magnetic substances, is readily related to the Heisenberg exchange integral, it may be possible to evaluate the variation of the integral with interionic distance when crystal structure data on the various gadolinium compounds are available. As in the case of neodymium the fairly large variation in Curie constant from one compound to another remains unexplained.

Summary

The magnetic susceptibilities of Eu_2O_3, $Eu_2(SO_4)_3 \cdot 8H_2O$, $EuSO_4$, Gd_2O_3, $GdCl_3$, and $Gd_2(SO_4)_3 \cdot 8H_2O$ have been measured from −190 to 70 or 100°. The effective Bohr magneton numbers for europium are in good agreement with quantum mechanical predictions. The susceptibility and electronic configurations of Eu^{++} are the same as those of Gd^{+++}. The Heisenberg exchange interaction forces for the gadolinium compounds are shown to be proportional to the magnetic concentration as in the case of neodymium.

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The Heat Capacity and Entropy of Nitrogen. Heat of Vaporization. Vapor Pressures of Solid and Liquid. The Reaction $^1/_2\ N_2 + {^1/_2}\ O_2 = NO$ from Spectroscopic Data

BY W. F. GIAUQUE AND J. O. CLAYTON[1]

Besides being one of the more important elements nitrogen is interesting as a light molecule possessing two non-combining forms comprised of the alternate rotation states. Thus one of the principal reasons for the present investigation is to decide whether the lack of equilibrium between the two forms persists into the solid state in some manner similar to that existing in solid hydrogen. It will be shown later that like iodine[1a] and unlike hydrogen, the type consisting of the odd rotational levels of the normal electronic state loses, in solid nitrogen, the rotational *a priori* weight of three associated with the lowest state in the gas. The three states are replaced by one and that, presumably, is a vibrational rather than a rotational state. This corresponds to the expectation of Pauling.[2]

The present work on nitrogen also includes a calculation of its free energy from band spectra.

Preparation of Nitrogen.—The nitrogen was prepared by passing gaseous ammonia into bromine water: $8NH_3 + 3Br_2 = 6NH_4Br + N_2$. About twenty-five or thirty moles of bromine was used for each preparation. In the first experiment ammonium bromide was used to increase the solubility at the start. However, the ammonium

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[1] Shell Research Fellow, Academic year 1929-1930.

[1a] Giauque, THIS JOURNAL, **53**, 507 (1931).

[2] Pauling, *Phys. Rev.*, **36**, 430 (1930).

bromide formed during reaction precipitated and increased the difficulty of dissolving the bromine from the layer on the bottom. Later a water solution of bromine was used at the start to minimize this difficulty. The reaction vessel was cooled with ice to prevent the heat of reaction from raising the vapor pressure of the bromine to an undesirable extent. The gas evolved usually contained excess bromine. Most of this was returned to the reaction flask by means of an ice jacketed condenser. The gas was passed through a train containing solid potassium hydroxide (sticks), anhydrous copper sulfate, a 50% solution of potassium hydroxide, concentrated sulfuric acid, solid potassium hydroxide (sticks) and phosphorus pentoxide. The anhydrous copper sulfate was used to absorb ammonia and indicate when ammonia was coming through the system due to depletion of bromine in the water layer.

All solutions were boiled under vacuum and the train was evacuated. This method precluded the presence of oxygen, which would have been difficult to remove. The nitrogen was distilled three times, a small first fraction and the last quarter being discarded each time. The very small first fraction was all that was considered necessary to discard as there were no possible impurities more volatile than nitrogen.

Heat Capacity Measurements and Data.—The apparatus, known as Gold Calorimeter II, and the method have been described previously.[3] Three preparations were used for the measurements. The amounts were measured volumetrically as previously described.[3b] In this connection the following constants were used in the equation.

Number of moles $= V \times P \times (D/M) \times 1/(1 + KT)\,[1 + \alpha(1 - P)]$
Gas density at 0° and 760 mm. $D = 1.25057$ g./l.[4,5,6a,b,7]
Molecular weight $M = 28.016$
Coefficient of thermal expansion $K = 0.0036777$[8,9a,b]
Coefficient of deviation from Boyle's law $\alpha = -0.00047$[10]
Gravitational acceleration (for Berkeley)[11] $= 979.973$ cm./sec.^{2}

The latter value was used to convert pressure measurements to the international scale. In correcting for the heat effect due to evaporation into the small gas volume above the liquid or solid nitrogen during a temperature rise, the density of the condensed material was necessary.

For liquid nitrogen Baly and Donnan[12] give $d = 1.1604 - 0.00455\,T$.

For solid nitrogen Dewar[13] gives 1.0265 at 20.6°K. and 0.8792 g./cc. at 63°K.

The volume of the gold calorimeter was 112.8 cc. at 20°.

The calorimetric data are given in Table I and are shown graphically in

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(3) (a) Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928); (b) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

(4) Gray, *J. Chem. Soc.*, **87**, 1601 (1905).

(5) Moles, *J. chim. phys.*, **19**, 283 (1921).

(6a) Moles and Clavera, *Añales soc. españ. fis. quim.*, **20**, 550 (1922).

(6b) Moles and Clavera, *J. chim. phys.*, **21**, 10 (1924).

(7) Baxter and Starkweather, *Proc. Am. Acad. Arts Sci.*, **12**, 703 (1926).

(8) Chappuis, *Trav. et Mem. bur. intern. des poids et measures*, 13 (1907).

(9a) Holborn and Otto, *Z. Physik*, **23**, 77 (1924).

