E			
	T °K	B cm ³ /mole	v^o cm ³ /mole c)
O ₂	90	- 229 a)	28.0
	77	- 312 b)	26.6
N ₂	77	- 245 b)	34.7
A	90	- 209 a)	29.1
a) Calculated (Chapter II)			
b) (Arm 55) c) (Bla 58)			

their measurements. The values of $RT \ln \gamma_1/\gamma_2$ listed by Armstrong et al. have been corrected by them for deviations from ideal mixing and gas imperfection. However, a term correcting for the change in the chemical potential of the liquids due to the pv change on mixing has been omitted. Addition of this correction and rather judicious drawing of the best curve through the experimental points results in usable, consistent data (see fig. III.6). Values of the constants used in the calculations for both systems are given in table III.3. The evaluation of G^E at various concentrations was accomplished simply by integrating graphically eqn. III.2. In the case of the A-O₂ system the excess Gibbs function was evaluated at 90° and then corrected to 86°K by successive approximations making use of the measured heat of mixing and eqn. III.1. Two cycles were required for convergence. The results of the calculation of G^E are shown in figs. III.3 and III.4 and tables III.1 and III.2. TS^E , the difference between the heat of mixing and the excess Gibbs function, is also given in the figures and in the tables.

4. DISCUSSION

From fig. III.3 it is evident that contrary to the expectations of Armstrong, Goldstein and Roberts (Arm 55) the mixtures of oxygen with nitrogen are not regular. There is an S^E and the heat of mixing cannot be represented by a function of the form x_1x_2h . The asymmetry of the curve with respect to the value at equimolar concentrations cannot be much improved by plotting H^E as a function of the volume fraction.

The argon-oxygen heats of mixing are in reasonable agreement with the one point measured by Pool and Staveley and reported in a review article (Par 59). This point is indicated in fig. III.4. The measured H^E is more symmetric than that calculated from the temperature

derivative of G^E as taken from the data of Clark, et al. (Row 59) but it is not of the parabolic form expected for a regular solution.

The excess entropy for both of the systems studied is rather small and because of the rather large uncertainties in the values of G^E and H^E it is probably only reliable with respect to order of magnitude.

It appears attractive to compare the measured thermodynamic properties of the mixture studied with those calculated from one of the modern theories of mixtures. A close look at the assumptions underlying these theories, however, should be a prerequisite to their application. Scott (Sco 56) has formulated the basic features of his work and that of the Prigogine school:

- (a) The intermolecular potential energy is assumed to be due to central forces only, and of the same form for all kinds of pairs, and may be written symbolically as $u(r) = \epsilon f(\sigma/r)$, where r is the distance between molecular centers, ϵ is the energy of a molecular pair at its equilibrium distance, and σ is the (low temperature) "collision diameter". Both liquids then conform to the same reduced equation of state, a function of the reduced temperature and a reduced volume.
- (b) The same reduced equation of state is assumed for the solution and a prescription is given for obtaining appropriate averages for the energy and volume parameters in the solution.

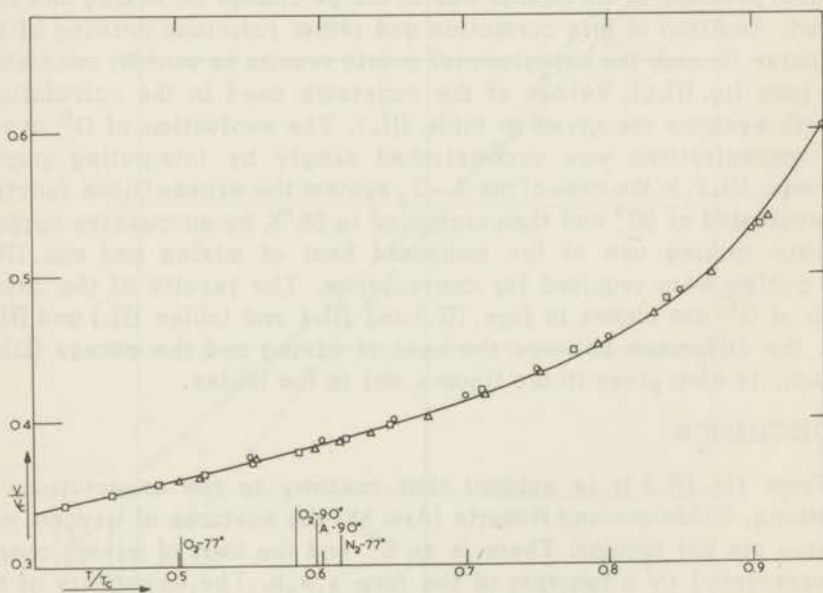


Fig. III.7 Reduced Orthobaric Volume vs. Reduced Temperature Reduction with critical constants. The vertical lines along the temperature axis indicate reduced temperatures for the pure liquids.

\circ A Δ N_2 \square O_2

One may test assumption (a) rather easily by plotting the reduced properties of the pure liquids as a function of a convenient reduced parameter such as the temperature. If the potential parameters used in the reduction are the correct ones, and if the law of corresponding states is followed, both sets of points will fall on the same universal curve. In fig. III.7 the reduced volume (reduction with critical volume)^o for liquid A, N₂ and O₂ is given as a function of the reduced temperature T^* . The correspondence between these liquids is, in this case, excellent.

However, for the calculation of the heat of mixing and other thermodynamic properties, use must be made of the configurational^{oo} enthalpy H' and this, in reduced form, is plotted against the reduced temperature in fig. III.8. Here the correspondence is very poor. As in the case for the volumes the reduction was done with critical constants.

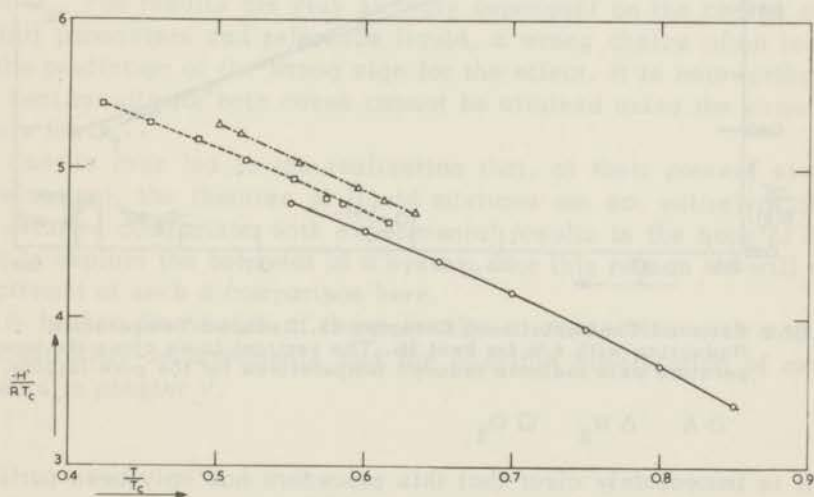


Fig. III.8 Reduced Configurational Enthalpy vs. Reduced Temperature
Reduction with critical temperature.

\circ A Δ N₂ \square O₂

^o Values of the various properties for the pure liquids used in this section have been taken from the tables given by Rowlinson (Row 59).

^{oo} Configurational properties are properties which are functions only of the relative positions of the molecules (i.e. their configuration) and not of the linear momenta or of the rotational or vibrational states. Hence, they may be calculated from the measured properties by subtracting the corresponding ideal gas value.

It is legitimate, however, to work in the opposite direction and to fit the potential parameters to the best representation of the data in agreement with the law of corresponding states, for accurate data on the potential force constants are scarce and one finds a large spread in the few known values. If $\log H'^*$ be plotted against $\log T^*$ for substances which conform to the law of corresponding states, a series of curves will result which coincide, or which can be made to coincide by a shift of coordinates. Because of the logarithmic scale the shifts required for coincidence directly give the change in potential parameter required for conformity. The results of such a fitting process are shown in fig. III.9.

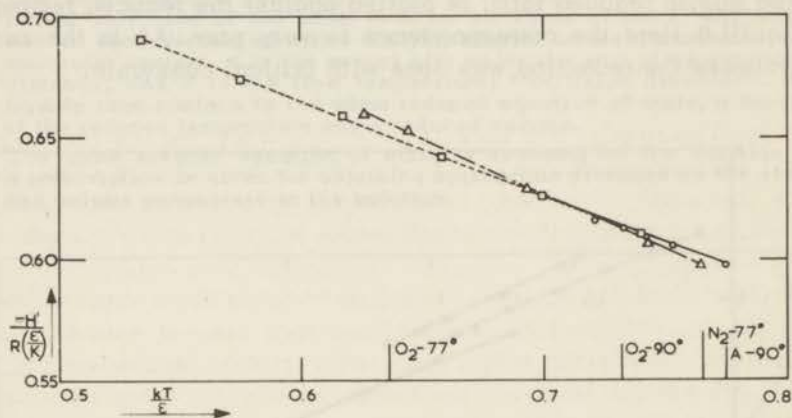


Fig. III.9 Reduced Configurational Enthalpy vs. Reduced Temperature Reduction with ϵ/k for best fit. The vertical lines along the temperature axis indicate reduced temperatures for the pure liquids.

