TABLE XI

PHYSICAL CONSTANTS AND MOLAL HEATS OF ADSORPTION OF AMMONIA AND THE METHYLAMINES

Gas	T, °C.	C_p/C_v	B. p. in °K. at 1 atm.	H_m at 25°, kg.-cal.	H_m at 40°, kg.-cal.
NH_3	132.4	1.317	234.6	14.8	14.9
CH_3NH_2	156.9	1.202	266.4	18.7	18.8
$(CH_3)_3N$	161.0	1.184	276.6	19.0	19.1
$(CH_3)_2NH$	164.6	1.149	280.3	20.1	20.0

Table XI shows that H_m for these gases does not change to any great extent with temperature over the range investigated.

Relation of Heat of Adsorption to Mesh Size and Previous History of Adsorbent.—The points obtained using 20–30 mesh silica gel fall on the curves obtained when 10–14 mesh gel was used. The previous use of the gel as an adsorbent for the gases investigated had no effect on the heat of adsorption provided the gel was degassed at 300° before it was used.

Summary

1. The adsorption isotherms of methylamine on alumina gel, silica gel and activated coconut charcoal have been determined at 0, 30 and 40°.

2. The heats of adsorption of ammonia, methylamine, dimethylamine and trimethylamine on silica gel at 25 and 40° have been determined.

3. It has been shown that the heat of adsorption does not change with mesh size nor the previous use of the gel as an adsorbent provided it is degassed at 300°.

4. It has been shown that the heat of adsorption does not change with temperature over the range investigated.

5. The heats of adsorption of these gases have been shown to be definite and reproducible.

AUSTIN, TEXAS RECEIVED JUNE 18, 1934

[CONTRIBUTION FROM THE RANDAL MORGAN LABORATORY OF PHYSICS, UNIVERSITY OF PENNSYLVANIA]

Specific Heat, Entropy and Free Energy of Gaseous Nitric Oxide Computed from the Spectroscopic Data

BY ENOS E. WITMER

In 1927 the writer[1] computed the specific heat of nitric oxide from the spectroscopic data of Jenkins, Barton and Mulliken[2] from 1 to 500°K. This was regarded as being of special interest because nitric oxide has a doublet normal level. Recently the entropy and the free energy were computed from the values of the partition sum and its derivatives (the P_1, P_2, P_3 used below) used in the computation of the specific heat. In the meantime, Johnston and Chapman[3] have published calculations of the thermodynamic properties of nitric oxide from the spectroscopic data. They, however, misinterpreted the data of Jenkins, Barton and Mulliken in regard to the value of the doublet separation of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states. Jenkins, Barton and Mulliken state on p. 171 of their article that the doublet separation is 124.4 cm.$^{-1}$. According to their footnote 38 this value was calculated from the figure 120.9 cm.$^{-1}$ obtained from Miss Guillery's[4] data (p. 144 of her paper) by adding on $9/4\, B_2'' - 1/4\, B_1''$ in the notation of Jenkins, Barton and Mulliken.

In order to understand the nature of the error made by Johnston and Chapman, it is necessary to write down the formulas for the energy levels of the two Π states which constitute the normal level of the nitric oxide molecule.

For the $^2\Pi_{1/2}$ state, the energy levels in cm.$^{-1}$ are

$$\begin{aligned} F_1'(v,J) = {} & (1.6754 - 0.01783v \pm 0.0011)(J + 1/2)^2 + \\ & (0.106 \pm 0.064)10^{-3}(J + 1/2)^3 - \\ & (0.506 \pm 0.137)10^{-5}(J + 1/2)^4 + \\ & 1892.119v - 14.4243v^2 + 0.04021v^3 - \\ & 0.001351v^4 \end{aligned} \tag{1}$$

Here J takes on the values $^1/_2$, $^3/_2$, . . . etc.