(9b) Holborn and Otto, *ibid.*, **30**, 320 (1924).

(10) "International Critical Tables."

(11) Sternewarte, Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Berlin, **1923**.

(12) Baly and Donnan, *J. Chem. Soc.*, **81**, 907 (1902).

(13) Dewar, *Proc. Roy. Soc.* (London), **A73**, 251 (1904).

TABLE I

HEAT CAPACITY OF NITROGEN

Molecular weight, 28.016. Series I, 2.7338 moles; Series II, 2.5855 moles; Series III, 2.5558 moles.

T, °K. mean	ΔT	C_p Cal. per degree per mole	Series	T, °K. mean	ΔT	C_p Cal. per degree per mole	Series
15.82	1.520	3.124	III	43.27	3.797	9.325	II
17.66	1.632	3.840	III	48.07	3.703	9.752	II
19.51	1.722	4.577	III	51.88	3.681	10.09	II
21.94	1.943	5.447	III	53.55	4.345	10.26	III
24.49	2.716	6.331	II	55.88	3.967	10.44	II
24.85	3.597	6.380	III	57.99	4.400	10.65	III
27.14	2.330	7.170	II	61.40	2.341	11.09	I
28.32	3.139	7.540	III	61.41	2.229	11.07	III
29.89	2.722	8.137	II	63.14	Melting Point		
31.29	2.656	8.643	III	65.02	2.184	13.33	I
32.84	1.929	9.397	III	68.41	4.455	13.45	I
34.42	0.185	10.28	III	70.28	4.149	13.45	I
34.68	.487	10.49	III	72.69	3.880	13.56	I
35.05	.315	10.84	III	74.57	4.228	13.59	I
35.33	.389	10.67	III	76.58	3.715	13.68	I
35.61	Transition			77.74	1.858	13.64	I
39.13	3.821	8.948	II				

Fig. 1. In calculating the energy one international joule was taken as 1.0004 absolute joules and 1 calorie (15°) was taken as 4.185 absolute joules.

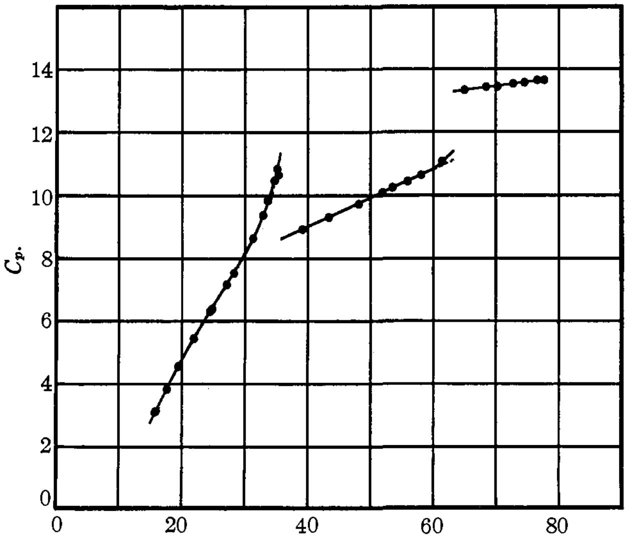

Fig. 1.—Heat capacity in calories per degree per mole of nitrogen.

Assuming that the slight rise in heat capacity below the melting point is due to premelting caused by impurity, it is computed that such impurity is not over three thousandths of one mole per cent. However, it is possible that even this small rise is characteristic of the pure substance.

The heat capacity of nitrogen has been measured by Eucken,[14] by Clusius[15] and by Wiebe and Brevoort.[16] The results of Clusius agree fairly well with those of the present investigation; the maximum deviation in the solid range is 4%. In the liquid range his measurements are consistently higher by 1.5%. The average deviation of Clusius' results from the above work is about 2%; the average algebraic deviation is 0.8%. The earlier work of Eucken agrees almost as well as that of Clusius. The results on the liquid are consistently 1.5% lower than the present work. The work of Wiebe and Brevoort covered only the liquid range at high pressures; the results of their work and the present work are in very satisfactory agreement in the neighborhood of the boiling point.

Transition and Melting Point Temperatures.—The transition and melting point temperatures were observed with various percentages transformed. All of the measurements were obtained on the material used in Series II. The transition temperature was observed over a period of fifteen hours. The melting point was observed on four occasions designated a, b, c and d, over periods of nineteen, thirty-five, eight and twelve hours, respectively. The data are given in Table II.

TABLE II

TRANSITION AND MELTING POINT TEMPERATURES OF NITROGEN

Transition temperature			Melting point		
Per cent. transformed	T, °K.	Series	Per cent. transformed	T, °K.	Series
25	35.59	II	50	63.12	IIb
25	35.59	II	50	63.12	IIb
70	35.63	II	60	63.12	IIb
70	35.64	II	75	63.10	IIb
Average	35.61 ± 0.05		10	63.14	IIc
			10	63.14	IIc
	Melting point		20	63.14	IIc
5	63.13	IIa	20	63.14	IIc
5	63.13	IIa	30	63.14	IIc
45	63.13	IIa	40	63.14	IIc
5	63.12	IIb	50	63.13	IIc
5	63.12	IIb	70	63.13	IId
			Average (c, d)	63.14 ± 0.05	

The conditions for measuring the melting point were not as satisfactory in Series a and b as in c and d, so that only the latter two were used in computing the final value 63.14. The experiments of series c were used for the triple point pressure measurements given in Table V. In Table III the data of previous observers have been collected.

