3. The temperature coefficient between 15° and 35° was found to be a linear function of the electromotive force. It decreased from 0.0000028 volts per degree for cells with an electromotive force of 1.01827 volts to —0.000013 volts per degree for cells with an electromotive force of 1.0210 volts, being zero for a cell with an electromotive force of 1.01873 volts.

4. Normal cells with electrolytes made by saturating a 0.015 *M* sulfuric acid solution with hydrated cadmium sulfate behaved in accordance with Wolff's temperature formula.

5. Mercurous sulfate prepared by reduction of mercuric sulfate with formaldehyde at 100° was no different in its behavior in normal cells from the electroltyic salt.

6. The differential heat of solution of hydrated cadmium sulfate in a slightly acid saturated solution was calculated.

NEWPORT, RHODE ISLAND

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 30]

THE ENTROPY OF DIATOMIC GASES AND ROTATIONAL SPECIFIC HEAT

BY RICHARD C. TOLMAN AND RICHARD M. BADGER

Received July 3, 1923

I. Introduction

Assuming the rigid "dumb-bell" model, the entropy of a diatomic gas at temperatures high enough so that the specific heat at constant pressure has become 7/2 *R*, is given by the equation

$$S = {}^7/_2\, RlnT - Rlnp + {}^3/_2\, RlnM + RlnJ + S_2 \tag{1}$$

where T is the absolute temperature, p is the pressure, M the molecular weight, J the moment of inertia of the molecule and S_2 a constant which has the same value for all diatomic gases composed of molecules of the assumed model. This equation has been derived by Tetrode,[1] Sackur[2] and Schames[3] on the basis of the quantum theory and by Tolman[4] from the theory of similitude or relativity of size, and using kinetic-theory data for calculating moments of inertia, has been shown[4] to agree with the available experimental data.

An important advance in the use of Equation 1 has been made by Urey.[5] In the first place he has used moments of inertia obtained from spectral data instead of kinetic-theory data in testing the equation,[6] and in the

---

[1] Tetrode, *Ann. Physik*, **38**, 434 (1912).

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

[3] Schames, *Physik. Z.*, **21**, 38 (1920).

[4] Tolman, THIS JOURNAL, **43**, 866 (1921).

[5] Urey, *ibid.*, **45**, 1445 (1923).

[6] Compare also Eucken, *Jahrb. Radioakt. Elektronik.* **16**, 361 (1920); *Z. Elektrochem.* **26**, 377 (1920).

second place he has obtained a theoretical value for the constant S_2 by making use of one of Reiche's equations for the rotational specific heat of diatomic gases. This latter possibility is of great interest since the work of Tetrode, Sackur and Schames did not make the theoretical value of this constant by any means certain, while the theory of the relativity of size gives no information as to the theoretical value of the constant.

Urey's method for determining the constant S_2 involved a laborious calculation of the whole rotational specific-heat curve from the absolute zero to a temperature where the rotational specific heat is approximately equal to R, followed by a graphical integration under this curve to determine the rotational entropy at the higher temperature, and was applied to only one of the several theoretical formulas for rotational specific heat which have been proposed. It is the purpose of the present article to show a simple mathematical method for obtaining the value of S_2 from various theoretical formulas for rotational specific heat, to apply the method to the 5 different formulas considered by Reiche[7] and to the new formula based on half-quantum numbers recently considered by Tolman,[8] and to compare the results obtained with the available experimental data.

II. The Additivity of Translational and other Forms of Entropy

The calculations presented in this article will be based on the assumption that the entropy of a gas can be calculated by putting it equal to the sum of the entropy given by the Sackur[9] equation, which it would have as a perfect monatomic gas, plus the additional quantity of entropy which corresponds to the increase in the value of the specific heat C_p over $5/2\ R$ as we proceed up from the absolute zero; in other words, that the total entropy is given by the equation

$$S = {}^5/_2 R \ln T - R \ln p + {}^3/_2 R \ln M + S_1 + \int_0^T (C_p - {}^5/_2 R) \frac{dT}{T} \qquad (2)$$

The above hypothesis was proposed by Tolman[10] and found to be correct within the probable limits of experimental knowledge for the case of the entropy of diatomic hydrogen at 25° using actual specific-heat data for the evaluation of the last term in Equation 2. No claim is made as to the theoretical justification for this hypothesis. An equivalent hypothesis was earlier employed by Langen[11] for the calculation of Nernst's chemical constants, making use, however, of the theoretically incorrect Einstein-Stern equation for the specific heat of diatomic gases.