○ A △ N₂ □ O₂

It is immediately clear that this procedure has only been partially successful. The slopes of the curves are different so that they can only be made to coincide over a short span of the reduced temperature, indicating that the law of corresponding states cannot be applied. Furthermore, the calculation of the heat of mixing essentially involves the deviation of this curve from a straight line (see (Pri 57)) and it is seen that the non-conformance to the corresponding states ideal is an effect at least equal in magnitude to the deviation from linearity of the curve. Equally large discrepancies are to be noted in the configurational specific heats and the configurational internal energy (Row 59). Thus in the case of A, O₂ and N₂ assumption (a) does not seem to be justified, and therefore it is reasonable to expect that (b) is also a doubtful assumption.

The application of a corresponding states theory to the problem of the excess volume is, at first glance, more promising, for as previously mentioned, the liquid volumes conform rather well to a universal function. Here, however, another difficulty presents itself as shown in fig. III.6 where the reduced temperatures corresponding to 90°K have been marked for A and O_2 and the reduced temperatures for N_2 and O_2 at 77°K have also been indicated. It is evident that those portions of the temperature-volume curve lying between the reduced temperatures of the pure components are almost linear. Any reasonable prediction of the excess volume made graphically is impossible, since it essentially entails a measurement of the non-linear character.

Of course, the excess functions can be calculated making use of analytical formulae, assuming that the various derivatives of the functions for the pure components are well known. Knaap et al. (Kna 61) have attempted this in the case of V^E for the mixtures of A and N_2 with O_2 . The results are very strongly dependent on the choice of potential parameters and reference liquid, a wrong choice often leading to the prediction of the wrong sign for the effect. It is noteworthy that the best results for both cases cannot be attained using the same constants for O_2 .

One is thus led to the realization that, at their present state of development, the theories of liquid mixtures are not entirely suitable for detailed comparison with experimental results in the hope of being able to explain the behavior of a system. For this reason we will make no attempt at such a comparison here.

A further discussion of these results in connection with magnetic susceptibility measurements and the possible dimerization of oxygen appears in chapter V.

The experimental apparatus described in this paper is designed to measure the rate of reaction between a gas and a solid surface. The reaction is assumed to be first order with respect to the gas concentration. The rate of reaction is measured by the change in the amount of gas in a closed system of known volume. The gas is introduced into the system by a syringe and the reaction is allowed to proceed for a certain time. The amount of gas remaining in the system is then measured by a gas buret. The rate of reaction is calculated from the change in the amount of gas and the time interval. The results are compared with the theoretical rate of reaction for a first order reaction. The agreement between the experimental and theoretical rates is within experimental error.

Of course, the correct location can be calculated regardless of the reaction order, provided that the volume of the gas is known. In this case, the rate of reaction is calculated from the change in the amount of gas and the time interval. The results are compared with the theoretical rate of reaction for a first order reaction. The agreement between the experimental and theoretical rates is within experimental error.

One is free to let the reaction take its own course, or to develop the reaction at fixed intervals or at certain points for comparison with experimental results in the form of a plot. The latter is the method of a system. For this reason we will use the method of such a comparison here.

A comparison of the results in comparison with theoretical results is shown in Figure 1. The theoretical results are shown in Figure 2. The agreement between the experimental and theoretical rates is within experimental error.

$$V = V_0 e^{-kt}$$

The results are compared with the theoretical rate of reaction for a first order reaction. The agreement between the experimental and theoretical rates is within experimental error. The rate of reaction is calculated from the change in the amount of gas and the time interval. The results are compared with the theoretical rate of reaction for a first order reaction. The agreement between the experimental and theoretical rates is within experimental error.

CHAPTER IV

THE MAGNETIC SUSCEPTIBILITY OF LIQUID MIXTURES CONTAINING OXYGEN

1. INTRODUCTION

We have previously shown how the measurements of Perrier and Onnes (Per 14) on the magnetic susceptibility of liquid mixtures of oxygen and nitrogen led Lewis (Lew 24) to suggest that a dimeric form of oxygen was responsible for its magnetic behavior. A detailed analysis of this data with respect to comparisons with other measurements on mixtures is not convenient, however, as the results are given only in terms of the susceptibility per gram oxygen at various effective densities of oxygen and not as a function of the concentration, and for some of the mixtures measurements were made at only two temperatures. Further, only mixtures with nitrogen were considered and thus new susceptibility studies were undertaken in order to gain more complete knowledge of the magnetic phenomena.

2. METHOD AND APPARATUS

The measurements were performed using a Hartshorn mutual inductance bridge, the construction and use of which has been extensively described previously (Mar 57, 58). A frequency of 227 Hz was used in all the studies and the coil system shown schematically in fig. IV.1 was especially constructed for the work. There are two secondary coils, S_1 and S_2 , wound from 0.1 mm povin insulated copper wire, which are connected in opposition to each other. The lower coil, which is wound around the sample bulb (15 cm^3), consists of 2001 turns and the upper coil, of 1990 turns, is wound around a piece of glass tubing similar in dimensions to that used for the sample volume. The primary coil, P , wound from 0.2 mm povin insulated wire, consists of 4942 turns and is wound about the glass jacket which encloses the secondary coils. It extends well beyond the ends of the inner coils to diminish the effect of field inhomogeneity. The annular space between the two coil systems was filled with gas for thermal conductivity, and holes above and below S_2 allow free circulation of gas within the coil. The filling capillary running through the center of the upper secondary coil is 1 mm in diameter.

Mixtures were prepared in a 3 l cylinder from laboratory stock gases (99.8% pure) and allowed to stand overnight before use. Nitrogen gas at 1 atm pressure was let into the space between the coils and the

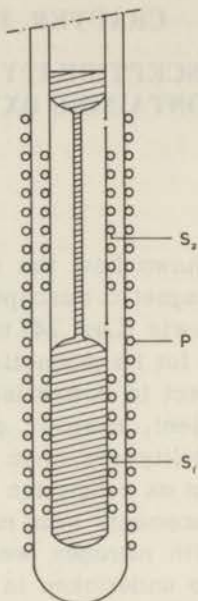


Fig. IV.1 Coil System

mixture was then condensed into the apparatus which was cooled with either liquid nitrogen or oxygen. Care was taken that the sample liquid level was well above the top of the primary coil so that even at the lowest temperature the contraction of the liquid could not bring the meniscus into the coil system. The temperature of the sample was taken as that of the bath and deduced from vapor pressure measurements. A heater at the bottom of the cryostat was used to dispel the temperature gradients which are the result of pumping on the refrigerant.

In the beginning, analysis of the mixtures was performed by sampling the gas remaining in the cylinder after filling, and analyzing it by thermal conductivity*, but results at low concentrations showed evidence of a systematic error leading to too low oxygen concentrations. Analysis by absorption in pyrogallol* of both the gas left in the cylinder and a sample taken from gas obtained by evaporating all of the liquid mixture condensed in the apparatus showed about 0.4% more O_2 in the latter sample. The reason for this difference is not completely clear; a possibility is imperfect mixing in the cylinder. Therefore, all points below 8% O_2 concentration were remeasured and the oxygen content determined from a sample taken from the evaporated mixture by absorption in pyrogallol. Taking this into account we estimate the overall accuracy in the measurement of the concentrations to be of the order of ± 0.005 in the mole fraction.

* We are indebted to Mr. H.v.Ee for the thermal conductivity analyses and Miss S.Henkes for the analyses by the absorption method.

Because of the large number of turns and the rather large sample volume it was possible to make measurements down to concentrations of about 3%, which at the highest temperature corresponds roughly to 0.4 turn on the bridge, whereas at 90°K, balancing of the bridge for pure oxygen gave a value of 10.6 turn. The uncertainty in the temperature of 0.1°K is, at worst, equivalent to a change of 0.01 turn in the bridge but a blank measurement with nitrogen showed a temperature dependent increase in the number of turns, which had a maximum at 77°K of 0.02 turn, while in the case of such a blank with argon an increase of 0.01 turn was found at 90°K. On the basis of the measurements on dilute mixtures this could correspond to a concentration of about 0.1% oxygen as impurity, but the effect decreased with decreasing temperature and was probably due to a change in the coil system induced by the addition of liquid to the sample volume. We have corrected for this effect but we accept 0.02 turn as the limit of the reliability of the susceptibility measurements, while the precision of the magnetic determinations is of the order of 0.1% as can be seen from the spread in the pure oxygen data shown in fig. IV.2.

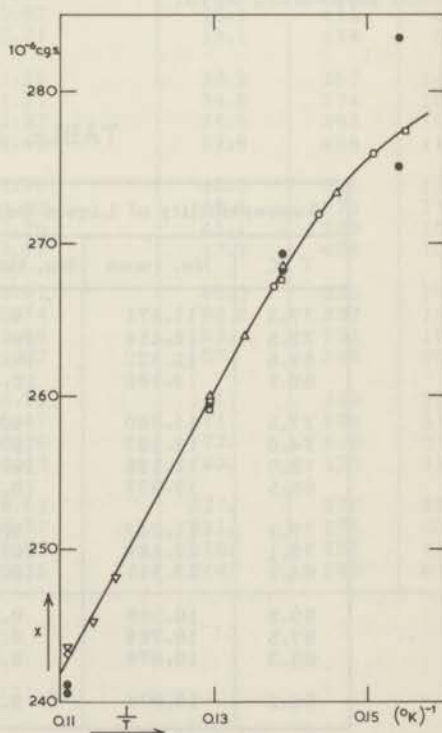


Fig. IV.2

Susceptibility per Gram of Liquid Oxygen as a Function of $1/T$
 The black circles are the measurements of Onnes and Perrier.
 Other symbols indicate different measuring days.