For the $^2\Pi_{3/2}$ state, we have

$$\begin{aligned} F_2'(v,J) = {} & (1.7239 - 0.01866v \pm 0.0015)(J + 1/2)^2 \\ & + (0.010 \pm 0.069)10^{-3}(J + 1/2)^3 - \\ & (0.871 \pm 0.135)10^{-5}(J + 1/2)^4 + \\ & 120.9 + 1891.976v - 14.4543v^2 + 0.04229v^3 \\ & - 0.001423v^4 \end{aligned} \tag{2}$$

Here J takes on the values 3/2, 5/2, . . . etc. The ± signs in the coefficients of the powers of $(J + 1/2)$ indicate the probable error. The

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(1) E. E. Witmer, *Phys. Rev.*, **29**, 918 (1927). The complete results for the specific heat were presented at a meeting of a section of the German Physical Society held in Goettingen in the winter of 1927–1928.

(2) F. A. Jenkins, H. A. Barton and R. S. Mulliken, *ibid.*, **30**, 150 (1927).

(3) H. L. Johnston and A. T. Chapman, THIS JOURNAL, **55**, 153 (1933).

(4) M. Guillery, *Z. Physik*, **42**, 121 (1927).

omission of the terms linear in $(J + 1/2)$ is due to the fact that the writer obtained these formulas from Jenkins, Barton and Mulliken before their work was quite complete and the exact values of the corresponding coefficients were still uncertain. The contributions of these terms to the thermodynamic quantities, however, are very small and decrease rapidly with increasing temperature.

The modern theoretical treatment of the diatomic molecule in Hund's case (a), which is realized in the normal state of nitric oxide, requires that the energy formulas be written in the following form

$$F_s(v,J) = B_s(v)[(J + 1/2)^2 - \Omega_s^2] + (s - 1)D + E_s(v) + \Delta F_s(v,J) \qquad (3)$$

In our case, $\Omega_s = s-1/2$ and s takes on the values 1 and 2. In eq. (3)

$$E_s(v) = \omega_s(v + 1/2) - x_s\omega_s(v + 1/2)^2 + \ldots \qquad (4)$$

and $\Delta F_s(v,J)$ represents the terms in the third and fourth powers of $(J + 1/2)$ in eqs. (1) and (2).

Putting the equations (1) and (2) into the form (3) requires a change in the zero point of the energy. The value of D comes out to be 124.4 cm.$^{-1}$ which is the same as $120.9 + 9/4B_2'' - 1/4B_1''$ given by Mulliken, the agreement being due to the fact that the other terms involved in the transformation from (1) and (2) to (3) do not contribute appreciably to the result.

Johnston and Chapman used the value 124.4 cm.$^{-1}$ in eq. (2) where 120.9 should have been used. This can be seen from the fact that they obtain the value 129.55 cm.$^{-1}$ for the separation between the ${}^2\Pi_{3/2}$ state for which $v = 0$ and $J = 3/2$ and the ${}^2\Pi_{1/2}$ state for which $v = 0$ and $J = 1/2$ instead of the value 126.13 cm.$^{-1}$ given by formulas (1) and (2). A similar misapprehension occurs on p. 307 of a paper by Gordon and Barnes,[5] where the value of 124.4 cm.$^{-1}$ is attributed to Jenkins, Barton and Mulliken and 120 to Schmid, Koenig and von Farkas,[6] thus indicating a disagreement which does not really exist.

The writer used the value 120.0 cm.$^{-1}$ in eq. (2) which was given to him directly by Jenkins, Barton and Mulliken before publication of their article. Schmid[7] and Jevons[8] give the value 120.9 for the doublet separation, while more recent work of Schmid, Koenig and von Farkas[6] seems to indicate that the true value is very close to 120.0 cm.$^{-1}$.

We give below the formulas used in computing the thermodynamic functions, omitting the contribution due to translation. They are then dependent merely on the partition sum, P_1, and its derivatives.[9]

Let

$$P(\mu) = \textstyle\sum_{s,v,J} p_s(v,J)e^{-\sigma_s(v,J)\mu+\sigma_0\mu} \qquad (5)$$

where

$$\left.\begin{aligned} \sigma_s(v,J) &= \frac{hc}{kT}F_s(v,J) \\ &\equiv \frac{c_2}{T}F_s(v,J) \\ \sigma_0 &\equiv \sigma_1(0, 1/2) \end{aligned}\right\} \qquad (6)$$

and

$$p_s(v,J) = 2(2J + 1) \qquad (7)$$

The factor 2 in (7) comes from Λ-type doubling. The σ_0 in eq. (5) is due to the fact that the energy is to be reckoned from the lowest state as the point of zero energy. μ is a parameter introduced for the sake of convenience in differentiation.