---

[7] Reiche, *Ann. Physik,* **58,** 657 (1919).

[8] Tolman, "Rotational Specific Heat and Half Quantum Numbers," to appear shortly in the *Physical Review.*

[9] Sackur, *Ann. Physik,* **36,** 968 (1911); **40,** 67 (1913).

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

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

III. General Equation for Rotational Specific Heat

Except for the case of diatomic hydrogen, we have no experimental specific-heat data that would permit the direct evaluation of the last term in Equation 2 and must resort to some theoretical expression for calculating the excess specific heat due to the rotation of our "dumb-bell" molecules.

For convenience let us define the quantities Q and σ by the equations

$$Q = \Sigma p_m e^{-m^2\sigma} \tag{3}$$

and

$$\sigma = \frac{h^2}{8\pi^2 JkT} \tag{4}$$

where p_m is the a-priori probability that a molecule will have the azimuthal quantum number m, J is the moment of inertia of the rigid "dumb-bell" molecule, h, k, and T have their usual significance and the summation Σ is to be taken over all the possible rotational states. It can then easily be shown[7] that the rotational specific heat is given by the equation

$$C_R = R\sigma^2 \frac{d^2 \ln Q}{d\sigma^2} \tag{5}$$

IV. Integration between Zero and T

With the help of Equation 5 we obtain for the rotational entropy at temperature T the expression

$$S_R = \int_0^T R\sigma^2 \frac{d^2 \ln Q}{d\sigma^2}\, d \ln T$$

Introducing the relation between σ and T given by Equation 4, we can transform the above expression as follows,

$$S_R = -\int_0^T R\sigma^2 \frac{d^2 \ln Q}{d\sigma^2}\, d \ln \sigma = R\left[\ln Q - \sigma \frac{d \ln Q}{d\sigma}\right]_0^T$$

$$= R\left(\ln Q_T - \sigma_T \frac{d \ln Q_T}{d\sigma} - \ln Q_0 + \sigma_0 \frac{d \ln Q_0}{d\sigma}\right) \tag{6}$$

Since the different theories of specific heat usually lead to simple expressions for $\ln Q$ at very low temperatures and at temperatures high enough so that the rotational specific heat has become R, the above expression for rotational entropy can easily be evaluated in the cases of interest without the necessity of determining the whole specific-heat curve.

V. Values of Q Given by Different Theories

Different hypotheses as to the value of the lowest possible azimuthal quantum number, and as to the relation between quantum number and a-priori probability have led to different expressions for Q. The following expressions for Q will be tested in this paper,—

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

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

III. $Q = \sum_1^\infty (2m+1)e^{-m^2\sigma}$

IV. $Q = \sum_1^\infty (m+1)e^{-m^2\sigma}$

V. $Q = \sum_1^\infty 2m\, e^{-m^2\sigma}$

VI. $Q = \sum_1^\infty 2n\, e^{-(n-1/2)^2\sigma}$

The first five of these expressions are the ones which were derived by Reiche[7] on the basis of the first form of quantum theory and different assumptions as to the lowest quantum number and as to a-priori probabilities, and the sixth is the one discussed by Tolman[8] derived on the new assumption that the lowest possible azimuthal quantum number is $^1/_2$. A statement of the hypotheses which have led to these different expressions for Q will be found in the paper of Tolman.[8] The expressions I and II are intrinsically not very probable since they lead to specific-heat curves with maxima at temperatures lower than the final asymptotic approach to the value R.