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(14) Eucken, *Ber. deut. physik. Ges.*, **18**, 4 (1916).

(15) Clusius, *Z. physik. Chem.*, **B3**, 41 (1929).

(16) Wiebe and Brevoort, THIS JOURNAL, **52**, 622 (1930).

TABLE III

SUMMARY OF AVAILABLE TRANSITION AND MELTING POINT TEMPERATURE DATA FOR NITROGEN

T, °K.		T, °K.	
	Transition temperature	62.6	(1904) Dewar[13]
35.5	(1916) Eucken[14]	62	(1906) Erdmann[20]
35.4	(1919) Clusius[15]	63.17	(1913) Von Siemens[21]
35.61	This research	63.24	(1915) Crommelin[22]
		63.1	(1916) Eucken[14]
	Melting point	63.12	(1927) Henning[23]
70–74	(1886) von Wroblewsky[17]	63.08	(1929) Clusius[15]
59	(1887) Olszewsky[18]	63.14	(1931) Verschoyle[24]
62.58	(1902) Fischer and Alt[19]	63.14	This research

Heats of Transition and Fusion.—The heats of transition and fusion were measured in the usual manner, starting the energy input a little below the transition or melting temperature and ending a little above. A correction for $\int C_p\, dT$ was made. The results are given in Table IV, which also includes the values given by other observers.

TABLE IV

HEATS OF TRANSITION AND FUSION OF NITROGEN

Molecular weight 28.016

ΔH Transition, calories per mole		ΔH Fusion	
54.79	Series II	172.7	Series II
54.63	Series III	172.4	Series III
54.71 ± 0.1	Average this research	171.9	Series I
53.8	(1916) Eucken[14]	172.3 ± 0.5	Average this research
51.4	(1929) Clusius[15]	168.7	(1916) Eucken[14]
		170.95	(1929) Clusius[15]

Vapor Pressures of Solid and Liquid Nitrogen.—Vapor pressures were measured on the same material used in the calorimetric measurements of Series II. The apparatus and method were approximately the same as previously described by Giauque, Johnston and Kelley.[25] A large diameter manometer was compared with a standard meter by means of a Gaertner cathetometer with an accuracy of 0.05 mm. of mercury. Correction was made for meniscus height.

The results have been represented by equations 1 and 2.

Solid nitrogen 54.78 to 63.14°K.

$$\log P\ (\text{cm.}) = (-381.6/T) + 7.41105 - 0.0062372\ T \qquad (1)$$

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(17) Von Wroblewsky, *Compt. rend.*, **102**, 1010 (1886).

(18) Olszewsky, *Wied. Ann. Physik*, **31**, 66 (1887).

(19) Fischer and Alt, *ibid.*, [4] **9**, 1149 (1903).

(20) Erdmann, *Ber.*, **39**, 1207 (1906).

(21) Von Siemens, *Ann. Physik*, [4] **42**, 871 (1913).

(22) Crommelin, *Proc. Roy. Acad. Amsterdam*, **17**, 959 (1915).

(23) Henning, *Z. Physik*, **40**, 775 (1927).

(24) Verschoyle, *Proc. Roy. Soc.* (London), **A230**, 189 (1931).

(25) Giauque, Johnston and Kelley, THIS JOURNAL, **49**, 2367 (1927).

Liquid nitrogen 63.14 to 78.01°K.

$$\log P\ (\text{cm.}) = (-339.8/T) + 6.71057 - 0.0056286\,T \qquad (2)$$

The observed and calculated values are given in Table V. The values are given to 0.001° because of the high relative consistency.

TABLE V

VAPOR PRESSURE OF NITROGEN

T, °K. observed	P int. cm. observed	ΔP obs. − calcd.	ΔT obs. − calcd.	Remarks
54.783	1.273	0.003	−0.009	Solid
55.875	1.710	.000	.000	Solid
56.930	2.244	− .010	.017	Solid
57.850	2.840	− .004	.006	Solid
58.741	3.526	− .009	.011	Solid
59.550	4.285	.004	− .004	Solid
60.670	5.526	− .006	.005	Solid
61.700	6.958	.017	− .011	Solid
63.136	9.396			Melting point
	9.400			Melting point
	9.401			Melting point
	9.405			Melting point
	9.397			Melting point
	9.406			Melting point
	9.401			Melting point
Average	9.401 ± 0.005	0.000	0.000	Melting point
64.555	12.105	− .015	.007	Liquid
65.968	15.446	.019	− .007	Liquid
67.367	19.391	.010	− .003	Liquid
68.799	24.255	.027	− .007	Liquid
70.356	30.565	.027	− .006	Liquid
71.947	38.244	− .011	.002	Liquid
73.422	46.673	− .022	.004	Liquid
75.035	57.474	− .028	.004	Liquid
76.528	69.125	+ .002	− .000	Liquid
78.008	82.323	− .002	.000	Liquid

The vapor pressures of the solid have been measured by Olszewsky[26] (at the melting point only), and by von Siemens.[21] The results of von Siemens agree quite well with this work, the greatest deviation being about 0.1°K. Verschoyle[24] has recently measured the triple point pressure. He obtained 9.360 cm. as compared with our value 9.401 cm. Holst's[27] recalculation of von Siemens' results leads to 9.35 cm.

The vapor pressure of liquid nitrogen has been measured by von Wroblewsky,[17] Olszewsky,[26] Baly,[28] Fischer and Alt,[19] Holst and Hamburger,[29] Henning and Heuse,[30] von Siemens[21] and by Cath.[31] Aside

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(26) Olszewsky, *Compt. rend.*, **99**, 133 (1884).

