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

THE HEAT CAPACITIES AND ENTROPIES OF DIATOMIC AND POLYATOMIC GASES

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The entropy of a monatomic gas is given within the limits of experimental error by the Sackur[1] equation,

$$S = R\ ln\ T^{3/2}M^{3/2}V + S. \qquad (1)$$

The constant S has been evaluated by Lewis[2] using the principle of ultimate rational units and equals —11.39±0.01, where M is the molecular weight and V is expressed in cubic centimeters.

The entropy equation for diatomic gases at high temperatures according to Tetrode[3] and Sackur[4] should have the form

$$S = R\ ln\ T^{5/2}M^{3/2}V\ I + S_2, \qquad (2)$$

where I is the moment of inertia of the rigid diatomic molecules of which the gas is assumed to be composed, and S_2 is a constant independent of the kind of gas. Latimer[5] has recently shown that the entropies of several diatomic gases at 25° are given with considerable accuracy by the equation

$$S_{298} = R\ ln\ M^{3/2}A_1{}^{1/2}A_2{}^{1/2} + S_0,$$

where A_1 and A_2 are the atomic weights of the 2 atoms comprising the molecule, and the constant S_1 was empirically determined. It has been pointed out by Tolman,[6] however, that the data employed by Latimer were not sufficient to distinguish between the validity of his equation and the earlier one of Tetrode and Sackur, and it was further pointed out that the earlier equation is derivable from the principle of similitude.

In the present article we shall calculate the entropy of gases by putting it equal to the sum of the entropy of a monatomic gas as given by Equation 1 plus the additional entropy due to the gradually increasing value of the specific heat of polyatomic gases over that for monatamic gases as we proceed up from the absolute zero. In the case of diatomic gases we shall take this additional specific heat as given with sufficient approximation by an equation[7] of Reiche's for the rotational specific heat of diatomic gases and shall make use of spectral data for determining the moment of inertia of the molecules of the gases.

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[1] Sackur, *Ann. Physik*, **36**, 598 (1911); **40**, 67 (1913).

[2] Lewis, *Phys. Rev.*, **18**, 121 (1921).

[3] Tetrode, *Ann. Physik*, **38**, 441 (1912).

[4] Sackur, *ibid.*, **40**, 87 (1913).

[5] Latimer, THIS JOURNAL, **43**, 818 (1921).

[6] Tolman, *ibid.*, **43**, 866 (1921).

[7] Reiche, *Ann. Physik*, **58**, 657 (1919). The reader should consult the original for the derivation of this equation.

This method of procedure agrees with Langen's calculation[8] of the relative moments of inertia of diatomic gases. His calculations, however, were based on the Einstein-Stern equation for the heat capacity of diatomic gases which does not correctly represent the experimental facts. Our general method of procedure also agrees with Tolman's calculation[9] of the entropy of diatomic hydrogen using the same assumption as to the possibility of adding the two entropies but using Eucken's experimental values for the molecular heat capacity of hydrogen. Tolman's method, however, was seriously limited, since hydrogen is the only diatomic gas for which we have or are soon likely to have actual experimental data on heat capacities at sufficiently low temperatures. Our work will also show that the equation of Tetrode and Sackur may be regarded as correct at high temperatures for the case of rigid diatomic molecules, and our work leads to a theoretical determination of the constant S_2 in that equation.

Of the several equations derived by various authors for the rotational specific heat of diatomic gases, that of Reiche's equations which agrees best with a moment of inertia for hydrogen approximately the same as that secured from band spectra seems most satisfactory and is adopted in this article. In deriving this equation Reiche uses directional quantization in a gravitational field to get the probability of the various energy states. The final equation of Reiche's which we have adopted is based on the assumption that the azimuthal quantum number cannot become zero. This leads to a rule of exclusion similar to that used in the case of electron orbits in electrostatic and magnetic fields and this agrees with the work of Stern and Gerlach[10] on magnetic moment of the silver atom and with Sommerfeld's[11] theory of the anomalous Zeeman effect. This equation then not only agrees with Eucken's heat-capacity data, with the possible exception of one point, but also agrees in theory with band spectra and direction quantization in magnetic fields.