VI. Evaluation of Rotational Entropy

We may now evaluate the rotational entropy as given by Equation 6 for the above six cases.

Case I. $Q = \sum\limits_0^\infty (2\,m + 1)e^{-m^2\sigma}$. At high temperatures we may evidently write the approximations

$$Q_T = \int_0^\infty (2\,m + 1)e^{-m^2\sigma}\,dm = \frac{1}{\sigma_T}\left(1 + \frac{1}{2}\sqrt{\pi\sigma_T}\right)$$

$$ln\,Q_T = -ln\,\sigma_T + \frac{1}{2}\sqrt{\pi\sigma_T},\ \text{and}\ \frac{d\,ln\,Q_T}{d\,\sigma} = -\frac{1}{\sigma_T} + \frac{1}{4}\sqrt{\frac{\pi}{\sigma_T}}$$

and at low temperatures the approximations

$$Q_0 = 1 + 3\,e^{-\sigma_0},\ ln\,Q_0 = 3\,e^{-\sigma_0}\ \text{and}\ \frac{d\,ln\,Q_0}{d\,\sigma} = -3\,e^{-\sigma_0}$$

Substituting into Equation 6, for the rotational entropy at temperature T, we obtain

$$S_R = R(-ln\,\sigma_T + \frac{1}{2}\sqrt{\pi\sigma_T} + 1 - \frac{1}{4}\sqrt{\pi\sigma_T} - 3\,e^{-\sigma_0} - 3\sigma_0\,e^{-\sigma_0})$$

Returning now to Equation 4 by which σ was defined

$$\sigma = \frac{h^2}{8\pi^2JkT}$$

we see that σ approaches zero at high temperatures and infinity at low temperatures so that for the case in which we are interested we have

$$S_R = R\,ln\,T + R\,ln\,J + R\,ln\frac{8\,\pi^2\,k}{h^2} + R \qquad (7)$$

and substituting S_R for $\int_0^T (C_p - {^5/_2}\,R)\,d\,ln\,T$ in Equation 2 we obtain for the total entropy of our diatomic gas

$$S = {^7/_2}\,R\,ln\,T - R\,ln\,p + {^3/_2}\,R\,ln\,M + R\,ln\,J + \left(S_1 + R\,ln\frac{8\,\pi^2\,k}{h^2} + R\right) \qquad (8)$$

where

$$S_2 = S_1 + R\,ln\,\frac{8\,\pi^2\,k}{h^2} + R \qquad (9)$$

is the constant of the entropy equation.

Since Reiche[7] and Tolman[8] have given simple values for $ln\,Q$ at high and low temperatures for the other theories of rotational specific heat, an entirely similar method of calculation can be used for evaluating the constants, using the other forms of Q that have been proposed. The results are given in Table I.

The second column gives the form of Q that has been considered and the third column the form found for S_2. Expressing entropies in calories per degree per mole, pressure in atmospheres, molecular weight in grams per mole, moment of inertia in grams cm. squared per mole, and using Lewis'[12] value, —2.63, for S_1, we have calculated the numerical values of S_2 given in the fourth column.

Since we shall generally be interested in the value for the entropy of gases at 1 atmosphere pressure and 25° C. = 298.1° K., we may substitute these values of pressure and temperature in Equation 1 and rewrite it in the form

$$S^\circ_{298\cdot1} = {}^3/_2 R\,ln\,M + R\,ln\,J + C_{298\cdot1} \qquad (10)$$

Numerical values of $C_{298\cdot1}$ are given in the last column of Table I.