(27) Holst, *Comm. Phys. Lab. Leiden* No. 148a (1915).

(28) Baly, *Phil. Mag.*, **49**, 517 (1900).

(29) Holst and Hamburger, *Z. physik. Chem.*, **91**, 513 (1916).

(30) Henning and Heuse, *Z. Physik*, **23**, 105 (1924).

(31) Cath, *Comm. Phys. Lab. Leiden*, No. 152d (1918).

from the pioneer work of Olszewsky and von Wroblewsky, most of these data agree fairly well with the present work. The nitrogen used by Fischer and Alt was impure, melting over a pressure range of from 8.64 to 9.40 cm. The following table gives the approximate average deviations of the above observers from the present work.

Baly	+0.2°	Von Siemens (converted to Leiden temp. scale)	+ 0.05°
Holst and Hamburger	− .07°	Cath	− .03°
Henning and Heuse	− .07°		
Von Siemens	− .03°		

The Boiling Point of Nitrogen.—From Equation 1 the boiling point was found to be 77.32°K. The values of other observers are given in Table VI.

TABLE VI

BOILING POINT OF NITROGEN

T, °K.	Observer	T, °K.	Observer
78.6	(1884) Olszewsky[26]	77.32	(1922) Kamerlingh Onnes[33]
80	(1886) von Wroblewsky[17]	77.35	(1924) Henning and Heuse[30]
77.54	(1900) Baly[28]	77.32	(1924) Mathias and Crommelin[34]
77.46	(1902) Fischer and Alt[19]	77.30	(1927) Dodge and Davis[35]
77.75	(1906) Stock and Nielson[32]	77.39	(1927) Henning[23]
77.30	(1918) Cath[31]	77.32	This research

Heat of Vaporization of Nitrogen.—The heat of vaporization was measured directly. The method has been described previously.[3a,b] The

TABLE VII

HEAT OF VAPORIZATION OF NITROGEN

Molecular weight 28.016

ΔH at 760 mm. cal. per mole	Moles N_2 evaporated	Time in minutes	Remarks
1332.4	0.21146	32	Series III
1331.8	.20607	31	Series III
1333.8	.18755	31	Series I
1333.7	.19166	32	Series I
1332.9 ± 1.0	Average this research		
1325.6	Vapor pressure data, using Berthelot's equation to correct for gas imperfection.		
1396	(1903) Shearer[36]		
1411	(1906) Dewar[37]		
1335	(1906) Alt[38]		
1363	(1916) Eucken[14]		
1402	(1922) Hammick[39]		
1337	(1925) Dana[40]		

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(32) Stock and Nielson, *Ber.*, **39**, 2066 (1906).

(33) Kamerlingh Onnes, *Comm. Phys. Lab. Leiden*, No. 156a (1922).

(34) Mathias and Crommelin, *Proc. Intern. Cong. Refrig.*, **41**, 89 (1924).

(35) Dodge and Davis, THIS JOURNAL, **49**, 610 (1927).

(36) Shearer, *Phys. Rev.*, [1] **17**, 469 (1903).

(37) Dewar, *Proc. Roy. Soc.* (London), **76A**, 325 (1906).

(38) Alt, *Ann. Physik*, **19**, 739 (1906).

(39) Hammick, *Phil. Mag.*, **44**, 509 (1922).

(40) Dana, *Proc. Am. Acad. Arts. Sci.*, **160**, 241 (1925).

results including a value calculated from our vapor pressure measurements are given in Table VII. The results of other observers are included.

The value obtained from the vapor pressure data is given no weight as compared to the direct determination.

The Entropy of Nitrogen.—A summary of the entropy calculation is given in Table VIII.

TABLE VIII

CALCULATION OF ENTROPY OF NITROGEN

0–10°K. Debye function ($h\nu/k$) = 68	0.458 E. U.
10–35.61°K., graphical	6.034
Transition 54.71/35.61	1.536
35.61–63.14°K., graphical	5.589
Fusion 172.3/63.14	2.729
63.14—Boiling point, graphical	2.728
Vaporization 1332.9/77.32	17.239
	36.31 ± 0.1 E. U.
Correction for gas imperfection assuming Berthelot gas	0.22
Entropy of ideal gas at boiling point	36.53 E. U.

The 0.22 E. U. correction for gas imperfection at the boiling point was obtained by combining Berthelot's equation of state with the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$. This leads to the correction $\Delta S = R(27T_c^3P/32T^3P_c)$. The critical temperature and pressure were taken as $T_c = 126.0$°K., and $P_c = 33.5$ atm.[41,42]

The above correction is not as certain as might be desired, but the good agreement obtained between the indirect and direct heats of vaporization supports the use of Berthelot's equation.