This equation for rotational heat capacity per mole is

$$C_r = R\sigma^2 \frac{\mathrm{d}^2 lnQ}{\mathrm{d}\sigma^2}, \tag{3}$$

provided we set $\sigma = \frac{h^2}{8\pi^2 IkT}$, and $Q = \Sigma\Sigma e^{-(n_1 + n_2)^2\sigma}$, and the expression for Q is summed over all integral values of n_2, the azimuthal quantum number, from 1 to ∞ and of n_1 from 0 to ∞. If n is set equal to the sum of n_1 and n_2, the expression Q becomes $Q = \sum\limits_{1}^{\infty} n e^{-n^2\sigma}$. If we substitute this

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[8] Langen, *Z. Elektrochem.*, **25**, 25 (1919).

[9] Tolman, THIS JOURNAL, **42**, 1185 (1920).

[10] Stern and Gerlach, *Z. Physik*, 9, 349 (1922).

[11] Sommerfeld, "Atombau," Friedr. Vieweg und Sohn., 3rd ed., **1922.**

expression in (3) and carry out the differentiation, we find

$$C_r = R\sigma^2 \left[\frac{\sum\limits_1^\infty n^5 e^{-n^2\sigma}}{\sum\limits_1^\infty n e^{-n^2\sigma}} - \left\{ \frac{\sum\limits_1^\infty n^3 e^{-n^2\sigma}}{\sum\limits_1^\infty n e^{-n^2\sigma}} \right\}^2 \right]. \tag{4}$$

In Curve I of Fig. 1, we have plotted the values of C_r/R calculated from Equation 4 using $I = 2.095 \times 10^{-41}$ g. cm.^{2} against *ln T*. The points show the experimental data of Eucken for hydrogen. In Curve II we have plotted a similar curve for a hypothetical gas with $I = 4.19 \times 10^{-41}$ g. cm.^{2} These curves can be superimposed by moving them along the *ln T* axis.

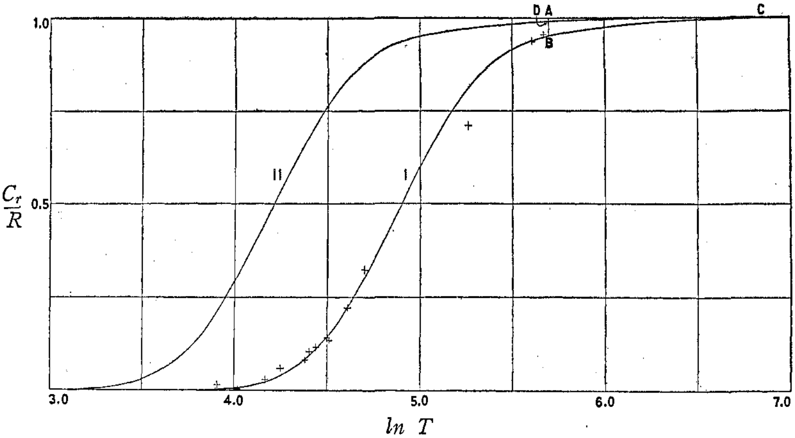

Fig. 1.—Heat capacity of hydrogen.

The Entropy Equation of Diatomic Gases

The entropy of a diatomic gas should be equal to the entropy due to its translational heat capacity, its volume, and its heat capacity of rotation. The equation for a monatomic gas gives the entropy due to the first two factors and therefore $S = R\, ln T^{3/2} M^{3/2} V - 11.39 + \int_0^T C_r \, d\, ln T$. In an exact sense there is no true entropy constant for a diatomic gas, since these curves in Fig. 1 never reach the value R but approach it asymptotically. However, if the C_r value of the gas at the temperature at which the entropy is to be calculated is nearly R and if there is no vibrational heat capacity, then a constant applicable at such a temperature can be calculated. Since C_r is a function of $I\ T$, that is, $C_r = f(I\ T)$, the heat capacity C_r is the same for all gases for the same value of $I\ T$, or at points such that $I_1/I_2 = T_2/T_1$, where I_1 and I_2 are the moments of inertia of two diatomic gases. Since under these conditions, $ln(I_1/I_2) = ln(T_2/T_1)$, it follows immediately that the curves secured by plotting C_r against *ln T* as in Fig. 1, can be superimposed by moving them along the $ln\ T$ axis by a distance $ln(I_1/I_2)$. The difference in entropy due to rotational heat capacity for these two gases is then $R\ ln(I_1/I_2)$, or $R\ ln(T_2/T_1)$ minus the area between the two curves above the point $ln\ T$, where T is the temperature at which the entropy is calculated. This area D B C is shown in Fig. 1 for hydrogen gas with $I = 2.095 \times 10^{-41}$ and the hypothetical gas having $I = 4.19 \times 10^{-41}$. When both curves come very close to the value R this area becomes negligible, as it would be at $ln\ T = 7$, as can easily be seen from the figure.