TABLE I

SUMMARY OF RESULTS

Case	Form of Q	Form of S_2	S_2	$C_{298\cdot1}$
I	$\sum_0^\infty (2\,m+1)e^{-m^2\sigma}$	$S_1 + R\,ln\,\frac{8\pi^2 k}{h^2} + R$	66.30	105.95
II	$\sum_0^\infty (m+1)e^{-m^2\sigma}$	$S_1 + R\,ln\,\frac{8\pi^2 k}{h^2} + R - R\,ln\,2$	64.92	104.57
III	$\sum_1^\infty (2\,m+1)e^{-m^2\sigma}$	$S_1 + R\,ln\,\frac{8\pi^2 k}{h^2} + R - R\,ln\,3$	64.12	103.77
IV	$\sum_1^\infty (m+1)e^{-m^2\sigma}$	$S_1 + R\,ln\,\frac{8\pi^2 k}{h^2} + R - 2R\,ln\,2$	63.54	103.19
V	$\sum_1^\infty 2\,m\,e^{-m^2\sigma}$	$S_1 + R\,ln\,\frac{8\pi^2 k}{h^2} + R - R\,ln\,2$	64.92	104.57
VI	$\sum_1^\infty 2\,n\,e^{-(n-1/2)^2\sigma}$	$S_1 + R\,ln\,\frac{8\pi^2 k}{h^2} + R - R\,ln\,2$	64.92	104.57

VII. Discussion of the Different Values of S_2

It will be noticed that three of the proposed theories of specific heat (II, V and VI) have led to the same value of S_2. Of these, Theory II is not entirely probable since it is based on the assumption that a-priori probabilities are to be calculated by counting positive and negative rotations only once, which does not agree with the Bohr correspondence principle. Theory V is perhaps as probable as any of those based on the assumption that the lowest possible azimuthal quantum number is unity, and Theory VI is the one based on the assumption that the lowest possible azimuthal quantum number is ${}^1/_2$.

Theory V is the one selected by Urey[5] for determining S_2 by graphical

---

[12] Lewis, *Phys. Rev.*, **18**, 121 (1921). See also Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 457.

integration under the specific-heat curve. Urey obtained in this way a value which, using our method of expression,[13] gives $S_2 = 64.93$, while we have obtained by a more direct mathematical treatment the practically identical value, $S_2 = 64.92$.

Since the different theoretical values for S_2 differ among themselves by a maximum of less than 3 cal./mole deg., an experimental decision as to the correct value for S_2 is difficult. Accurate values for the entropy and moment of inertia are both needed, the possible deviation from the assumed rigid "dumb-bell" model must be considered, and the assumption that the specific-heat curve has already reached the value $C_p = 7/2\,R$ must be scrutinized.

Moments of inertia calculated from the *classical* formula for the wave lengths of the maxima of infra-red double bands

$$J = kT\left\{\frac{\lambda_1\,\lambda_2}{\pi c\,(\lambda_2-\lambda_1)}\right\}^2$$

are evidently less suitable for exact tests than those calculated on the basis of the quantum theory from a complete knowledge of the rotation spectrum, and moments of inertia calculated on the basis of the quantum theory from band or many-lined spectra in the visible or ultraviolet are not completely satisfactory since they presumably correspond to the molecule in an excited condition rather than in the normal condition which contributes to specific heat at moderate temperatures.

The following table presents all the figures for the calculated and experimental values of the entropy of diatomic gases at 25° C. and 1 atmosphere that we have felt justified in including. The data upon which some of the figures are based are far from satisfactory, as will be indicated in the discussion that follows. Hydrogen has been omitted since the specific heat is still considerably below $7/2\,R$ at 25°, and the moment of inertia would have to be obtained from the many-lined spectrum that corresponds to an excited condition of the molecule. Carbon dioxide and hydrogen cyanide have been included since the spectral data for these substances indicate that the structure of the molecule is linear and that they behave like rigid diatomic molecules.

The first column of the table gives the formula of the substance, the second column the value of the moment of inertia in grams cm. squared which was used for the calculation, the third column the experimental value of the entropy as determined by thermodynamic methods, and the remaining columns the values of the calculated entropies using the six different formulas developed in this paper, together with the deviations from the experimental values. The values of entropy calculated by the three formulas II, V and VI which agree have been put in a single column.

---

[13] Urey used volumes instead of pressures in his entropy equation. It is easy to show that the constants for the two methods of expression differ by $R\ ln\ R$.