The entropy for the ideal gas state may be compared with the value calculated from band spectra data.

$$S = \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - R\ln P - \frac{5}{2}R - 7.267 + R\ln Q + RT\frac{\mathrm{d}\ln Q}{\mathrm{d}T} \qquad (3)$$

$$Q = \Sigma p e^{-\epsilon/kT}$$

$$\epsilon_{\text{rotation}} = \left[B_e + \alpha\left(v + \frac{1}{2}\right)\right]m^2 + \left[D_e + \beta\left(v + \frac{1}{2}\right)\right]m^4$$

$$\epsilon_{\text{vibration}} = \omega_e\left(v + \frac{1}{2}\right) + \omega_e\chi_e\left(v + \frac{1}{2}\right)^2$$

The Raman spectrum data of Rasetti[43] give $B_e = 2.003$, $\alpha = -0.023$ (estimated by analogy with carbon monoxide and the relationship $\chi_e B_e/\alpha$ = const. due to Birge), $D_e = -5.773 \times 10^{-6}$ and $\beta = 8.61 \times 10^{-8}$. For the vibration constants Birge and Hopfield[44] give $\omega_e = 2359.61$ and $\omega_e\chi_e = -14.445$. All of the above constants have been converted to the conven-

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(41) Kamerlingh Onnes, Dorsmann and Holst, *Comm. Phys. Lab. Leiden*, **145b** (1914).

(42) Pickering (Review), *Sci. Papers Bureau Stand.*, **21**, 608 (1926).

(43) Rasetti, *Phys. Rev.*, **34**, 367 (1929).

(44) Birge and Hopfield, *ibid.*, **29**, 212 (1927).

tional system which refers the molecular constants to the hypothetical state of zero vibration. To save labor in summing the rotational Boltzmann factors we have made use of the expression

$$Q = e^{hc(B/4)+(D/16)/kT}\left(\frac{kT}{hc}\right)\left[1+\frac{1}{12}\left(\frac{hc}{kT}\right)-\frac{2D}{B^2}\left(\frac{kT}{hc}\right)+\frac{12D^2}{B^4}\left(\frac{kT}{hc}\right)^2+\dots\right] \qquad (4)^{45}$$

and its derivative in evaluating the entropy. The results are given in Table IX. The Q given by Equation 4 has been reduced to one-half its value because of the molecular symmetry of nitrogen and the effect of nuclear spin has been eliminated.

TABLE IX

COMPARISON OF CALORIMETRIC AND SPECTROSCOPIC ENTROPIES OF NITROGEN

		Calorimetric	
T, °K.	Spectroscopic	Actual gas	Corrected to ideal state
77.32	36.416	36.3 ± 0.1	36.5 E. U.
298.1	45.788	....	45.9

The "calorimetric" value at 298.1°K. was obtained by adding the spectroscopic increase to 36.5.

The agreement is very satisfactory and since the effect of nuclear spin has been neglected in the calculation, it indicates that the limiting high temperature nuclear spin entropy remains in the solid state below the temperatures of liquid hydrogen.

It also indicates that nitrogen is not rotating in the solid state in a manner similar to hydrogen. This is important since it supports the suggestion[46] that no substances, with the possible exception of some containing symmetrically located hydrogen atoms in the molecule, will possess entropy due to the effect of rotation in the solid state below the temperatures of liquid helium, thus complicating extrapolation. Absence of this rotation is assumed in the ordinary application of the third law.

Had nitrogen rotated in a manner similar to hydrogen the calorimetric entropy would have been decreased by $(1/3)R \ln 3 = 0.73$ E. U. This is computed as follows: the nuclear spin of the nitrogen atom is 1 Bohr unit of angular momentum. This leads to the spin statistical weights 6 and 3 for the even and odd rotational levels of the normal electronic state. Thus in the gas at extremely low temperatures three-ninths of the molecules would be unable to lose the rotational statistical weight associated with the state $j_{(\text{rot.})} = 1$, thus leading to a zero point entropy of $(1/3)R \ln 3$. However, the experimental data show that the rotational weight of three has been lost in the solid state.

It is equally interesting that the lack of equilibrium between the two non-combining states of nitrogen is not altered by the solid. This is

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(45) Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

(46) Giauque, *ibid.*, **52**, 4816 (1930).

evident since, as mentioned above, the high temperature limiting spin entropy remains at low temperatures.

If all of the nitrogen molecules were changed to the form of lowest energy the entropy caused by nuclear spin would be $R \ln 6$, whereas the experimental facts correspond to $(6/9)\ R \ln 9 + (3/9)\ R \ln 9 = R \ln 9$, indicating the presence of the high temperature proportions of the two forms.

The Free Energy of Nitrogen.—From the band spectra data given above and the equation

$$\frac{F^\circ - E_0^\circ}{T} = -\frac{3}{2} R \ln M - \frac{5}{2} R \ln T + R \ln P + 7.267 - R \ln Q^{47}$$

the values of $(F^\circ - E_0^\circ)/T$ have been calculated and are given in Table X.

The values given in heavy type have been directly calculated. The others have been interpolated with a difference plot constructed by means