In order to use such an equation as (2), let us choose as a reference gas one having a moment of inertia of unity. We can take this as 1 g. cm.^{2} per mole or as 1 g. cm.^{2} per molecule. We shall use the former unit. If the latter is used all constants secured must be increased by $R\ ln\ N$ where N is Avogadro's number. The entropy due to the heat capacity C_r of gas A is equal to the area under the curve for this reference gas from 0 to T minus the area between this curve and the curve for gas A, if the moment of inertia of A is less than that of the standard gas, as of course is the case with such a large value of I for the standard gas. Let C_r and S_r be the heat capacities of rotation and entropy due to the rotational heat capacity, respectively, of A, and let C be the rotational heat capacity of our reference gas, then

$$S_r = \int_0^T C_r\, \mathrm{d}\, ln\ T = \int_0^T C\, \mathrm{d}\, ln\ T - R\ ln \frac{I_R}{I_A}$$

or since I_R, the moment of inertia of the reference gas, is unity

$$S_r = \int_0^T C\, \mathrm{d}\, ln\ T + R\ ln\ I_A = \int_0^T C\, \mathrm{d}\, ln\ T + R\ ln\ T + R\ ln\ I_A. \quad (5)$$

The substitution $\int_0^T C\, \mathrm{d}\, ln\ T = \int_0^1 C\, \mathrm{d}\, ln\ T + R\ ln\ T$ can be made, since the heat-capacity curve of our reference gas would already be sensibly R at 1° K. It is evident that $\int_0^1 C\, \mathrm{d}\, ln\ T$ is the constant for the entropy due to C_r. Using Equation 4 for the calculation of C and counting the squares, we get 67.56 for this constant, and then by adding Equation 1 which gives the entropy due to volume and translational heat capacity and Equation 5 we get for the total entropy equation for a diatomic gas. This equation applies only to gases having a value of C_r equal to R and no vibrational heat capacity at the temperature for which the entropy is to be calculated. The equation does not give the correct entropy for hydrogen by the amount of the area A B C which must be added to that calculated.

We can use the equation secured above together with data on the moments of inertia secured from band spectra to calculate accurate values of the entropies of several gases. The moments of inertia have been secured from the following sources; Kratzer's[12] calculations for hydrogen fluoride,

[12] Kratzer, *Z. Physik*, **3**, 289 (1920).

chloride and bromide from Imes' data,[13] the constant 2B for the 3883 cyanogen band as given by Kratzer[12] for nitrogen, the maxima of the double bands of carbon monoxide at 4.67μ and nitric oxide at 5.33μ from the data of E. v. Bahr[14] and Warburg and Leithauser,[15] using the formula based on classical theory which gives fairly accurate results, namely,

$$I = kT\left[\frac{\lambda_1\lambda_2}{\pi c(\lambda_2 - \lambda_1)}\right] \tag{6}$$

in which λ_1 and λ_2 are the maxima of the double band and c is the velocity of light.

Table I gives the moments of inertia, the distances between the nuclei in the diatomic molecules, the atomic radii as given by Bragg,[16] the entropies calculated from Equation 6 and the experimental values with the author in whose paper the observed value is found.

Table I

Moment of Inertia and Entropy of Diatomic Gases

Substance	$I \times 10^{40}$	$l \times 10^{8}$	$r \times 10^{8}$	S_{298} (calc.)	S_{298} (obs)	Reference
H_2	0.2095 (Reiche)	0.502	....	29.25	29.2	17
	0.19 (band spectra)	....	....	....	....	..
N_2	14.4	1.13	0.65	45.59	45.6	18
HF	1.325	0.92	0.67 (F)	39.84	....	..
HCl	2.594	1.265	1.05 (Cl)	42.95	43.3	17
HBr	3.258	1.407	1.19 (Br)	45.79	....	..
CO	14.7	1.14	0.77 (C)	45.6	45.6	19
NO	14.3	1.08	....	45.3	49.3	17