3. RESULTS

The results of the measurements on pure liquid oxygen are given in table IV.1. The susceptibility, χ , is first listed in terms of the difference between the number of turns required to balance the bridge when the secondary coil was empty and when it was filled. The correction mentioned above has been applied to these data. These results have also been expressed in the number of turns per gram mixture by dividing by the density taken from the recent measurements by Blagoi and Rudenko (Blā 58) and they have been converted into cgs units per gram relative to the measurements of pure liquid oxygen at 77°K by Onnes and Perrier (Kam 10). Thus, a conversion factor obtained from the ratio of the old Leiden value for the susceptibility (259.6×10^{-6} cgs/g) at the nitrogen boiling point to the average value of the number of turns per gram for oxygen at the same temperature (9.86) was used to establish the absolute value of the susceptibility. In fig. IV.2 these data are plotted against the reciprocal of the temperature. The dark circles represent the early Leiden data (Kam 10) and the other symbols indicate different measuring days.

TABLE IV.1

Susceptibility of Liquid Oxygen from 65 to 90°K				
T °K	No. turns	No. turns/g	χ /g cgs	- θ °K
77.3	11.871	9.86	259.7	43.0
72.5	12.454	10.15	267.4	44.4
69.6	12.822	10.33	272.1	45.3
66.3	13.182	10.49	276.2	46.9
77.3	11.880	9.87	259.9	43.0
74.6	12.197	10.02	264.0	43.8
72.0	12.536	10.19	268.6	44.4
68.5	12.937	10.38	273.6	45.8
77.3	11.847	9.84	259.2	43.3
72.1	12.489	10.16	267.7	44.7
64.5	13.345	10.54	277.8	48.0
90.2	10.586	9.25	243.7	38.1
87.5	10.766	9.31	245.3	39.9
85.3	10.978	9.40	247.7	40.9
90.2	10.574	9.24	243.4	38.2

TABLE IV.2

Susceptibility of Liquid Mixtures of Nitrogen and Oxygen						
x_{O_2}	T °K	No. turns	No. turns/g _{mix.}	$\chi/g_{\text{mix.}}$ cgs	χ/g_{O_2} cgs	$-\theta^\circ\text{K}$
0.029	77.3	0.410	0.50	13.7	400	0.3
	74.1	0.442	0.53	14.3	420	0.1
	69.4	0.494	0.58	15.6	460	-1.0
	66.5	0.511	0.59	15.9	470	0.5
0.035	77.3	0.467	0.57	15.4	385	4.0
	73.5	0.493	0.59	15.9	398	5.1
	69.9	0.534	0.62	16.9	423	4.1
	66.1	0.579	0.66	17.9	448	3.8
0.039	77.3	0.507	0.62	16.6	377	5.7
	73.6	0.549	0.65	17.6	400	4.7
	70.2	0.574	0.67	18.1	411	6.0
	65.8	0.622	0.71	19.1	434	6.3
0.082	77.3	1.051	1.25	33.2	357	14.
	73.3	1.126	1.31	34.8	374	10.
	70.3	1.198	1.37	36.5	392	10.
	66.4	1.265	1.42	37.8	406	11.
0.103	77.3	1.283	1.50	40.0	345	13.
	73.4	1.409	1.62	43.1	372	11.
	70.1	1.504	1.70	45.1	389	10.
	66.1	1.604	1.77	47.1	406	10.
0.266	77.3	3.333	3.61	95.3	325	19.
	74.0	3.505	3.74	98.8	337	19.
	70.2	3.722	3.89	103.	351	19.
	66.0	3.963	4.07	107.	366	20.
0.539	77.3	6.472	6.26	165.	289	31.
	73.5	6.804	6.47	171.	299	31.
	70.0	7.161	6.70	177.	310	31.
	67.0	7.495	6.93	183.	320	31.
0.825	77.3	9.811	8.62	227.	270	39.
	74.3	10.161	8.77	231.	275	40.
	70.4	10.535	8.97	236.	281	41.
	66.7	11.037	9.25	244.	290	41.

TABLE IV.3

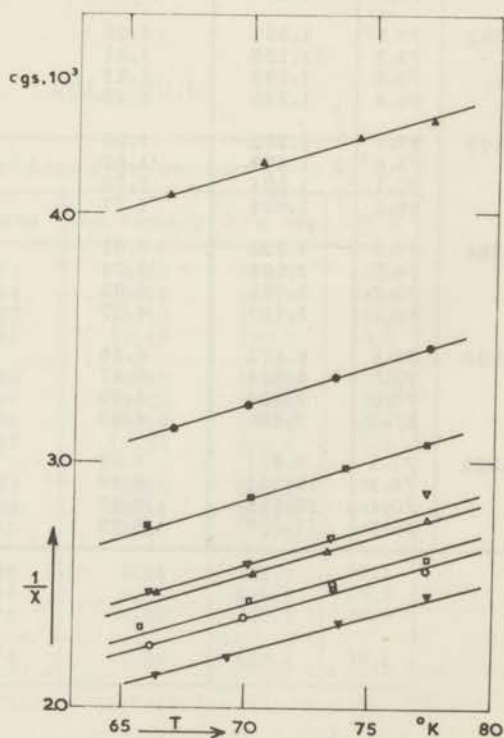
Susceptibility of Liquid Mixtures of Argon and Oxygen at 90°K					
x_{O_2}	No. turns	No. turns/g _{mix.}	$\chi/g_{mix.}$ cgs	χ/g_{O_2} cgs	$-\theta^{\circ}K$
0.025	0.345	0.25	7.1	356	-2.3
0.031	0.419	0.31	8.5	341	1.5
0.032	0.452	0.33	9.2	340	1.9
0.208	2.725	2.04	54.2	311	10.3
0.256	3.400	2.57	68.0	315	9.2
0.373	4.755	3.66	96.6	299	14.5
0.487	5.990	4.69	124.	287	18.9
0.780	8.726	7.24	191.	258	31.0

In tables IV.2 and IV.3 the work on the mixtures with nitrogen and with argon is reported. The susceptibility per gram mixture in cgs units has been corrected for the diamagnetic susceptibility of the diluent, and the densities of the mixtures have been calculated from those of the pure components neglecting the volume change on mixing, which is an

Fig. IV.3

Reciprocal of the Susceptibility per gram Oxygen in O_2-N_2 Liquid Mixtures as a Function of T

x_{O_2} = 0.029 ▼
 .035 ○
 .039 □
 .082 △
 .103 ▽
 .266 ■
 .539 ●
 .825 ▲



effect smaller than the experimental error in the susceptibility measurement (Kna 61). In the case of the argon mixtures data has only been taken at 90°K because of the small temperature range over which argon is liquid. The results for the nitrogen mixtures in the temperature range 65–77°K are plotted as $1/\chi$ per gram oxygen against T in fig. IV.3 and χ for the argon mixtures is shown as a function of the concentration in fig. IV.4, which is a curve typical of all the mixtures studied.

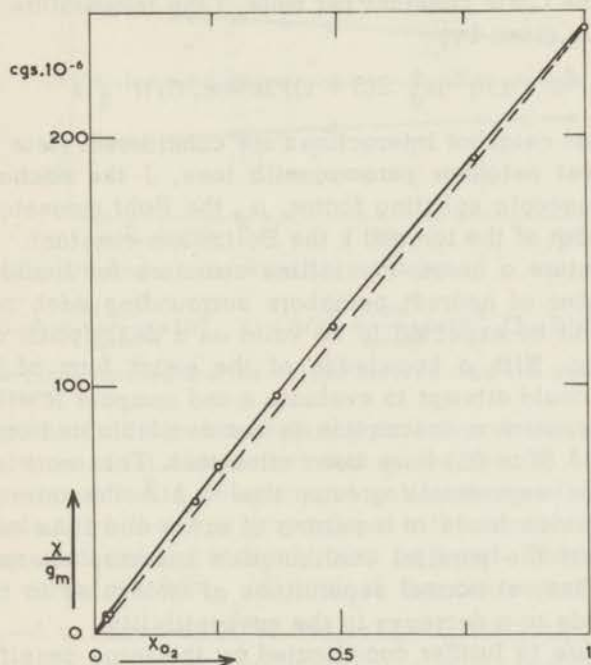


Fig. IV.4 Susceptibility per Gram Mixture of O_2 -A Liquid Mixtures as a Function of the Oxygen Concentration

The dashed line represents the value on the basis of a linear concentration dependence.