TABLE X

$-(F^\circ - E_0^\circ)/T$ FOR N_2 AND N

T, °K.	N_2	N	T, °K.	N_2	N
298.1	**38.834**	**31.655**	2200	53.239	**41.583**
300	**38.876**	**31.686**	2300	53.587	**41.804**
350	39.949	**32.452**	2400	53.922	**42.015**
400	**40.877**	**33.115**	2500	**54.246**	**42.219**
450	41.697	**33.700**	2600	54.558	**42.414**
500	**42.431**	**34.224**	2700	54.859	**42.601**
550	43.096	**34.697**	2800	55.150	**42.782**
600	43.705	**35.129**	2900	55.432	**42.957**
650	44.265	**35.527**	3000	**55.706**	**43.125**
700	44.786	**35.895**	3100	55.970	43.287
750	**45.272**	**36.238**	3200	56.228	43.445
800	45.729	**36.558**	3300	56.479	43.599
850	46.158	**36.859**	3400	56.723	43.747
900	46.566	**37.143**	3500	**56.960**	43.891
950	46.953	**37.412**	3600	57.191	44.032
1000	**47.322**	**37.667**	3700	57.417	44.168
1050	47.674	**37.909**	3800	57.637	44.302
1100	48.011	**38.140**	3900	57.852	44.432
1150	48.335	**38.361**	4000	**58.062**	**44.559**
1200	48.646	**38.572**	4100	58.267	44.682
1250	48.947	**38.775**	4200	58.468	44.803
1300	49.235	**38.970**	4300	58.664	44.921
1400	49.785	**39.338**	4400	58.855	45.036
1500	**50.301**	**39.681**	4500	**59.044**	**45.150**
1600	50.787	**40.001**	4600	59.228	45.261
1700	51.247	**40.303**	4700	59.409	45.369
1800	51.684	**40.586**	4800	59.586	45.475
1900	52.100	**40.855**	4900	59.760	45.580
2000	**52.497**	**41.110**	5000	**59.929**	**45.682**
2100	52.875	**41.352**			

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(47) Giauque, THIS JOURNAL, **52**, 4808 (1930).

of comparison with the function for a rigid rotator and the harmonic oscillator. This method is so accurate that the interpolated values have about the same accuracy as the directly calculated ones.

The $(F^\circ - E_0^\circ)T$ for atomic nitrogen has also been included in Table X. The values below 3000°K. are taken from tables of this function for the elements in course of preparation by Roy Overstreet and one of us. Only the normal electronic ^4S state and to a small extent the ^2D levels at 19202 cm.$^{-1}$ and ^2P levels at 28808 cm.$^{-1}$ [48] are occupied below 5000°K.

The Dissociation of Nitrogen.—The heat of dissociation of the nitrogen molecule is known only very roughly. However, accepting the value 7.90 volts = 182,000 calories per mole[49] we may make a provisional calculation of the dissociation constant. When a more reliable value of ΔE_0° becomes available, it may very easily be combined with the values of $\Delta[(F^\circ - E_0^\circ)/T]$ for $N_2 = 2N$ which are given in Table XII.

$$\frac{\Delta F^\circ}{T} = -R \ln K = \Delta\left(\frac{F^\circ - E_0^\circ}{T}\right) + \frac{\Delta E_0^\circ}{T}$$

A few values of K based on the above value of ΔE° are also given in Table XII.

The Reaction $^1/_2\ N_2 + {}^1/_2\ O_2 = NO$.—Nitric oxide and oxygen have previously been investigated calorimetrically by Johnston and Giauque.[50,3b] Johnston and Chapman[51] have obtained the free energy of nitric oxide in connection with their calculation of the heat capacity of this substance and Johnston and Walker[52] have similarly obtained the free energy and dissociation of oxygen. The present work on nitrogen completes the information necessary for considering the free energy of formation of nitric oxide.

Thomsen and Berthelot have both measured the heat of formation of nitric oxide. From their data ΔE_0° may be calculated.

$$\Delta E_0^\circ = \Delta H_T - \Delta(H_T^\circ - E_0^\circ) = \Delta H_T - \Delta\left(\frac{5}{2} RT + RT^2 \frac{d \ln Q}{dT}\right)$$

$$(H^\circ_{298.1} - E_1^\circ) \text{ for } N_2 = 2072.9$$

From the calculations of Giauque and Johnston[3b] $(H_{298.1}^\circ - E_0^\circ)$ for O_2 = 2070.4 and from Johnston and Giauque[50] $(H_{298.1}^\circ - E_0^\circ)$ for NO = 2216.8

$$\Delta(H_{298.1}^\circ - E_0^\circ) = 2216.8 - (2072.9/2) - (2070.4/2) = 145.1 \text{ calories per mole}$$

Berthelot[53] found ΔH = 21,600 cal. (20°) = 21,575 cal. (15°) per mole, ΔE_0° = 21,430. Thomsen[54] found ΔH = 21,575 cal. (20°) = 21,550 cal. (15°) per mole. ΔE_0° = 21,400. ΔE_0° may also be evaluated from determinations of the equilibrium constant.

$$\Delta E_0^\circ/T = -R \ln K - \Delta[(F^\circ - E_0^\circ)/T]$$

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(48) Compton and Boyce, *Phys. Rev.*, **33**, 145 (1929).

(49) Lozier, *Phys. Rev.*, **44**, 575 (1933) (dissociation of N_2 revised in proof).

(50) Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

(51) Johnston and Chapman, *ibid.*, **55**, 153 (1933).

(52) Johnston and Walker, *ibid.*, **55**, 172 (1933).

(53) Berthelot, *Ann. chim. phys.*, **20**, 255 (1880).

(54) Thomsen, see "Thermochemistry," 1908.

In Table XI are given the various values of ΔE_0° obtained from the equilibrium amounts of nitric oxide resulting when air was heated.

TABLE XI

ΔE_0° FOR $^1/_2\,N_2 + {}^1/_2\,O_2 = NO$ FROM EQUILIBRIUM MEASUREMENTS AND SPECTROSCOPIC DATA

T, °K.	ΔE_0°	Author
1811	22150	Nernst[55]
1873	20110	Briner, Boner and Rothen[56]
1877	22550	Nernst and Jellinek[55]
2033	22700	Nernst
2195	22710	Nernst
2580	22800	Nernst–Finckh[55]
2675	23190	Nernst–Finckh

All of the values tabulated deviate considerably from those of Thomsen and Berthelot and in the case of Nernst and his co-workers the trend increases the uncertainty.