The agreement in the case of hydrogen points only to the accuracy of the shape of curve given by Reiche's equation, since the experimental value quoted was secured by using the monatomic gas equation and adding to this result the area under a smooth curve drawn through the experimental data of Eucken. Other experimental values for hydrogen are somewhat higher than the calculated entropy. Lewis, Gibson and Latimer[18] have calculated from the heat capacity of water and the change of entropy for the reaction $2H_2 + O_2 = 2H_2O$, the value 31.8, and from Kammerlingh Onnes' thermal data on hydrogen at low temperatures, the value 30.78. They estimate the possible error, however, as about 1.5 entropy units. The moment of inertia tabulated is that required to give the best agreement with the experimental heat-capacity data. The Fulcher[20] bands of hydrogen give 1.9×10^{-41} g. cm.^{2} for the moment of inertia and this agree-

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[13] Imes, *Astrophys. J.*, **50**, 251 (1919).

[14] v. Bahr, *Verh. deut. phys. Ges.*, **15**, 726 (1913).

[15] Warburg and Leithauser, *Ann. Physik*, **28**, 313 (1909).

[16] W. L. Bragg, *Phil. Mag.*, **40**, 169 (1920).

[17] Eastman, This Journal, **44**, 1008 (1922).

[18] Lewis, Gibson and Latimer, *ibid.*, **45**, 80 (1923).

[19] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923.**

[20] Fulcher, *Astrophys. J.*, **37**, 60 (1913).

ment is satisfactory. The calculated entropy for hydrogen fluoride is for the unassociated gas and therefore is not exact. The formula should give correct values at 90° or above for this gas, since it is practically all dissociated at these temperatures. The agreement between the calculated and the observed values for hydrogen chloride, nitrogen, carbon monoxide, and nitric oxide are within the experimental limits of accuracy even though the deviation is quite large in the case of nitric oxide. The observed entropy for nitric oxide is calculated from equilibrium measurements of Haber for the reaction, $N_2 + O_2 = 2\ NO$, in the neighborhood of 2500°. This calculation then requires a very great extrapolation since the heat capacity of nitric oxide has been determined only at a few points at room temperatures and below by Heuse.[21] These data indicate that the entropy of nitric oxide at 298° K. is less than that given above for the observed value. However, we may be dealing with a gas which does not follow the equation given. This point will be discussed further in connection with oxygen.

An error of 1% in the moment of inertia makes an error of only 0.02 entropy unit. The error in the constant due to the probable error in h^2, since h is 6.5543 ± 0.0025,[22] would be entirely negligible. The accuracy of the constant is, therefore, limited by the accuracy with which we can plot the experimental points and count the squares. This we estimate as about 0.01 unit and the probable error of the monatomic gas constant is ±0.01. Then the greatest error in the constant for a diatomic gas is 0.02 entropy unit. Since the values of I for nitrogen, hydrogen fluoride, hydrogen chloride and hydrogen bromide are accurate to about 1%, these entropies are accurate to about 0.04 entropy units. It is difficult to estimate the probable errors in the moments of inertia of carbon monoxide and nitric oxide since the lines have not been resolved. A rough estimate of the errors in these moments of inertia is 10% and this gives an error of ±0.2 entropy unit for these gases. This estimate for nitric oxide is on the assumption that the above equation applies.

Further checks on this equation can be secured by calculating the moments of inertia and the distances between nuclei from observed entropies. Table II gives the results of three such calculations.

TABLE II

THE MOMENT OF INERTIA OF DIATOMIC GASES

Substance	$I \times 10^{40}$	$I \times 10^{8}$	$r \times 10^{8}$	S_{298}(obs)	Reference
O_2	41	1.8	0.65	48.0	5
HI	4	1.6	1.40 (I)	47.5	23
Cl_2	109	1.9	1.05	52.6	23

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[21] Heuse, *Ann. Physik*, [4] **59**, 94 (1918).

[22] Birge, *Phys. Rev. N. S.*, **14**, 361 (1919).

[23] Eastman, THIS JOURNAL, **45**, 80 (1923).

It is interesting to note that the distance between nuclei secured for hydrogen iodide is about that predicted from the data on hydrogen fluoride, chloride and bromide from band spectra (See Table I). Chlorine has a heat capacity at constant volume somewhat greater than $5/2\ R$ but the entropy due to vibrational heat capacity is not large and the distance between nuclei calculated seems to be quite reasonable. If the entropy is in error by 1 entropy unit, a factor of 1.286 must be applied to the distance between nuclei.