4. DISCUSSION

According to Kamerlingh Onnes and Perrier their results showed that (a) the deviations from Curie's law shown by pure liquid oxygen are not an immediate consequence of the temperature, but are related to the density, and (b) the magnetic susceptibility of oxygen increases with dilution in mixtures, approaching the Curie's law value at infinite dilution. The present work is qualitatively in agreement with these observations and we shall now try to consider these properties in more detail on the basis of antiferromagnetic exchange and the Lewis model of chemical equilibrium, respectively.

a. Antiferromagnetic Treatment

It is well known (see e.g. (Nag 55)) that for a crystal containing paramagnetic ions exhibiting exchange, the magnetic susceptibility at relatively high temperatures may be described by:

$$\chi = C/(T - \theta)$$

where C is the Curie constant per mole, T the temperature and θ a constant which is given by:

$$\theta = zJg^2 \mu_{\beta}^2 S(S + 1)/3k \equiv zJC/N$$

if only nearest neighbor interactions are considered. Here z is the number of nearest neighbor paramagnetic ions, J the exchange integral, g the spectroscopic splitting factor, μ_{β} the Bohr magneton, S the spin quantum number of the ion and k the Boltzmann constant.

If we picture a quasi-crystalline structure for liquid oxygen, i.e. a fixed number of nearest neighbors surrounding each molecule, this formula should be expected to be valid as a description of the oxygen susceptibility. With a knowledge of the exact form of the exchange integral one could attempt to evaluate θ and compare it with experiment. Unfortunately, such a description is not available and only rough calculations of J (Kan 55) have been attempted. This work shows that at intermolecular separations greater than 1.3 \AA the interaction of two oxygen molecules leads to a pairing of spins and it is only at shorter distances that the parallel configuration becomes energetically more favorable. Thus, at normal separations of molecules in the liquid the exchange leads to a decrease in the susceptibility.

The picture is further complicated by the large density changes in the liquid accompanying temperature changes. The exchange integral is dependent on the distance between molecules so that θ should have a density dependence. In fig. IV.5 values of $-\theta/\rho$, $-\theta/\rho^2$ and $-\theta/\rho^3$ for pure oxygen have been plotted. The θ values have been obtained by fitting each of the points to a Curie-Weiss law and ρ is the density in moles/cm³. It is obvious that between 65 and 90°K θ is quadratically dependent on the density and probably temperature independent.

It should be noted here that deviations from the Curie-Weiss law are not unusual for antiferromagnetics at temperatures near the value of $-\theta$ and that these departures are attributable to short-range ordering (Kas 56). However, if we compare the behavior of liquid oxygen to that of crystals with a crystalline anisotropy small as compared to the magnetic interaction, such as the simple salts of manganese, we see that at temperatures twice the value of θ , deviations from the Curie-Weiss law are negligible (Nag 55). Hence, it does not seem plausible that it

is the ordering process which excites the changes in θ in oxygen. Furthermore, the dependence of θ on z can be neglected, as diffraction studies on the liquid (Sha 42, Hen 60) indicate that the number of nearest neighbors is practically temperature independent.

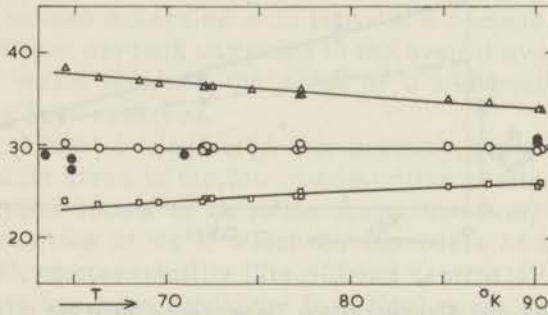


Fig. IV.5 Density Dependence of θ for Liquid Oxygen

$$\Delta - \theta/\rho \frac{^{\circ}\text{Kcm}^3}{\text{mole}} \times 10^2 \quad \circ - \theta/\rho^2 \frac{^{\circ}\text{Kcm}^6}{\text{mole}^2} \times 10^3 \quad \square - \theta/\rho^3 \frac{^{\circ}\text{Kcm}^9}{\text{mole}^3} \times 10^4$$

The black circles are the values derived from the data of Onnes and Perrier.

If we assume that the change in the exchange integral is dependent on the density we must also detect this in the results for the mixtures, but experiments on solid solutions of antiferromagnetic with diamagnetic materials show that θ is proportional to the concentration (Nag 55) and this type of dependence should also be found. Therefore, we have plotted the value of $-\theta/(x_{\text{O}_2} \rho^2)$ against the concentration of oxygen, x_{O_2} , for O_2 -A mixtures at 90°K and for O_2 - N_2 mixtures at 77°K in figs. IV.6 and IV.7, respectively. The horizontal line obtained for the mixtures with argon seems to lend weight to our assumptions, at least

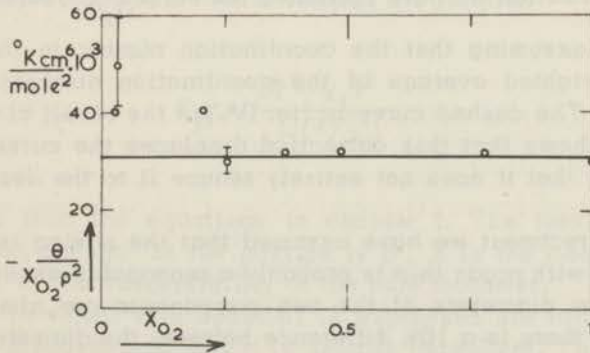


Fig. IV.6 Density and Concentration Dependence of θ for O_2 -A Liquid Mixtures at 90°K

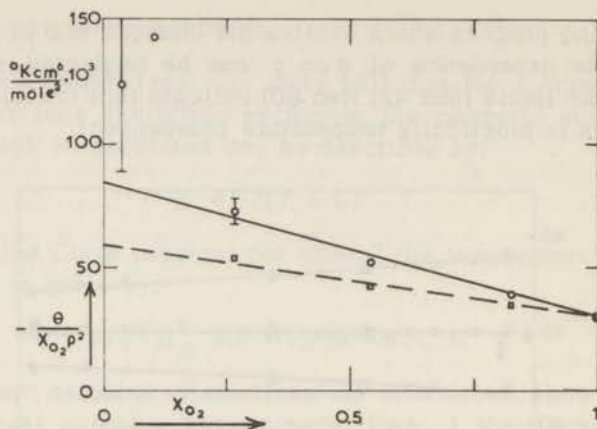


Fig. IV.7 Density and Concentration Dependence of θ for O_2-N_2 Liquid Mixtures at $77^\circ K$

The dashed curve shows values of $-\theta/(x_{O_2} z \rho)$ adjusted to the same scale as the upper curve.

down to concentrations of about 20%. In mixtures with a lower oxygen content the accuracy rapidly decreases as indicated by the lines in the graph so that it is not possible to draw any conclusions concerning the low oxygen concentration range.

For the mixtures with nitrogen, however, there is a rather large slope to the line. This is not surprising, for results of x-ray (Sha 42) and neutron (Hen 60) diffraction measurements indicate that while argon and oxygen at $90^\circ K$ both have coordination numbers of 8, at $77^\circ K$ oxygen has 6 nearest neighbors and nitrogen 12, and it can be seen from eqn. IV.1 that the change in coordination number must influence θ . In a very rough approximation we have corrected the $-\theta/(x_{O_2} \rho^2)$ values for N_2-O_2

at $77^\circ K$ by assuming that the coordination number in the mixture is simply a weighted average of the coordination numbers of the pure components. The dashed curve in fig. IV.7 is the result of this calculation and it shows that this correction displaces the curve in the right direction but that it does not entirely reduce it to the desired horizontal line.

In this treatment we have assumed that the mixing is random. For the mixtures with argon this is probably a reasonable assumption, since the molecular diameters of the two components are almost identical (Hir 54), but there is a 10% difference between the diameters of oxygen and nitrogen molecules so that in this case a departure from random

mixing is not unlikely (see (Pri 57)). However, even the problem of the volume distribution of a mixture of two different size hard spheres has not been solved (Pri 57), so that it is not possible to give a quantitative description of the effect of this size difference on the oxygen distribution in the mixtures with nitrogen. An ordering, either in terms of clustering of oxygen molecules or in terms of a decrease of the average distance between oxygens compared to the overall average distance in the mixture, would increase the value of θ and could lead to the results that have been observed.

Once again it must be indicated that because of inaccuracy there can be little weight given to the low concentration points. Finally, the θ values for oxygen appear to be rather large. However, solid oxygen undergoes a transition at 44°K which on the basis of susceptibility (Kam 10, Kan 55), compressibility (Ste 60) and neutron diffraction (Hen 60) measurements has been attributed to a Néel point. In its simplest form the theory for antiferromagnetism predicts that above the Néel point the antiferromagnetic will follow a Curie-Weiss law with a θ equal to the Néel temperature. If we use the value for $-\theta/\rho^2$ which is representative of the pure liquid oxygen measurements, namely $29 \times 10^3 \text{°K cm}^6/\text{mole}^2$, and multiply this by the square of the oxygen density at 44°K we find a θ value of 58°K. Considering the crudity of such a calculation and the fact that more refined theories lead to θ 's higher than the Néel temperature it seems reasonable to accept this as support for the model used above.

b. Chemical Treatment

The chemical approach chosen by Lewis to explain the susceptibility data was based on the calculation of the equilibrium constant K_ρ from the magnetic measurements through the relation

$$K_\rho = \frac{\rho(\chi/\chi_1)^2}{1 - (\chi/\chi_1)}$$

which follows from the equations in chapter I. The total number of grams of oxygen per cm^3 in the mixture is ρ' , χ is the measured susceptibility and χ_1 the susceptibility of the pure monomer.