The partition sum P_1 is then given by the equation

$$P(1) = P_1 \qquad (8)$$

We define further

$$P_2 = -\frac{\partial P(\mu)}{\partial\mu}\bigg|_{\mu=1} = \textstyle\sum_{s,v,J} p_s(v,J) \times [\sigma_s(v,J) - \sigma_0]\, e^{-\sigma_s(v,J)+\sigma_0} \qquad (9)$$

$$P_3 = \frac{\partial^2 P(\mu)}{\partial^2\mu}\bigg|_{\mu=1} = \textstyle\sum_{s,v,J} p_s(v,J) \times [\sigma_s(v,J) - \sigma_0]^2\, e^{-\sigma_s(v,J)+\sigma_0} \qquad (10)$$

In terms of the P's we can now write the specific heat,[10] the entropy and the free energy, as follows

$$\frac{C}{R} = \frac{\partial^2}{\partial\mu^2}\log P(\mu)\bigg]_{\mu=1} = \frac{P_3}{P_1} - \left(\frac{P_2}{P_1}\right)^2 \qquad (11)$$

$$\frac{S}{R} = \log P_1 - \frac{\partial \log P(\mu)}{\partial\mu}\bigg]_{\mu=1} = \log P_1 + \frac{P_2}{P_1} \qquad (12)$$

$$-\frac{F - E_0^\circ}{RT} = \log P_1 \qquad (13)$$

In these formulas, C, S and F are, respectively, the specific heat, the entropy and the free energy arising from all degrees of freedom except translation. E_0° is the additive energy constant at the absolute zero.[9]

At the higher temperatures an approximation formula for $P(\mu)$ was used because direct summation became too laborious. It was obtained as

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[5] A. R. Gordon and C. Barnes, *J. Chem. Phys.*, **1**, 297 (1933).

[6] R. Schmid, T. Koenig and D. von Farkas, *Z. Physik*, **64**, 84 (1930).

[7] R. Schmid, *ibid.*, **49**, 428 (1928).

[8] W. Jevons, "Report on Band-Spectra of Diatomic Molecules," London, 1932.

[9] *Cf.* also Giauque, This Journal, **52**, 4808 (1930).

[10] *Cf.* E. C. Kemble and J. H. Van Vleck, *Phys. Rev.*, **21**, 653 (1923).

follows. Substituting from eq. (3) in (5) and neglecting for the moment $\Delta F_s(v,J)$, we obtain

$$P^0(\mu) = \sum_{s,v} \sum_{j=\Omega_s+1/2}^{\infty} 4je^{-\beta_s(v)[j^2-\Omega_s^2]\mu} \times e^{-[(s-1)\rho+\epsilon_s(v)-\sigma_0]\mu} \quad (14)$$

The superscript zero in $P^0(\mu)$ indicates the omission of $\Delta F_s(v,J)$. Further

$$\left.\begin{aligned} \beta_s(v) &= hc\,\frac{B_s(v)}{kT} \\ \rho &= hc\,\frac{D}{kT} \\ j &= J + 1/2 \\ \epsilon_s(v) &= hc\,\frac{E_s(v)}{kT} \end{aligned}\right\} \quad (15)$$

Now, at temperatures so high that the rotational energy approaches its classical value, integration can be substituted for summation without introducing any serious error. Hence

$$\sum_{j=\Omega_s+1/2}^{\infty} 4je^{-\beta_s(v)[j^2-\Omega^2_s]\mu} = e^{\beta_s(v)\Omega_s^2\mu} \int_{\sqrt{\Omega^2_s-\lambda}}^{\infty} 4je^{-\beta_s(v)j^2\mu}\,dj = \frac{2e^{\beta_s(v)\lambda\mu}}{\beta_s(v)\mu} \quad (16)$$

Initially the lower limit of the integral in (16) was taken as Ω_s, but it was found that a very much better approximation was obtained by using the limit indicated, taking $\lambda = 0.0745$.