A comparison with the radii of atoms given by Bragg shows that the distances calculated from band spectra and from the entropy equation are somewhat less than Bragg's data, except in the case of oxygen. It seems very likely that the distances between nuclei in the gaseous state should differ somewhat from those in the solid state; but since oxygen differs more than the others and in the opposite sense and since the distance between nuclei in nitric oxide is 1.08×10^{-8}, in nitrogen is 1.13×10^{-8} and in carbon monoxide is 1.14×10^{-4}, it seems very probable that oxygen does not follow Equation 6. Also a study of its band spectrum by Runge[24] showed that it is quite peculiar in that half quantum numbers appear to be necessary to account for the positions of the lines. A similar fact was observed by Curtis[25] for the band spectrum of helium. It may be also that nitric oxide belongs with oxygen and helium in this respect. The entropy calculated for nitric oxide is less than that observed and if we used 1.1×10^{-8} as the distance between nuclei for oxygen the entropy calculated would also be too low. Moreover, these two gases are paramagnetic and it may be that this unusual type of band spectrum and the high entropy may be related to the magnetic character. We can look at this question in another way. If the atoms have tetrahedral symmetry and in nitric oxide, carbon monoxide, and nitrogen we imagine them placed with 2 faces in coincidence and in oxygen with 2 edges in coincidence, the ratio of the distances between centers would be 1.73, and this would explain the difference. However, a more complete investigation of the band spectra of these gases is necessary before this question can be answered.

The Entropy of Diatomic Gases Having Vibrational Energy

The vibrational energy of diatomic molecules seems to be due to an inharmonic oscillator so that they do not have a fundamental frequency of which all others are exact multiples. If the oscillator were harmonic in character we could expect that the vibrational heat capacity would be the same function of the fundamental frequency and that, therefore, a constant for the entropy due to vibrational heat capacity could be secured in a manner similar to that employed in getting the constant for entropy of rotation. The vibrational frequencies are given by the equation $\nu = n\nu_0\ (1 + nx)$

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[24] Runge, *Physica*, **1**, 254 (1921).

[25] Curtis, *Proc. Roy. Soc.*, **89**, 146 (1914).

in which ν_0 and x are constants characteristic of the gas. Therefore, it seems that no constant can be secured for the entropy due to this heat capacity. It would be of great interest to secure the heat capacity of such a gas as chlorine, bromine or iodine over a range of temperature of 0° to a few hundred degrees. Lenz[26] has interpreted certain lines in the fluorescent spectrum of iodine secured by Wood as being due to vibrational changes. These give $\nu_0 = 213$ and x as very nearly equal to zero. The correlation of such data with heat capacities and entropies would be highly desirable but at the present time we do not have sufficient data on heat capacities and band spectra of the same gases to do this.

Entropy of Polyatomic Gases

Sufficient heat-capacity data on polyatomic gases are not yet available to permit a similar calculation of the entropy constants for gases of this type except in the case of gases whose molecules have tetrahedral symmetry. By using the method of Reiche for the dumbbell molecule, but setting all three moments of inertia equal to I instead of two equal to I and the third about the figure axis equal to L, and quantizing in exactly the same way, we find for the rotational heat capacity

$$C_r = R\sigma^2 \frac{d^2 \ln Q}{d\sigma^2} \tag{9}$$

where

$$Q = \Sigma\Sigma\Sigma\, e^{-\frac{h^2}{8\pi^2 kT}\left[\frac{(n_1 + n_2)^2 - n^2_3}{I} + \frac{n^2_3}{I}\right]}, \text{if } n_2 > n_3,$$

and

$$Q = \Sigma\Sigma\Sigma\, e^{-\frac{h^2}{8\pi^2 kT}\left[\frac{(n_1 + n_3)^2 - n^2_3}{I} + \frac{n^2_3}{I}\right]}, \text{if } n_2 < n_3,$$

and

$$\sigma = \frac{h^2}{8\pi^2 I kT}.$$

The n_3 terms are retained in order to get the probabilities of the energy states. If the summations are carried out over all integral values of n_2 from 1 to ∞ and n_1 and n_3 from 0 to ∞ following the same general rule used by Reiche in securing his equation for hydrogen, namely, that the azimuthal quantum number cannot be 0, and setting $n = n_1 + n_2$, if $n_2 > n_3$, or $n = n_1 + n_3$, if $n_2 < n_3$, we find