The units in which this constant is expressed are rather unusual and it has the disadvantage that it is density dependent. Therefore, we introduce another constant K here which is defined in terms of the mole

fractions. It is related to the measured susceptibility in a manner entirely analogous to that of K_ρ and is given by:

$$K = \frac{x_2^2}{x_4} = \frac{4 \left(\chi / \chi_1 \right)^2}{\left[\left(1 - \left(\chi / \chi_1 \right) \right) \left[\left(\chi / \chi_1 \right) + 1 + 2 \left(n_a / n_t \right) \right] \right]}$$

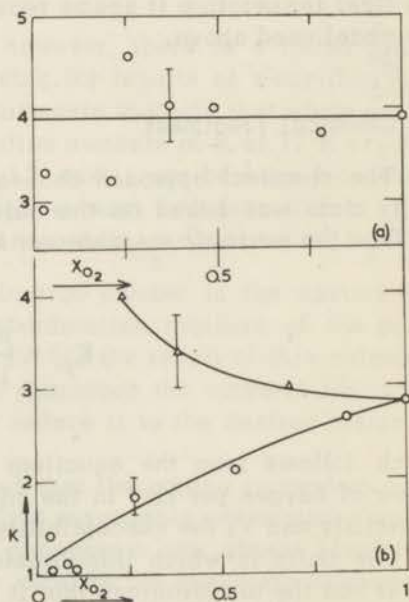
The mole fractions x of monomer and dimer are denoted by 2 and 4 respectively, n_a is the number of moles of diluent, n_t the total number of moles of oxygen in the mixture and the other terms in the susceptibility are defined as above for K_ρ .

Lewis derived χ_1 by extrapolating the Perrier and Onnes data on O_2-N_2 mixtures to infinite dilution and obtained 430×10^{-6} , 469×10^{-6} and 518×10^{-6} cgs/g at 77.4, 70.9 and 64.2 °K, respectively. However, this extrapolation is doubtful for in all three cases these values lie about 6% higher than the susceptibility of an ideal paramagnetic with spin 1 and are then, of course, higher than the value of the susceptibility of the gas. The value of K is particularly sensitive to χ / χ_1 , so that if the Curie's law value for χ_1 is used for the evaluation of the equilibrium constant the results differ greatly from those derived by Lewis. The values for K based on the Curie's law χ_1 are shown in fig. IV.8.

Fig. IV.8

K as a Function of the Mole Fraction of Oxygen in Liquid Mixtures
 χ_1 is taken from Curie's law.

- (a) \circ O_2-A 90°K
 (b) \square O_2-N_2 77°K Perrier and Onnes
 \circ 77°K This research



The mixtures with argon are in reasonable agreement with an equilibrium constant assumption but neither the old Leiden measurements nor the present ones for O_2-N_2 lead to a constant value for K . (Also a marked difference between the constant derived from the present studies and that from the Perrier and Onnes data can be seen in the figure. The earlier results for the susceptibility of the mixtures are higher than those found in this work, and as has been mentioned above, this also leads to a dubious value for the susceptibility at infinite dilution. The reason for this difference is not clear as it seems to lie outside of the experimental error of both of the studies.)

The lack of constancy for the K derived from the O_2-N_2 mixtures cannot be interpreted as proof of the inapplicability of the chemical treatment to this system. An equilibrium constant written in terms of mole fractions can only be considered as an approximation, for all the effects of inideality in the mixture have been neglected. In order to stringently apply this treatment it is necessary to substitute activities for mole fractions, but we do not have sufficient information to be able to make this improvement.

For the sake of completeness the value of K for each of the measured points for pure oxygen has been calculated and these data are compared in fig. IV.9 where $\ln K$ is plotted against $1/T$. The straight line dependence of these constants on the reciprocal of the temperature can be represented by an equation of the form

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

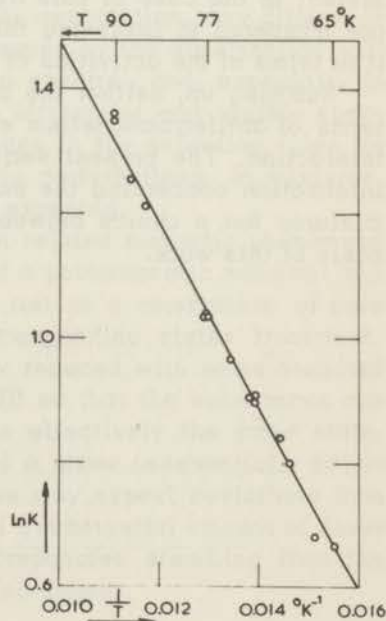


Fig. IV.9 $\ln K$ vs. $\frac{1}{T}$ for Pure Oxygen
between 65 and 90 $^\circ\text{K}$

Here A is not necessarily equal to ΔH , the heat of the reaction, because in a system where the non-ideality is not small compared to the heat of reaction an equilibrium constant written in terms of concentrations can also have the above temperature dependence but the constant A then includes terms which stem from the non-ideality. At best, we can say that if such a chemical treatment is valid the heat of the reaction is probably of the order of a few hundred calories, i.e. the slope of the line, if interpreted as being $\Delta H/R$, where R is the gas constant in cal/mole, gives a value of about 150.

5. CONCLUSIONS

It has been shown that a purely physical treatment of the magnetic susceptibility of pure liquid oxygen and its mixtures with argon can lead to a consistent picture of the oxygen-oxygen interaction but that the measurements on the mixtures with nitrogen can be only qualitatively explained. However, there are indications that a better knowledge of the distribution of the molecules in the liquid could improve this picture. Further, as will be shown in the following chapter, a magnetic interaction stemming from exchange which can be described by an r^{-6} potential and leading to an interaction of roughly 5°K per pair of molecules is not in disagreement with other data concerning the intermolecular potential of oxygen.

On the other hand, the Lewis chemical treatment is equally as consistent in the case of pure oxygen and the oxygen-argon mixtures. We are hampered in improving this treatment by our inability to formulate it in terms of the activities of the monomer and the dimer.

Summing up, neither the chemical hypothesis nor the description in terms of antiferromagnetism entirely explains the nature of the oxygen interaction. The present series of measurements has contributed new information concerning the magnetic behavior of liquid oxygen and its mixtures but a choice between the two models cannot be made on the basis of this work.

CHAPTER V

SURVEY OF PHYSICAL PROPERTIES AND CONCLUSIONS

1. INTRODUCTION

In the almost forty years since the publication of Lewis' paper the status of the O_4 hypothesis has little changed. The results of a number of experiments have similarly been in concordance with the postulate of a dimer but there has been no irrefutable proof of its existence. On the other hand, some experiments appear to be inconsistent with the double molecule. It is our intention to review a number of physical measurements performed on oxygen and its mixtures and try to evaluate their worth as evidence for the dimer.

Perhaps the most risky part of such a compilation is the definition of the term dimer. In the case where a normal covalent or ionic bond is established between the two monomers there is little arbitrariness in the definition of a new species, but if we accept the Lewis hypothesis we are dealing with a bond which is less than 0.1 as strong as even the weakest chemical bond. Therefore, we choose to define a dimer as two molecules which interact over a period of time long compared to the time between intermolecular collisions so that the vibrational and rotational degrees of freedom cannot be treated as those of two independent particles.

The choice of the properties to be discussed has, of course, been limited to those which would be affected by association. Any difference in the vibrational and rotational modes caused by the dimerization will be noticeable in the infrared and Raman spectra, and, especially in the oxygen system, a large change in the ultraviolet and visible spectrum should be seen as a result of changes in the selection rules for electronic transitions caused by magnetic perturbations. In mixtures, deviations from Beer's law are also to be expected.

The magnetic susceptibility and other related magnetic phenomena are obviously of importance in the case of a paramagnetic monomer and a diamagnetic dimer. Also high on the list is a comparison of pure oxygen with other substances in a corresponding states treatment. Various properties can be systematically reduced with some standard parameters as was described in chapter III so that the substances can be compared with each other in what is effectively the same state. If the interaction between a monomer and a dimer is essentially different from that between three monomers we may expect deviations from the behavior of 'normal' substances and if a substantial amount of dimer is present in the system apparent discrepancies stemming from the change in the number of molecules will also appear.

If the dimerization affects the intermolecular potential we must also expect a change in the transport properties. Here, however, we must be careful in drawing conclusions. The existence of an associated species in equilibrium with a monomer does not imply that at each intermolecular collision a reaction will take place. Indeed, in bimolecular reactions the probability of each collision being successful chemically has been known to vary from 1 to 10^{-8} depending on the system (Hin 51) so that it is possible that a modification of the intermolecular potential will act only in a small fraction of the molecular encounters and thus will make no noticeable contribution to the transport properties. It should be noted that the thermal conductivity can be very sensitive to association. The temperature gradient induces a corresponding concentration gradient and a convection process tending to transport the heat of the reaction will add to the heat of thermal motion carried by the molecules.