It seems best to adopt a value $\Delta E_0^\circ = 21{,}400$ based on the work of Thomsen and Berthelot. This is equivalent to $\Delta H_{298} = 21{,}500$ calories per mole for the formation of nitric oxide.

Using the above data the values of $\Delta[(F^\circ - E_0^\circ)/T]$, $\Delta F^\circ/T$ and K have been calculated for the reaction $^1/_2\ N_2 + {}^1/_2\ O_2 = NO$. The results are given in Table XII.

TABLE XII

FREE ENERGY OF FORMATION OF NITRIC OXIDE AND $\Delta[(F^\circ - E_0^\circ)/T]$ FOR THE DISSOCIATION OF NITROGEN

	$^1/_2\,N_2 + {}^1/_2\,O_2 = NO$			$N_2 = 2N$	
T, °K.	$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$\Delta F^\circ/T$	$K = \frac{[NO]}{[N_2]^{1/2}\,[O_2]^{1/2}}$	$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$k = [N]^2/[N_2]$
298.1	2.527	69.261	7.26×10^{-16}	24.476	1×10^{-128}
300	2.532	68.801	9.15×10^{-16}	24.496	
350	2.592	58.551	1.59×10^{-13}	24.955	
400	2.639	50.861	7.64×10^{-12}	25.353	
450	2.675	44.881	1.55×10^{-10}	25.703	
500	2.708	40.092	1.73×10^{-9}	26.017	1×10^{-74}
550	2.735	36.174	1.24×10^{-8}	26.298	
600	2.755	32.912	6.40×10^{-8}	26.653	
650	2.777	30.146	2.58×10^{-7}	26.789	
700	2.790	27.781	8.47×10^{-7}	27.004	
750	2.806	25.727	2.38×10^{-6}	27.204	
800	2.818	23.932	5.88×10^{-6}	27.387	
850	2.831	22.345	1.31×10^{-5}	27.560	
900	2.840	20.938	2.65×10^{-5}	27.720	
950	2.850	19.676	5.00×10^{-5}	27.871	
1000	2.859	18.541	8.86×10^{-5}	28.012	2×10^{-34}
1050	2.867	17.514	1.49×10^{-4}	28.144	
1100	2.877	16.578	2.38×10^{-4}	28.269	

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(55) Nernst, *Z. anorg. Chem.*, **49**, 213 (1906).

(56) Briner, Boner and Rothen, *J. chim. phys.*, **23**, 788 (1926).

TABLE XII (*Concluded*)

T, °K.	$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$\Delta F^\circ/T$	$K = \frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}}$	$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$k = [N]^2/[N_2]$
1150	2.879	15.730	3.65×10^{-4}	28.387	
1200	2.888	14.945	5.41×10^{-4}	28.498	
1250	2.892	14.228	7.76×10^{-4}	28.603	
1300	2.897	13.565	1.08×10^{-3}	28.705	
1400	2.906	12.380	1.97×10^{-3}	28.891	
1500	2.915	11.352	3.30×10^{-3}	28.061	4×10^{-21}
1600	2.922	10.453	5.19×10^{-3}	29.215	
1700	2.929	9.659	7.74×10^{-3}	29.359	
1800	2.936	8.953	1.10×10^{-2}	29.488	
1900	2.943	8.320	1.52×10^{-2}	29.610	
2000	2.948	7.752	2.02×10^{-2}	29.723	4×10^{-14}
2100	2.954	7.236	2.62×10^{-2}	29.829	
2200	2.959	6.768	3.32×10^{-2}	29.927	
2300	2.963	6.341	4.11×10^{-2}	30.021	
2400	2.967	5.950	5.01×10^{-2}	30.108	
2500	2.970	5.590	6.00×10^{-2}	30.192	5×10^{-10}
2600	2.974	5.257	7.09×10^{-2}	30.270	
2700	2.977	4.949	8.29×10^{-2}	30.343	
2800	2.980	4.663	9.57×10^{-2}	30.414	
2900	2.982	4.397	1.09×10^{-1}	30.482	
3000	2.985	4.148	1.24×10^{-1}	30.544	3×10^{-7}
3100	2.989	3.914	1.40×10^{-1}	30.604	
3200	2.991	3.697	1.56×10^{-1}	30.662	
3300	2.994	3.491	1.73×10^{-1}	30.719	
3400	2.997	3.297	1.90×10^{-1}	30.771	
3500	2.999	3.115	2.09×10^{-1}	30.822	2×10^{-5}
3600	3.001	2.943	2.27×10^{-1}	30.873	
3700	3.003	2.781	2.47×10^{-1}	30.919	
3800	3.003	2.629	2.66×10^{-1}	30.967	
3900	3.003	2.484	2.86×10^{-1}	31.012	
4000	3.003	2.347	3.07×10^{-1}	31.056	7×10^{-4}
4100	3.005	2.215	3.28×10^{-1}	31.097	
4200	3.005	2.090	3.49×10^{-1}	31.138	
4300	3.005	1.972	3.71×10^{-1}	31.178	
4400	3.006	1.858	3.93×10^{-1}	31.217	
4500	3.004	1.752	4.14×10^{-1}	31.256	1.0×10^{-2}
4600	3.004	1.648	4.36×10^{-1}	31.294	
4700	3.002	1.551	4.58×10^{-1}	31.329	
4800	3.002	1.456	4.81×10^{-1}	31.364	
4900	3.002	1.365	5.03×10^{-1}	31.400	
5000	3.003	1.277	5.26×10^{-1}	31.435	8×10^{-2}

Table XIII summarizes the observed and calculated values of the equilibrium constant for the reaction $^1/_2\ N_2 + {}^1/_2\ O_2 = NO$. The measurements were made by determining the amount of NO formed in air at high temperatures. In calculating the equilibrium constants the composition of dry air was taken as 78.03% oxygen and 20.99% nitrogen.[57]

(57) "I. C. T.," Vol. I, p. 393.