Substituting from eq. (16) into (14) we obtain

$$P^\circ(\mu) = \sum_{s,v} \frac{2e^{\beta_s(v)\lambda\mu}}{\beta_s(v)\mu} e^{-[(s-1)\rho+\epsilon_s(v)-\sigma_0]\mu} \quad (17)$$

P_1°, P_2° and P_3° can be obtained from (17) by making use of eqs. (8), (9) and (10).

We consider now the effect of the terms involving the higher powers of $(J + 1/2)$ in (3). The contribution of these terms to the P's and the thermodynamic quantities is very small; therefore, their contribution was computed as a correction to the values obtained by the formula above. This correction, which increases with temperature, was largest in the case of the specific heat, amounting to 0.0046 cal./deg./mole at 500°K. The formulas used in making the correction were obtained by letting

$$e^{-\frac{hc\mu}{kT}\Delta F_s(v,J)} = 1 - \frac{hc\mu}{kT}\,\Delta F_s(v,J)$$

and substituting integration for summation in the case of the rotational part, as in eq. (16). The resulting $P(\mu)$ could then be written

$$P(\mu) = P^0(\mu)[1 + \theta(\mu)]$$

In this way the corrections to the thermodynamic quantities could be obtained in terms of quantities θ_1, θ_2 and θ_3, which are defined by eqs. (8), (9) and (10) by substituting everywhere θ for P.

TABLE I

VALUES CORRESPONDING TO THE STARRED TEMPERATURES WERE OBTAINED BY DIRECT SUMMATION

T, °K.	C_p	S	$-(F - E_0^\circ)/T$
1*	5.1191	10.612	5.625
2*	6.2642	14.413	9.073
3*	6.7552	17.166	11.418
4*	6.8707	19.128	13.110
5*	6.9079	20.667	14.474
10*	6.9442	25.472	18.908
20*	6.9723	30.289	23.531
30	7.137	33.143	26.291
40	7.396	35.232	28.278
50*	7.6176	36.907	29.840
60	7.743	38.300	31.203
70	7.801	39.514	32.256
80	7.798	40.546	33.222
90	7.762	41.467	34.090
100*	7.7112	42.282	34.869
110	7.653	43.018	35.579
120	7.596	43.677	36.222
130	7.540	44.283	36.821
140	7.489	44.841	37.376
150	7.442	45.356	37.890
160	7.400	45.833	38.369
170	7.362	46.277	38.819
180	7.329	46.703	39.251
190	7.299	47.100	39.655
200	7.272	47.467	40.031
220	7.226	48.159	40.740
240	7.188	48.785	41.387
300	7.133	50.386	43.033
400	7.158	52.439	45.140
500	7.295	54.048	46.766

The results of our calculations for the specific heat at constant pressure, the entropy and $-(F - E_0^\circ)/T$ are given in Table I in calories per degree per mole. These values include the contribution due to translational motion. The value of R used was that given by Birge,[11] R = 1.9864 cal./deg./mole and 30.008 was used as the molecular weight of nitric oxide. The value of $c_2 = hc/k$ for the values in Table I is 1.4317 cm. deg., the value given by Birge.[11] The original computations were made with c_2 = 1.4294 cm. deg., but the final results were corrected to the value given above by means of simple correction formulas which are easily derived. In no case did this correction exceed 0.005 cal./deg./mole and in the case of the specific heat it did not exceed 0.0015 cal./deg./mole. The values of the specific heat from 1 to 5°K., inclusive, however, were recomputed with c_2 = 1.4317. Λ-type doubling was taken into account, but not nuclear spin. At the starred temperatures in Table I, P_1, P_2 and P_3 were evaluated by direct summation and the

(11) R. T. Birge, *Phys. Rev.*, Suppl. 1, 1 (1929).

thermodynamic quantities computed to five, or more, significant figures. At all the other temperatures the P's were evaluated by the use of the approximation formulas mentioned above. In order to determine the accuracy of the approximation formulas comparisons with the values obtained by direct summation were made at 20, 50 and 100°K.; the differences between corresponding values of the thermodynamic quantities never exceeded 0.0021 cal./deg./mole, the discrepancy in the values of the specific heat at 20°K. The agreement apparently improved with temperature, as is to be expected theoretically. At 100°K. the discrepancy between the two values of the specific heat was less than 0.0003 cal./deg./mole and in the case of the entropy and $(-(F - E_0°)/T)$ there was complete agreement to five significant figures.