The thermodynamic properties of mixtures may also be expected to give evidence for complex formation. Association is a form of ordering and this must affect the entropy of the system, while the change in concentration of the associated species with temperature or dilution will also be represented by energy effects stemming from the heat of reaction and there will also be a change in the number of moles of the components in the system.

Finally, there are a number of miscellaneous measurements such as x-ray diffraction, which, under certain conditions, might be useful as proof of complex formation. During the course of the following discussion we will also make use of comparisons of oxygen with NO, nitric oxide. We do not claim that the hypothetical $(O_2)_2$ is related to $(NO)_2$, but the existence of the latter species has been proven beyond any doubt and it is instructive to see what effect this double molecule formation has on the physical properties of its mixtures with its monomer. The heat of formation of the nitric oxide complex is of the order of 4000 cal/mole so that it is a relatively stable species.

2. SPECTRA

The infrared spectra of liquid and gaseous oxygen show an absorption at 1550 cm^{-1} which cannot be attributed to a single oxygen molecule (Cra 49, Smi 50). However, a similar absorption at 2330 cm^{-1} has also been observed for nitrogen (Cra 49) and it appears that it can be accounted for by dipole transitions induced by intermolecular forces at collisions (Cho 56). Furthermore, Smith and Johnston (Smi 52) report that there is a shoulder at 1610 cm^{-1} which is also present in solid γ -oxygen, and which disappears on dilution with nitrogen. They are not certain if this is attributable to the dimer.

A study of the rotational wings of the Raman bands in liquid oxygen (Cra 52) has shown that their extent and the intensity distribution are in satisfactory agreement with the theoretical distribution, so that the rotation of the molecules is essentially free. The authors reason that if there were an oxygen dimer the intensity distribution in the vibrational band would not have been so close to the theoretical. Also, for a dimer there could be a splitting of the Q branch, but secondary components were not found.

For comparison, the infrared and Raman spectra for nitric oxide show large differences between the gas at room temperature which is monomeric and the liquid at the boiling point which is essentially pure dimer. There is a splitting of various bands and new frequencies are observed (Smi 51).

In a long series of articles beginning in 1955, Dianov-Klokov has carefully considered the absorption for oxygen between 12,600 and 3000 Å. Mixtures of oxygen with nitrogen (Dia 55,56a) and with argon and krypton (Dia 56b) were also investigated. In a discussion of the results (Dia 59) he points out that the transitions observed correspond to the series proposed by Ellis and Kneser in 1934. All the bands may be described in terms of five electronic-vibrational transitions, i.e. transitions induced by the interaction of two molecules in a complex. By making assumptions concerning the symmetry of the complex he is able to explain the intensities and their temperature variation. However, it is not possible to tell whether these interacting groups exist only at collisions or whether they have a long life. He is inclined to believe that they are merely 'statistical' complexes and the data is not adequate to assign them to an interaction with paired or unpaired electron spins. Beer's law is not followed by these bands but their variation with concentration is more complex than has been reported previously and there is no correlation with the square of the concentration as expected for a dimerization reaction.

It is typical of oxygen that the position and form of the ultraviolet and visible bands do not change very much from one phase to another. Thus, all of the visible and ultraviolet spectra found for the liquid have also been observed in the gas. In 1928 Wulf (Wul 28) calculated an equilibrium constant for the dimerization reaction from the density dependence of the ultraviolet spectra and he found a value of 1.2 g/cm^3 for K_p at room temperature, which is considerably less than that derived from the low-temperature susceptibility measurements. On the other hand, Steiner (Ste 33), on the basis of experiments at different densities and with the addition of a foreign gas, showed that the Ellis and Kneser explanation in terms of collision induced transitions

of the anomalous electronic spectra is probably correct. Further, he cautioned that it is dangerous to try to assign a one-to-one correspondence to spectral and magnetic effects for it cannot be shown that interactions which perturb spectral levels also cause corresponding changes in the magnetic properties, so that it is possible that not all collisions effective in a spectral sense will alter other properties.

In passing let us note that in the case of NO a strong continuous absorption below 2600 Å in both the liquid and the gas (Ber 47, Dor 51) has been demonstrated to be due to the double molecule.

In closing this section we point out that the only positive evidence for the existence of the oxygen dimer is the shoulder found in the infrared spectra. It is very unlikely that a double molecule would not lead to any change in the vibrational frequencies and tend to hinder the free rotation in the liquid. We also see that the explanation of the anomalous ultraviolet and visible spectra does not rest on the assumption that anything other than a short-lived complex exists.

3. MAGNETIC PROPERTIES

In the previous chapter we have thoroughly discussed the magnetic susceptibility of liquid oxygen and its mixtures and shown that the measurements can give no unequivocal proof of the existence of a dimer.

The susceptibility of the gas has been measured as a function of the temperature (Wie 31) and of the temperature and the density (Wol 29, Kan 39). At normal pressures Curie's law is followed to the boiling point but deviations similar to those for the pure liquid are found at very high densities. In a discussion of some of these results Wiersma and Gorter (Wie 32) have shown that an equilibrium constant of the Lewis type can be derived from them which is in excellent agreement with that calculated by Lewis.

Recently, Buckingham and Pople (Buc 56), in a discussion of the magnetic properties of dense gases, pointed out that three types of binary collisions are possible for oxygen molecules in a $^3\Sigma$ ground state. The spins of the individual molecules can interact to give a total spin for the collision pair of 0, 1 or 2 and these collisions have a priori weights of 1/9, 3/9 and 5/9. The authors show that it is possible to expand the magnetic susceptibility in a virial type of expansion in the density wherein the second virial coefficients for each of the different types of collision are multiplied by the net susceptibility change on collision and their statistical weights. The measured susceptibility is dependent on the signs and the sizes of these contributions and although with the present information it is not possible to quantitatively apply this treatment to the susceptibility of the dense gas, it can qualitatively explain the observed deviations from Curie's law. It

should be remarked, however, that only small differences between the three different virial coefficients (which could arise from differences in the depth of the potential well of about 2–3°K) are necessary to explain the observed deviations.

Results somewhat analogous to those for the susceptibility of the liquid oxygen mixtures have been found for both the Kerr (Gui 36a, 36b, 37) and the Faraday effects (Lai 33, 36). Again the effects are not directly proportional to the oxygen concentration in the mixtures, but the interpretation in terms of a dimer hypothesis is more difficult than that for the susceptibility because there can be a non-negligible contribution from the diamagnetic dimer. Guillien (Gui 37) assumed that the specific Kerr constant of oxygen in its mixtures was made up of a linear combination of the Kerr constants of the monomer and dimer. Using K_{ρ} , the equilibrium constant proposed by Lewis, he calculated the concentration of the single and the double species for two compositions of a nitrogen–oxygen mixture. Using these concentrations and the measured value of the Kerr constant at those compositions he evaluated the specific Kerr constants for the two types of molecules and then calculated the variation of the Kerr constant of the mixture with concentration, each time deriving the monomer–dimer ratio from the equilibrium constant. The theoretical curve so calculated fits the experimental curve only at the points where it has been fitted to the experiment and has the wrong curvature.

The thermal variation of the electro- and magneto-optical effects has also been studied for the pure liquid (Gui 37, Gau 52). It is anomalously high and unpredicted by the theory, which is a free molecule approach. No attempt has been made to explain these anomalies quantitatively in terms of $(O_2)_2$.

Serber, who has developed a molecular theory for the Faraday effect, pointed out that the magneto-optical rotation for oxygen gas was anomalous (Ser 32) and that this was probably due to the fact that the measurements were performed at high densities where a considerable amount of the dimer was certain to be present. More recently, however, low pressure measurements (Ing 56) have shown the same deviation and a more comprehensive theory has been developed (Hou 60) which successfully describes these results.

Like oxygen, gaseous NO obeys Curie's law at normal temperatures and densities. At lower temperatures, however, deviations have been observed (Wie 30) and are understandable because the $^2\pi$ splitting is of the order of kT (Vle 32). In the liquid the susceptibility is almost entirely quenched (Biz 37). The Faraday effect in the liquid is also anomalous (Biz 38).

Aside from the considerations in the previous chapter no further conclusions concerning $(O_2)_2$ can be drawn on the basis of the above-

mentioned work. Qualitatively it is perhaps possible to explain some of these anomalies on the basis of dimerization, but an exchange model might do just as well. Clarification of the optical effects must await a more comprehensive theory.

4. CORRESPONDING STATES CONSIDERATIONS

A number of attempts have been made to apply the law of corresponding states to liquids. In chapter III we have shown that while for some properties this gives rather good results, for others the deviations for even the noble gases may be large. However, a correlation by Staveley and Tupman (Sta 50) of the entropies of vaporization of a large number of liquids has shown that this is a rather good basis for discriminating between associated and non-associated liquids. They find that there is no abnormality in the entropy of vaporization as a function of the temperature since oxygen, chlorine, nitrogen and carbon monoxide all lie on the same line within 1%. Quantitatively this means that in the evaporation of a mole of oxygen (which if we believe the dimer hypothesis consists of 40% double molecules) to a gas which is monomeric, the contribution to the heat of vaporization at 90°K due to the breakup of $(O_2)_2$ cannot be greater than about 18 cal/mole of oxygen. Thus, the outer limit for the heat of the reaction including the effect of the ideality of the mixture is about 80 cal/mole of dimer, and considering the uncertainty in the law of corresponding states, this is not necessarily in disagreement with the existence of a dimer. It has been found that the deviations for NO are of the order of 30%.