TABLE XIII

OBSERVED AND CALCULATED EQUILIBRIUM CONSTANTS FOR THE FORMATION OF NITRIC OXIDE

T, °K.	%NO	$K_{\text{obs.}}$	$K_{\text{calcd.}}$	Observer
1811	0.37	0.0093	0.0114	Nernst[55]
1873	.79	.0198	.0140	Briner, Boner and Rothen[56]
1877	.42	.0104	.0142	Nernst and Jellinek[55]
2033	.64	.0160	.0221	Nernst
2195	.97	.0243	.0328	Nernst
2580	2.05	.0523	.0687	Nernst-Finckh[55]
2675	2.23	.0580	.0798	Nernst-Finckh

The observations differ quite appreciably from the calculated values. However, the agreement is perhaps all that might be expected when the difficulty of experiment at such high temperatures is considered. A redetermination of the heat of formation of nitric oxide seems very desirable. Such a determination with the advantage of modern technique would, when combined with the tabulated values of $\Delta[(F^\circ - E_0^\circ)/T]$, yield equilibrium constants with an insignificant error.

We wish to express our thanks to Dr. R. W. Blue for assisting with the experimental work.

Summary

The heat capacity of the two crystalline forms and of liquid nitrogen has been measured from 15°K. to the boiling point.

The transition, melting and boiling points are 35.61, 63.14 and 77.32°K., respectively.

The calorimetric heats of transition, fusion and vaporization (at 760 mm.) are 54.71, 172.3 and 1332.9 calories per mole, respectively.

From the calorimetric measurements and the third law of thermodynamics the entropy of nitrogen at its boiling point was found to be 36.3 ± 0.1 E. U. A 0.2 E. U. correction for gas imperfection, using Berthelot's equation, gives 36.5 E. U. as the entropy of the ideal gas at 77.32°K.

The entropy was also calculated from band spectrum data. At 77.32°K. the value was found to be 36.416 E. U. in excellent agreement with the experimental 36.5. At 298.1°K., $S = 45.788$ calories per degree per mole. None of the above entropy values contain the amount of entropy due to nuclear spin. The absolute entropy at 298.1°K. is $45.788 + R \ln 9 = 50.154$ E. U.

It has been concluded that, although lack of equilibrium between the two series of "non-combining" states of nitrogen persists into the solid state at 13°K., no molecular rotation remains in the solid at this temperature, as is the case in hydrogen.

The vapor pressure of solid and liquid nitrogen has been measured and the results have been represented by the equations: solid nitrogen 54.78 to 63.14°K., $\log_{10} P \text{ (cm.)} = -(381.6/T) + 7.41105 - 0.0062372\,T$; liquid

nitrogen 63.14 to 78.01°K., $\log_{10} P$ (cm.) $= -(339.8/T) + 6.71057 - 0.0056286\ T$.

The free energies and equilibrium constants for the reactions $^1/_2\ N_2 + {^1/_2}\ O_2 = NO$ and $N_2 = 2N$ have been calculated to 5000°K. with the assistance of spectroscopic data. The free energy of formation of nitric oxide was found to be $\Delta F^\circ_{298.1} = 20{,}650$ calories per mole.

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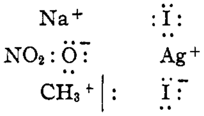
The Electronic Structure of Inorganic Complexes

BY WILLIAM ALBERT NOYES

Soon after Arrhenius proposed his theory of ionization a distinction was made between "heteropolar" and "homopolar" compounds. This corresponds closely to our distinction between ionic and covalent compounds. Chemists have very generally supposed that ionic compounds react very rapidly and that covalent compounds react slowly or not at all. Professor Kahlenberg, many years ago, showed the illusory nature of such a method of distinguishing the two classes of compounds but, because his views of ionization were considered heterodox, the facts which he stated have been too generally disregarded.

The fact that covalent methyl iodide reacts with silver nitrate in an alcoholic solution almost or quite as rapidly as ionic sodium iodide demonstrates that the two classes of compounds cannot be distinguished by the speed of their reactions.



$$\begin{array}{rl} Na^+ & :\underset{\cdot\cdot}{\overset{\cdot\cdot}{I}}: \\ NO_2:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^- & Ag^+ \\ CH_3{}^+\,\Big|\,: & \underset{\cdot\cdot}{\overset{\cdot\cdot}{I}}:^- \end{array}$$

Both reactions are ionic but the positive methyl has only an ephemeral existence.

Instead of speed of reactions we must rely on other properties to distinguish between covalences and ionic valences. The most important of these are conductivity in solutions, molecular weights in solutions, Sugden's parachor, optical activity and, especially, electronic structure. The last can frequently be inferred with a high degree of probability.

That there is an absolute balance between the positive charge of the nucleus of an atom and the negative charges of the electrons surrounding the nucleus is universally accepted by chemists and physicists. That every ion consisting of a single atom has a stable group of electrons the sum of whose negative charges overbalances or underbalances the positive charge of its nucleus and that in every complete molecule the sum of the