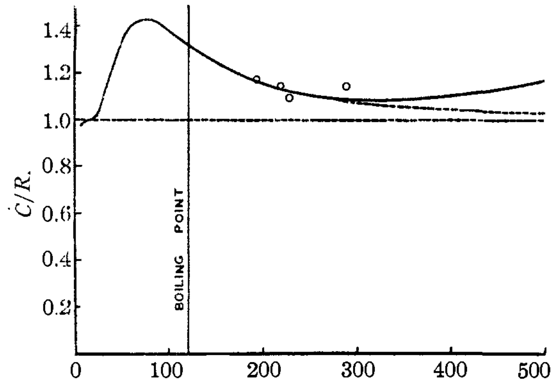

Fig. 1.—Specific heat of NO.

In Fig. 1 the values of $(C_p/R - 5/2)$ are plotted against the absolute temperature. The circles are the experimental values of Scheel and Heuse.[12] The dotted curve beginning at about 275°K. differs from the continuous curve in that the contribution due to vibration has been omitted. The multiplet contribution is represented by the excess of the ordinate over unity below 275°K. and by the excess of the ordinate of the dotted curve over unity above 275°K. The maximum in the curve occurs at $\rho = 2.399$, corresponding to a temperature of 73.55°K.

Before proceeding to a comparison of our values with those of Johnston and Chapman, it is necessary to consider briefly the general nature of the contributions to the thermodynamic functions due to the multiplicity. The writer[13] has developed formulas for the contributions to the specific heat, entropy and free energy of a diatomic gas whose molecules have a multiplet normal electronic state belonging to Hund's case (a). It can be shown by means of these formulas that if we plot the *multiplet contributions* to the thermodynamic functions against temperature, curves with the same multiplicity but different values of D (multiplet spacing) will differ only in their scale along the temperature axis, any given point of the curve being displaced toward higher temperatures with increasing D. It should be noted also that the multiplet contributions to the entropy and $-(F - E_0°)/T$ are monotone increasing functions of T. With the aid of the formulas referred to we have computed the theoretical errors in Johnston and Chapman's values due to their error in the doublet spacing, *viz.*, 4.4 cm.$^{-1}$. These results are given in Table II. The errors were computed at 73.55°K. because it is the location of the maximum in the specific heat curve and the error in the entropy has its maximum at that point. The errors were also computed at 138.03°K. because the error in $(-(F - E_0°)/T)$ has its maximum here. It can be shown that the errors due to this source in all the thermodynamic quantities here considered are zero at $T = 0$°K. and at $T = \infty$. Practically this means that at sufficiently high temperatures these errors are negligible.

TABLE II

THEORETICAL ERRORS IN THE RESULTS OF JOHNSTON AND CHAPMAN IN CAL./DEG./MOLE.

T, °K.	ΔC_p	ΔS	$\Delta(-(F - E_0°)/T)$
20	−0.0055	−0.0008	−0.0001
30	− .0261	− .0068	− .0011
40	− .0376	− .0163	− .0037
50	− .0316	− .0244	− .0071
60	− .0189	− .0292	− .0104
73.55	.0000	− .0311	− .0143
100	+ .0207	− .0275	− .0183
138.03	+ .0252	− .0197	− .0197
200	+ .0186	− .0114	− .0183
300	+ .0103	− .0056	− .0149
400	+ .0063	− .0033	− .0122
500	+ .0041	− .0021	− .0103

We shall now compare our values with those of Johnston and Chapman. Before we do this, however, it is necessary to take into consideration the fact that they apparently used values of R and c_2 from the "International Critical Tables," which differ from those used by us. Their value of c_2 is thus 1.433 cm. deg., whereas ours is 1.4317.