The values of the moments of inertia for the first four gases in Table II are the ones used by Urey.[5] The value for hydrogen chloride is based on Ime's data for the infra-red bands and hence is very accurate. The value for nitrogen is from the constant $2B$ for the 3883 cyanogen band as given by Kratzer, and hence suffers from the grave doubt as to whether this band is due to nitrogen or cyanogen. The values for carbon monoxide and nitric oxide are calculated by the classical formula from the separation of the maxima of infra-red bands and hence are not exact.

TABLE II

$S_{298\cdot1}$ FOR GASES WITH A LINEAR MOLECULE

Substance	$J \times 10^{40}$	S exptl.	S_{I}	Dev.	S_{III}	Dev.	S_{IV}	Dev.	$S_{\mathrm{II, V, VI}}$	Dev.
HCl	2.594	43.3	44.3	1.0	42.1	1.2	41.6	1.7	42.9	0.4
N_2	14.4	45.6	46.9	1.3	44.8	0.8	44.2	1.4	45.6	0.0
CO	14.7	45.6	47.0	1.4	44.8	0.8	44.2	1.4	45.6	0.0
NO	14.3	49.3	47.1	2.2	45.0	4.3	44.4	4.9	45.8	3.5
CO_2	50	49.4	50.8	1.4	48.6	0.8	48.0	1.4	49.4	0.0
HCN	33	49.1	48.9	0.2	46.3	2.8	45.7	3.4	47.1	2.0

The treatment of carbon dioxide is based on the assumption that this behaves like a diatomic gas with the carbon atom in the middle between the oxygen atoms. The moment of inertia is that obtained by Barker[14] from infra-red spectra, who concludes from the spectral data that the molecule is linear in structure rather than triangular. It is a matter of great interest that the inverse calculation of the moment of inertia of carbon dioxide from thermodynamic data was made by Eucken,[15] before Barker's results were known. Eucken in his calculations used the language of Nernst's chemical constants rather than that of entropy and used what was equivalent to an empirical rather than a theoretical value for the constant S_2. He obtained the value for carbon-dioxide $J = 50 \times 10^{-40}$ g. cm. squared in complete agreement with the later spectral work of Barker who was himself unfamiliar with Eucken's work, which had appeared only a few months earlier.

Hydrogen cyanide is also treated as a rigid linear structure. The moment of inertia has been calculated from the separation between the maxima $\lambda_1 = 13.60\mu$, and $\lambda_2 = 14.33\mu$ measured by Burmeister.[16] The spectral data now available show no evidence of a third moment of inertia. If we assume radii for the atoms that are consistent with those found for these same atoms in other gases, it seems necessary to assume that the hydrogen atom is between the carbon and nitrogen atoms in order to account for the large moment of inertia, $J = 33 \times 13^{-40}$. The assumption of such a structure is undoubtedly bizarre but finds some support from the theory of hydrogen bonds proposed by Latimer and Rodebush.[17]

[14] Barker, *Astrophys. J.*, **55**, 391 (1922).

[15] Eucken, *Z. physik. Chem.*, **100**, 159 (1922).

[16] Burmeister, *Verh. D. phys. Geo.*, **15**, 589 (1913).

[17] Latimer and Rodebush, THIS JOURNAL, **42**, 1431 (1920).

The experimental values of the entropies of the diatomic gases are those given by Eastman.[18] The experimental values for the triatomic gases have been calculated from the free-energy data of Lewis and Randall.[19] The values for nitric oxide and hydrogen cyanide may be greatly in error owing to the insufficiency of the thermodynamic data.