$$Q = \sum_1^\infty n^2 e^{-n^2\sigma} \tag{10}$$

At high temperatures this can be transformed into the integral

$$\int_0^\infty n^2 e^{-n^2\sigma}\, dn = \frac{1}{4}\sqrt{\frac{\pi}{\sigma^3}}$$

and this gives a value for C_r of $3/2\,R$ as demanded by classical theory. If we carry out the summation for n_2 from 0 to ∞ as well as for n_1 and n_3 we find

$$Q = \sum_0^\infty (n + 1)^2 e^{-n^2}.$$

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[26] Lenz, *Physik. Z.*, **21**, 291 (1920).

Other ways of summing these states could be employed but we shall use Equation 10, since this follows the same rule as that used successfully in the case of hydrogen. Table III, Col. 3, gives the values of C_r/R calculated from Equations 9 and 10 using 2.232×10^{-41} g. cm.^{2} for the moment of inertia. The curve for these values passes through the lower experimental points as shown in Fig. 2. The points plotted are the experimental data of Muller,[27] Masson,[27] Capstick,[27] Millar,[28] Heuse,[21] and Dixon, Campbell and Parker[29] for methane. This agreement is not satisfactory and from other considerations which follow, we believe that the values secured at 142° and 158° K. are in error. Assuming that the hydrogen nuclei are at the corners of a tetrahedron the moment of inertia used for this curve gives 0.37×10^{-4} cm. as the distance between the hydrogen nuclei. This distance seems to be too small when compared with the distance secured for diatomic gases given in Tables I and II.

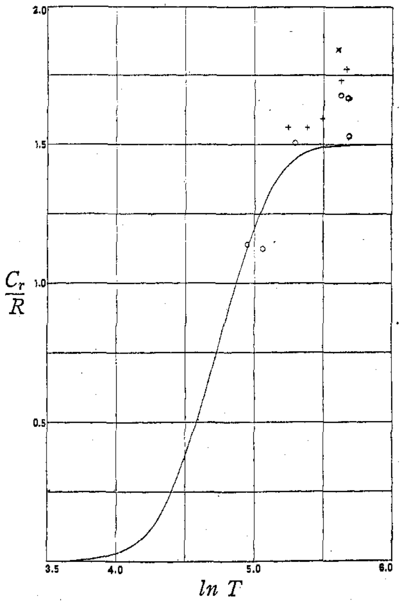

Fig. 2.—Heat-capacity curve for gases with tetrahedral symmetry. Heat capacity of methane.

× Dixon, Campbell and Parker

O Millar ⟜ Capstick

+ Heuse ṓ Masson

Using Equations 9 and 10 and employing the same reasoning as used in securing the constant of Equation 6, we find for the entropy equations for a polyatomic gas whose molecules have tetrahedral symmetry

$$S = R\, ln\, T^{3/2}M^{3/2}V - 11.39 + {}^{3}/{}_{2}\, R\, ln\, T + R\, ln\, I + 99.14$$

or

$$S = R\, ln\, T^{3}M^{3/2}VI + 87.75. \qquad (11)$$

The entropy of methane calculated by this equation using $I = 2.232 \times 10^{-41}$ is 34.25 entropy units. Moreover, any curve drawn through the two lower points and falling off rather rapidly to $C_p = 5/2\ R$ as all observed heat capacity curves do, (for example the curve of any solid or of hydrogen gas) would give an entropy for methane approximately the same as that calculated by equation (11). However, Lewis and Randall[19] get from equilibrium measurements for the reaction, $C + 2\ H_2 = CH_4$, 41 entropy units, and this does not seem to be in error by more than 2 units. It seems im-

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[27] See Haber "Thermodynamics of Technical Gas Reactions," Longmans and Co., pp. 236, 239.

[28] Millar, *Thesis* for degree of Doctor of Philosophy, University of California, 1922.