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(12) Scheel and Heuse, *Ann. Physik*, [4] **40**, 473 (1913). *Cf.* also Heuse, *ibid.*, [4] **59**, 86 (1919).

(13) E. E. Witmer, *J. Chem. Phys.*, **2**, 618 (1934).

This, however, would make a difference of 0.0026 cal./deg./mole at most in the thermodynamic quantities under consideration—in the specific heat of 0.0009 or less. The value of R given by the "International Critical Tables" is 1.9869 cal./deg./mole, which is 0.0005 in excess of the value used by us. This difference in the value of R produces considerable differences in the computed values of the entropy and $(-(F - E_0°)/T)$ less in the case of the specific heat. When the values of Johnston and Chapman are "corrected" for this difference in the value of R, it is found that the differences between our values and their values are just about what they should be according to Table II. This is a check on both calculations. Outside of the errors arising from their incorrect value of the doublet spacing, only one error has been found in their work. This is in the value of the specific heat at 4°K., where there should be almost complete agreement, since the $^2\Pi_{3/2}$ level is not yet excited at that temperature. Their value exceeds ours by 0.015 cal./deg./mole. Since we recomputed our value, this difference is apparently due to an error on their part.

It should be borne in mind, in considering the importance of the discrepancies arising from differences in the values of the physical constants, that the probable error due to uncertainty in the spectroscopic data of Jenkins, Barton and Mulliken is of the order of 0.005 cal./deg./mole, as estimated by Johnston and Chapman. The error introduced by the incorrect value of the doublet separation in the work of Johnston and Chapman is several times this probable error within a considerable range, and also exceeds, on the whole, the differences traceable to discrepancies in the values of the physical constants.

In conclusion, the writer wishes to thank Prof. E. C. Kemble, who suggested calculating the specific heat of nitric oxide, which was done at Harvard University in 1927; and the Faculty Research Committee of the University of Pennsylvania for providing funds for an assistant, Dr. A. V. Bushkovitch, who made the calculations of the entropy and the free energy.

Summary

The specific heat, entropy and free energy of nitric oxide in the ideal gaseous state have been computed for the temperature range from 1 to 500°K. from the spectroscopic data.

The values obtained do not agree entirely with those recently published by Johnston and Chapman. This is due principally to the fact that they used an incorrect value of the doublet separation in their computation; the effect of this error is distorted somewhat by differences in the respective values of the physical constants used by Johnston and Chapman and by us. The magnitude of the error affecting their values is several times larger than their estimated probable error throughout the greater part of the range from 1 to 500°K.

PHILADELPHIA, PA. RECEIVED JUNE 18, 1934

[CONTRIBUTION FROM THE LABORATORY OF CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

The Solubility of Sulfur Dioxide at Low Partial Pressures. The Ionization Constant and Heat of Ionization of Sulfurous Acid[1]

BY H. F. JOHNSTONE AND P. W. LEPPLA

In some work on the rate of oxidation of sulfur dioxide by oxygen in stationary liquid films it has been necessary to know the solubility of the gas at partial pressures considerably lower than those previously reported. The opportunity has thus been given to make further application of the theory of interionic attraction to the field of intermediate electrolytes. Using the method of Sherrill and Noyes[2] the ionization constants of sulfurous acid have been calculated at 0, 10, 18, 25, 35 and 50° from the recent conductivity data of Maass and his co-workers.[3] By means of these constants the molalities of the un-ionized molecules, both in our dilute solutions and in the more concentrated solutions for which the vapor pressures were measured by Maass, have been

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(1) This paper contains a part of the results of a coöperative research, Project No. 34, with the Utilities Research Commission of Chicago, entitled "A Study of Stack Gases." Published by permission of the Director of the University of Illinois Engineering Experiment Station.

(2) Sherrill and Noyes, THIS JOURNAL, **48**, 1861 (1926); *cf.* also MacInnes, *ibid.*, **48**, 2068 (1926); MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

(3) Campbell and Maass, *Can. J. Research*, **2**, 42 (1930); Morgan and Maass, *ibid.*, **5**, 162 (1931).