It would be dangerous to draw from the figures in Table II an absolutely definite conclusion as to the correct theory of rotational specific heat and rotational entropy. The derivations assumed are (1) a rigid dumb-bell molecule whose moment of inertia does not change with speed of rotation, (2) rotational energy for the molecule but no vibrational energy, (3) a specific-heat curve that has already reached 7/2 R at the temperature in question. Our spectral knowledge of hydrogen chloride is enough to tell us that Conditions 1 and 2 will be nearly met by this molecule, but the assumption that the specific heat is already 7/2 R is not justified for this gas at 25°C., owing to the small value of J. Nitrogen must be excluded for an exact test owing to the probability that the bands used belong to cyanogen rather than nitrogen. Carbon monoxide and nitric oxide are unsuitable for exact tests since their moments of inertia had to be calculated from the classical formula. Furthermore, the experimental value for the entropy of nitric oxide may be greatly in error. Carbon dioxide is not suitable since the value of the specific heat is apparently already greater than 7/2 R at 25°. Finally, in the case of hydrogen cyanide both the spectral data and the thermodynamic data are unsatisfactory.

In spite of these difficulties, we feel that the tentative conclusion may be drawn in favor of the rotational entropy given alike by Theories II, V and VI. If we eliminate nitric oxide and hydrogen cyanide where the experimental values of the entropy may be greatly in error, we note an almost perfect correspondence between the experimental entropy and the value given by Theories II, V and VI. Under all the circumstances it would seem best to use for the present the values of S_2 and $C_{298\cdot1}$, given by these theories.

VIII. Summary

1. A direct mathematical method has been developed for determining the theoretical values of the constants S_2 and $C_{298\cdot1}$ in the equations for the entropy of diatomic gases,

$$S = {}^7/_2\, R\, ln\, T - R\, ln\, p + {}^3/_2\, R\, ln\, M + R\, ln\, J + S_2$$

$$S_{(298\cdot1^\circ,\ 1\ \mathrm{atm.})}, = {}^3/_2\, R\, ln\, M + R\, ln\, J\; C_{298\cdot1}$$

2. Six different theories which have been proposed for rotational specific heat all based on the first form of quantum theory, but based on different theories as to a-priori probabilities and as to the lowest possible

---

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

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

azimuthal quantum number, have been used to determine the theoretical values of S_2 and $C_{298\cdot 1}$ and the results compared with experimental values.

3. In the absence of further evidence, the best values for S_2 and $C_{298\cdot 1}$ are 64.92 and 104.57, respectively. (Entropy in calories, temperature in degrees centigrade absolute, pressure in atmospheres, molecular weight in grams per mole, moment of inertia in gram cm. squared per mole.)

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 31]

THE TEMPERATURE COEFFICIENT OF PHOTOCHEMICAL REACTION RATE

BY RICHARD C. TOLMAN

RECEIVED JULY 9, 1923

I. Introduction

Let us consider a photochemical reaction, aA + bB + . . . ⟶ Products, taking place at some given temperature T, under the influence of radiation from an external source, the frequency of the radiation being ν, and its energy density throughout the reacting mixture being u_ν. If we confine our attention to cases where the rate of reaction is proportional to the energy density u_ν and where the law of Guldberg and Waage is followed, we may write for the rate of the above reaction the expression,

$$-\frac{dC_A}{dt} = k_\nu u_\nu C_A^a C_B^b \dots \tag{1}$$

The quantity k_ν occurring in Equation 1 may be called the *specific photochemical reaction rate.* It is the rate at which the reaction would proceed if the reacting substances were present at *unit concentration* and subjected to radiant energy of frequency ν and *unit energy density.* The quantity k_ν is a parameter, independent of the concentration and energy density, but dependent on the temperature T and frequency ν. The temperature T is to be taken as that which would exist if the illumination from the external source were cut off. It is the purpose of the following article to present a theoretical treatment of the change in k_ν with T.

In an earlier article,[1] the writer has already shown that for a *monomolecular* photochemical reaction, the temperature coefficient of photochemical reaction rate will be given by the equation

$$\frac{\partial \ln k_\nu}{\partial T} = \frac{\bar{\bar{\epsilon}} - \bar{\epsilon}}{kT^2} \tag{2}$$

where $\bar{\bar{\epsilon}}$ is the average energy of the molecules which pick up radiant energy and react, $\bar{\epsilon}$ is the average energy of all the molecules and k is Boltzmann's constant. In the article referred to, the above equation

---

[1] Tolman, THIS JOURNAL, **42,** 2506 (1920).