[29] Dixon, Campbell and Parker, *Proc. Roy. Soc.*, **100A**, 1 (1921).

possible, therefore, to reconcile these two sets of data with the suggestion used so successfully for diatomic gases, namely.

$$S = R\ ln\ T^{3/2}M^{3/2}\ V - 11.39 + \int_0^T C_r\ d\ ln\ T.$$

If the entropy of methane is taken as 41 and the reverse calculation made by Equation 11 we find 2.14 × 10^{-41} g. cm.^{2} for the moment of inertia, 1.13 × 10^{-8} cm. for the distance between the hydrogen nuclei and 0.69 × 10^{-8} cm. for the distance between the hydrogen and carbon nuclei. Cols. 1 and 3 of Table III give the data on the heat-capacity curve using this moment of inertia. As above, a factor of 1.286 must be applied to the distances if the entropy is in error by 1 unit. These quantities are in agreement with what would be expected from Bragg's calculations within the wide limits of error of our calculation. We believe this agreement justifies the conclusion that the lower heat capacity data are incorrect and that Equation 11 gives a correct relationship between the moment of inertia and the entropy of this type of gas.

TABLE III

HEAT CAPACITY OF METHANE

C_r/R	T $I = 2.232 \times 10^{-41}$	T $I = 2.14 \times 10^{-40}$	C_r/R	T $I = 2.232 \times 10^{-41}$	T $I = 2.14 \times 10^{-40}$
.0066	44.81	4.673	1.2711	156.9	16.36
.0262	53.78	5.608	1.3921	179.3	18.69
.0351	58.25	6.074	1.4513	201.7	21.03
.0913	67.22	7.010	1.4801	224.1	23.37
.1791	76.17	7.943	1.4920	246.5	25.70
.3667	89.62	9.345	1.4967	268.9	28.04
.7336	192.0	11.68	1.4998	448.1	46.73
1.0555	134.4	14.02	....	....	....

The entropy equation (11) for gases whose molecules have tetrahedral symmetry is not nearly so useful at present as the equation for diatomic gases, since all such gases and vapors for which we have secured heat capacity data have more than 6 degrees of freedom and, therefore, must have vibrational heat capacity. This equation is suggested only for gases having 3 degrees of rotational freedom and no energy of vibration at the temperature at which the entropy is to be calculated. It is possible that the equation could be applied to silicane, SiH_4. However, the greatest value of this constant must be in its possible use in getting the entropy of gases having vibrational energy since the entropy of any gas should be

$$S = R\ ln\ T^{3/2}M^{3/2}V - 11.39 + \int_0^T C_r\, d\, ln + \int_0^T C_v\ d\ ln\ T \qquad (12)$$

where C_v refers to vibrational heat capacity. For a diatomic gas this becomes

$$S = R\ ln\ T^{5/2}M^{3/2}VI + 56.17 + \int_0^T C_v\ d\ ln\ T, \qquad (13)$$

and for a gas with tetrahedral symmetry

$$S = R \ln T^3 M^{3/2} VI + 87.75 + \int_0^T C_v \, d \ln T. \qquad (14)$$

Equations 13 and 14 point out the importance of evaluating the last terms from band spectra.

The author wishes to thank Professor R. T. Birge of the Department of Physics at this institution for his help in interpreting the band spectra data, and the members of this department for many valuable suggestions.

Summary

1. The entropy constant for diatomic gases having no vibrational energy is evaluated.

2. The entropies of hydrogen, hydrogen fluoride, hydrogen chloride, hydrogen bromide, nitrogen, carbon monoxide and nitric oxide are calculated from the equation secured and comparisons made where possible with experimental entropy determinations.

3. The moments of inertia of oxygen, hydrogen iodide and chlorine are calculated from their observed entropies and attention is called to the probability that oxygen and possibly nitric oxide do not follow the equation given.

4. The entropy equation for diatomic gases having vibrational heat capacity is discussed.

5. The constant for the entropy equation of gases whose molecules have tetrahedral symmetry is secured and the dimensions of the methane molecule are calculated.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE HEAT OF SOLUTION OF THALLIUM IN DILUTE THALLIUM AMALGAMS

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In connection with a study of the properties of solid thallium amalgams[1] an investigation of the heat of solution of thallium in mercury and in dilute thallium amalgams was commenced. The preliminary results obtained appear to possess interest by virtue of their bearing upon recently published work dealing with the thermodynamics of these amalgams.

The negative heat of solution of thallium in fairly concentrated liquid amalgams had been previously determined[2] by an isothermal method, which was applicable only to endothermic changes and could not, there-

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[1] Richards and Smyth, THIS JOURNAL, **44**, 524 (1922).

[2] Richards and Daniels, *ibid.*, **41**, 1756 (1919).