In the case of two other properties of the liquid, the vapor pressure and the rectilinear diameter, Cook and Rowlinson (Coo 53) have shown that the deviations from the corresponding states ideal are consistent with departures from spherical symmetry of the intermolecular potential, which are to be expected for diatomic molecules. For gases, the law of corresponding states is helpful in analyzing equation of state data. The reduced equations of state of oxygen and nitrogen can be compared if they are plotted against the reduced density, and this is illustrated in fig. V.1 where PV/RT is given as a function of the logarithm of the Amagat density. Such a graph shows that the behavior of the two gases is the same and the agreement is good up to the critical density even if low temperature data are used (Kam 24a, 24b).

The theories for dense gases are not at present capable of describing the viscosity at high densities but several attempts have been made to do this with semi-empirical equations. Coremans (Cor 60) has shown in a corresponding states treatment that up to 49 atm the viscosity of oxygen can be represented by such an equation within 5%. High

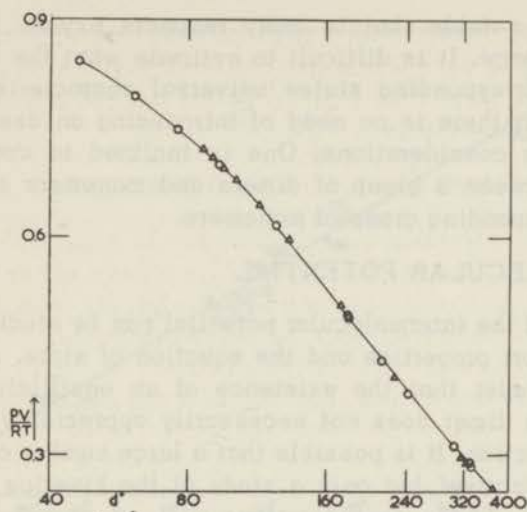


Fig. V.1 PV/RT vs. Reduced Density
Reduction by shifting the N_2 curve.

○ O_2 △ N_2

density measurements of the thermal conductivity have been made by Ziebland (Zie 59) on oxygen, argon and nitrogen and the reduced thermal conductivity is compatible with the law of corresponding states up to densities three times the critical density within the experimental error (see fig. IV.2).

Oxygen is markedly anomalous with respect to the triple point temperature and the heat of fusion. However, one must be careful in ascribing this to an ordering caused by dimerization, for in the case of NO, where the associating has been proven, there is no such effect.

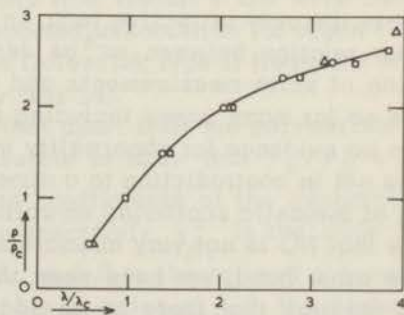


Fig. V.2

Reduced Thermal Conductivity vs.
Reduced Density
Reduction with critical parameters.
From (Zie 59).

△ O_2 ○ N_2 □ Ar

It is thus notable that in many respects oxygen behaves like a 'normal' substance. It is difficult to estimate what the departures from the various corresponding states universal characteristics should be but we see that there is no need of introducing an association on the basis of these considerations. One is inclined to conclude that the interaction between a group of dimers and monomers is equivalent to that of a corresponding group of monomers.

5. INTERMOLECULAR POTENTIAL

The form of the intermolecular potential can be studied by considering the transport properties and the equation of state. Again, we must caution the reader that the existence of an equilibrium between the monomer and a dimer does not necessarily appreciably affect the collision cross-section. It is possible that a large number of the collisions is chemically 'active', but only a study of the kinetics of the reaction can affirm this. These considerations will, of course, have a bearing on the validity of the conclusions to be drawn from negative results with respect to proof of the existence of a dimer.

Proof of the similarity between the oxygen, argon and nitrogen potentials is given by the excess second virial coefficients determined in chapter II. Such a small excess shows that the oxygen-nitrogen and oxygen-argon interactions are not much different from the interactions for the pure gases. Further proof that a Lennard-Jones type of potential is reasonable for oxygen can also be found in an analysis of viscosity measurements. Whalley and Schneider (Wha 52) have demonstrated that one set of potential parameters is sufficient to fit viscosity measurements on oxygen between 80 and 730°K, ruling out any temperature dependent terms of note in the potential.

The attractive term in the intermolecular potential caused by the dispersion forces can be linked to the polarizability, α , of the molecule. If this is the only attractive term, in a logarithmic plot there should be a linear relation between $\epsilon\sigma^6$ as derived from transport properties or equation of state measurements and α . Brandt (Bra 56) has shown that this is so for many gases including oxygen, as noted in fig. V.3. There is then no evidence for abnormality in the potential function for oxygen. This is not in contradiction to a dimer hypothesis as long as the contribution of inelastic scattering on collision is small. It is also interesting to note that NO is not very anomalous although the data are very scarce. On the other hand, we have seen that the antiferromagnetic exchange model requires that there be an additional attractive term in r^{-6} with an energy of interaction of about 5°K. This is less than 5% of the depth of the Lennard-Jones potential well and, as the potential parameters are not known with such accuracy, it would go unnoticed.

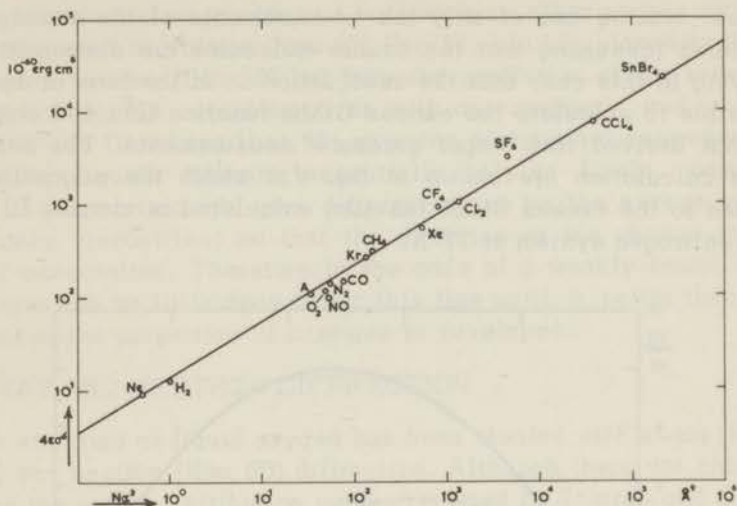


Fig. V.3 Na^3 vs. $4\epsilon^{06}$
From (Bra 56). The point for hydrogen was not in the original graph.

Finally, it is remarkable that the ϵ and σ values that one obtains from a corresponding states treatment of liquid and high density data are in very good agreement with those directly obtained from low density measurements.

6. EXCESS PROPERTIES OF MIXTURES

The excess properties of mixtures should be expected to reveal some evidence for association, as the dilution of oxygen must also break up complexes. As early as 1910, Dolezalek (Dol 10) attempted to explain the deviation from ideality of oxygen-nitrogen mixtures as being due to the formation of double molecules. However, he attempted to show that all positive deviations from Raoult's law were caused by polymerization, and so he also reported association for argon (Dol 19). In recent years a more generalized Dolezalek type of treatment has been developed by Prigogine and Defay (Pri 54).

Starting with the assumption that apart from the polymerization the mixture behaves ideally it is possible to show that $\gamma_A/\gamma_B = 1/x_{A_1}^0 \beta$, where γ_A and γ_B are the activity coefficients of the associating and the non-associating component, respectively, $x_{A_1}^0$ is the mole fraction of monomers in the pure liquid A, and β is the ratio of the number of moles of monomer to the total number of moles of A in the mixture. It is possible to determine β and $x_{A_1}^0$ from some physical property which varies directly with the concentration of monomer.

Thus, making use of only the measurements of the susceptibility of mixtures (assuming that the double molecules are diamagnetic) and specifying in this case that the association is in the form of dimers, it is possible to calculate the excess Gibbs function G^E , and compare it with that derived from vapor pressure measurements. The results of such a calculation are shown in fig. V.4 where the magnetic G^E is compared to the excess Gibbs function calculated in chapter III for the oxygen-nitrogen system at 77°K.

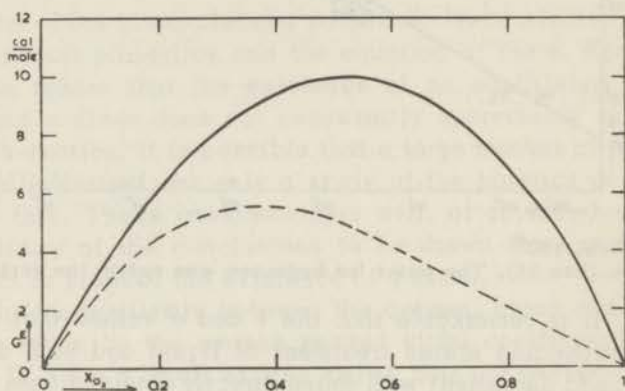


Fig. V.4 G^E from Vapor Pressure Data and from Magnetic Measurements for O_2-N_2 at 77°K
 Vapor pressure ————— Magnetic - - - - -

It can immediately be seen that the Gibbs function drawn from the vapor pressure measurements is considerably larger and more symmetric than the same function calculated from the magnetic data and, according to the theory, these differences must be attributed to non-ideality of the mixture of monomer, dimer and diluent, which is not in disagreement with the results for the dependence of K on concentration discussed in chapter IV. To explain the lack of congruity of the two curves on this basis we must assume that the portion of G^E which is not the result of association is asymmetric in a direction opposite to that of the excess Gibbs function calculated from the magnetic data. This is not too unreasonable, but we are also faced with the fact that similar systems studied in the same temperature range (e.g. $A-N_2$), which show no sign of association, also have thermodynamic excess properties of the same order of magnitude (Row 59). Hence, the oxygen mixtures are not abnormal in this respect and it is not necessary that a dimer hypothesis be relied upon for a clarification of the results of these studies.

The literature also provides us with work on other excess properties of mixtures, such as volume (Kna 61, Poo 57, Bla 58), viscosity (Gal 41) and surface tension (Bla 59) but here the prediction of the results for even normal liquids cannot be made with any certainty, and as shown by Lutskii and Obukhova (Lut 59) mixtures of a normal component with associating liquids differing essentially only in dipole moment and degree of association can give different signs for the excess volumes and excess viscosities, so that the direction of the change is not a proof of association. Therefore, in the case of a weakly bound oxygen dimer there can be little done along this line until a better theoretical treatment of the properties of mixtures is developed.

7. X-RAY AND NEUTRON DIFFRACTION

The structure of liquid oxygen has been studied with x-ray (Kee 37, Sha 42) and neutron (Hen 60) diffraction. Although there are characteristics in the radial distribution curves reported by Sharrah and Gingrich and by Henshaw which might have some connection with a dimer, both studies suffer from diffraction effects caused most probably because data was not taken to sufficiently high angles (Kan 51) and a ghost peak at 2.2 \AA was found in both investigations. Further, Borgen and Finbak (Bor 54) have shown that in the x-ray study there is a periodicity in the published atomic distribution curve which makes it suspect as a large diffraction ripple. They show that if this is true a maximum should also be found at 0.24 \AA and starting with the published intensity curve they have found a peak between 0.2 and 0.3 \AA .

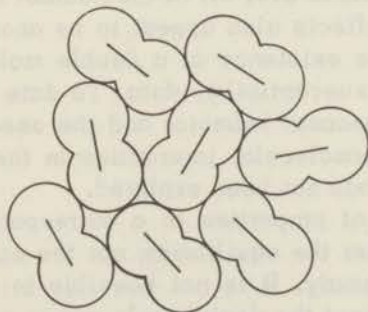


Fig. V.5 Proposed Packing of Oxygen Molecules in the Liquid From (Bor 54).

From the electronic distribution curve alone it appears that the structure of the liquid can be represented by a packing of spheres, for maxima are found at 1.23 , between 3.8 and 4.5 (broad peak) and at 6.9 \AA^{-1} (see fig. V.5) thus ruling out a specific $\text{O}_2\text{-O}_2$ distance characteristic

of a dimer. The similarity between the neutron diffraction data and the x-ray work makes it also suspect of similar diffraction effects and it is thus difficult to make use of these results in support of any dimer hypothesis.

8. PROPERTIES OF THE SOLID

Solid oxygen will not be considered here in detail. A discussion of its properties is complicated by the existence of three phases, the crystal structures of which have not been unambiguously determined. Studies with x-ray diffraction indicate the possibility of a pairing of oxygen molecules in γ -oxygen (Veg 35, Kee 36) but if any bond exists it must be very weak because the molecules are said to rotate freely and independently. As has been pointed out in the previous chapter evidence for a Néel point at 44°K is in support of an antiferromagnetic treatment.

9. CONCLUSIONS

Let us review the results of this survey. The magnetic susceptibility measurements on liquid oxygen are the source of the speculation about the existence of $(O_2)_2$; yet, as we have seen, although the measurements are not inconsistent with this model, a chemical equilibrium is not necessary for an understanding of the results. We should note that the essential difference between antiferromagnetic exchange and dimerization is that in the latter hypothesis the interaction must be specifically two-molecule, while the magnetic exchange is made up of the sum of interactions over all of the nearest neighbors.

Other magnetic effects also appear to be anomalous, but the use of them as proof for the existence of a double molecule has rested only on analogy with the susceptibility data. To date no real link has been made between the abnormal behavior and the association, and the consequences of an intermolecular interaction in the case of the Faraday and the Kerr effects has not been explored.

The comparison of properties in a corresponding states treatment has shown that neither the equilibrium nor the non-equilibrium properties display any anomaly. It is not possible to evaluate the worth of this as evidence against the double molecule in a quantitative way, but these results indicate that if such a species exists the combination dimer-monomer must be very nearly equivalent to the interaction of three monomers. Conclusions based on the form of the intermolecular potential are subject to the qualification mentioned concerning the probability of the reaction with collision. We must, however, accept the fact that the form of the potential seems to be very well established and

that it is not dissimilar to that of non-associating gases.

Spectral studies have yielded important results. The total absence of changes in the infrared and Raman spectra is entirely inconsistent with the postulate of a dimer. The anomalous electronic spectra do not require the existence of a stable species for their clarification.

Summing up, there has been no direct experimental evidence for the existence of $(O_2)_2$. Further, effects attributed to this species are also explainable in terms of normal interactions observed in many other systems. Thus, we are led to the conclusion that the hypothesis is not at all plausible and unless its existence be proved on the basis of a direct experiment such as the determination of the collision cross-sections of oxygen at low temperatures with a molecular beam, we must look to a detailed analysis of magnetic exchange for the delineation of the character of oxygen.

The first of these is the fact that the...
 The second is the fact that the...
 The third is the fact that the...
 The fourth is the fact that the...
 The fifth is the fact that the...
 The sixth is the fact that the...
 The seventh is the fact that the...
 The eighth is the fact that the...
 The ninth is the fact that the...
 The tenth is the fact that the...

CONCLUSION

In conclusion, it is clear that the...
 The first point to note is that...
 The second point to note is that...
 The third point to note is that...
 The fourth point to note is that...
 The fifth point to note is that...
 The sixth point to note is that...
 The seventh point to note is that...
 The eighth point to note is that...
 The ninth point to note is that...
 The tenth point to note is that...

It is therefore clear that the...
 The first of these is the fact that...
 The second is the fact that...
 The third is the fact that...
 The fourth is the fact that...
 The fifth is the fact that...
 The sixth is the fact that...
 The seventh is the fact that...
 The eighth is the fact that...
 The ninth is the fact that...
 The tenth is the fact that...

The final point to note is that...
 The first of these is the fact that...
 The second is the fact that...
 The third is the fact that...
 The fourth is the fact that...
 The fifth is the fact that...
 The sixth is the fact that...
 The seventh is the fact that...
 The eighth is the fact that...
 The ninth is the fact that...
 The tenth is the fact that...

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SAMENVATTING

In dit proefschrift worden twee soorten experimenten beschreven, die tot doel hebben nadere gegevens te verkrijgen omtrent de bestaansmogelijkheid van een dimeer van het zuurstof molecuul, $(O_2)_2$. Het eerste hoofdstuk geeft een overzicht van de historische achtergrond van de dimeer hypothese. Metingen van de magnetische susceptibiliteit van vloeibare zuurstof-stikstof mengsels hebben voor de eerste maal aanwijzingen voor deze hypothese gegeven. Het tweede hoofdstuk, waarin metingen van de exces tweede viriaal coëfficiënt van gasmengsels bij $90^\circ K$ besproken worden, dient als inleiding tot het derde hoofdstuk, waarin de thermodynamische eigenschappen van vloeibare mengsels van zuurstof met argon en stikstof worden beschreven. Met een calorimeter zijn mengwarmte metingen aan deze mengsels uitgevoerd. Uit de kook- en dauwpunts-bepalingen zijn de exces chemische potentialen voor deze mengsels berekend en vervolgens zijn met behulp van de mengwarmte de exces entropiën bepaald.

In het vierde hoofdstuk worden de magnetische eigenschappen besproken. Door middel van een inductie methode zijn magnetische susceptibiliteitsmetingen uitgevoerd van vloeibaar zuurstof en vloeibaar zuurstof-argon en zuurstof-stikstof mengsels. De resultaten worden besproken in verband met een antiferromagnetisch model en met de dimeer hypothese. In het vijfde hoofdstuk wordt een overzicht gegeven van metingen van andere fysische grootheden. Geconcludeerd wordt, dat beschrijving met behulp van magnetische wisselwerking de voorkeur verdient boven de dimeer hypothese.

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