

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

THE HYDROGEN, CHLORINE, HYDROGEN CHLORIDE EQUILIBRIUM AT HIGH TEMPERATURES

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RECEIVED OCTOBER 28, 1931

PUBLISHED MAY 7, 1932

The experimental investigation of chemical equilibria presents many difficulties. For gaseous equilibria nearly all of these are avoided when spectroscopic data are available for such determinations. Since the energy levels of molecules are independent of temperature the troublesome matters of temperature control and accurate measurements are eliminated. Moreover, even the higher energy levels may be excited for observation under conditions where the gas remains at conservative temperatures. Questions as to whether equilibrium has been reached, or if reached been shifted by quenching, do not enter. The energy levels of gas molecules at moderate pressures are independent of equilibrium conditions and in fact are usually best investigated under conditions where the gases exist separately.

The necessary equations and an example of their application have been given previously.¹

$$\frac{F^\circ - E_0^\circ}{T} = -\frac{3}{2}R \ln M - \frac{5}{2}R \ln T + R \ln P - C - R \ln R - R \ln Q \quad (1)$$

where $F^\circ = H^\circ - TS^\circ$ and the various symbols have their usual significance, the superscript referring to the standard state. E_0° is the energy of the molecules when all are in the lowest level ($T = 0^\circ\text{K.}$). $Q = \sum p e^{-\epsilon/kT}$ the summation being taken over all energy levels that are occupied by appreciable numbers of molecules. p is the *a priori* probability of the level concerned. The values of all constants used are those given by the "International Critical Tables." $R = 1.9869$ calories per mole per degree. $C + R \ln R = -7.267$ calories per mole per degree.

The amount of calculation involved in the evaluation of Q by means of summing the individual Boltzmann terms is very considerable except for the lighter molecules and low temperatures. Thus one of the principal purposes of this paper is to discuss an approximation method by which Q may be evaluated without loss in accuracy.

The rotational levels of a diatomic molecule are usually represented with a high degree of accuracy by the expression

$$\epsilon_r = Bm^2 + Dm^4 + Fm^6 + \dots \quad (2)$$

where $m = j + 1/2$ and j is the rotational quantum number. The terms Dm^4 , Fm^6 , etc., arise from the fact that molecules are not rigid. The effect of these terms becomes considerable at large values of m .

$$p = 2j + 1 = 2m$$

¹ (a) Giauque, *THIS JOURNAL*, **52**, 4808 (1930); (b) *ibid.*, **52**, 4816 (1930).

Then

$$\begin{aligned}
 Q &= \sum 2me^{-hc(Bm^2 + Dm^4 + Fm^6 + \dots)}/kT \\
 &= \sum 2me^{-Bhcm^2/kT} \cdot e^{-Dhcm^4/kT} \cdot e^{-Fhcm^6/kT} \dots \\
 &= \sum 2me^{-Bhcm^2/kT} \left[1 - \frac{Dhcm^4}{kT} + \frac{1}{2} \left(\frac{Dhcm^4}{kT} \right)^2 \dots \right] \\
 &\quad \left[1 - \frac{Fhcm^6}{kT} + \frac{1}{2} \left(\frac{Fhcm^6}{kT} \right)^2 \dots \right] \\
 &= \sum 2me^{-Bhcm^2/kT} \left[1 - \frac{Dhcm^4}{kT} - \frac{Fhcm^6}{kT} + \frac{1}{2} \left(\frac{Dhcm^4}{kT} \right)^2 + \right. \\
 &\quad \left. \left(\frac{Dhcm^4}{kT} \right) \left(\frac{Fhcm^6}{kT} \right) + \frac{1}{2} \left(\frac{Fhcm^6}{kT} \right)^2 \dots \right] \quad (3)
 \end{aligned}$$

As a first approximation integration may be substituted for summation, thus

$$\begin{aligned}
 Qe^{-\epsilon_0hc/kT} &= \int_0^\infty 2me^{-Bhcm^2/kT} dm - \int_0^\infty \frac{2Dhc}{kT} m^5 e^{-Bhcm^2/kT} dm - \\
 &\quad \int_0^\infty \frac{2Fhc}{kT} m^7 e^{-Bhcm^2/kT} dm + \int_0^\infty \left(\frac{Dhc}{kT} \right)^2 m^9 e^{-Bhcm^2/kT} dm + \\
 &\quad \int_0^\infty 2DF \left(\frac{hc}{kT} \right)^2 m^{11} e^{-Bhcm^2/kT} dm \dots \quad (4)
 \end{aligned}$$

The factor $e^{-\epsilon_0hc/kT}$ which accompanies Q is due to the fact that the integrals assume zero m as the reference point of energy whereas the reference point which we are to use is one in which $m = 1/2$. This is done since we believe it is preferable to confine our calculations to observable states.

Integrating

$$\begin{aligned}
 Qe^{-\epsilon_0hc/kT} &= \frac{kT}{Bhc} \left[1 - 2! \frac{D}{B^2} \left(\frac{kT}{hc} \right) - 3! \frac{F}{B^3} \left(\frac{kT}{hc} \right)^2 \right. \\
 &\quad \left. + \frac{4!}{2!} \frac{D^2}{B^4} \left(\frac{kT}{hc} \right)^2 + 5! \frac{DF}{B^5} \left(\frac{kT}{hc} \right)^3 \dots \right] \quad (5a)
 \end{aligned}$$

However, as is well known, the substitution of an integral for the summation of discrete terms introduces a small error. A treatment of this problem for the case of rigid diatomic molecules has been given by Mulholland² and by Sutherland.³

They find

$$\sum 2me^{-Bhcm^2/kT} = \frac{kT}{Bhc} \left[1 + \frac{Bhc}{12kT} \dots \right] \quad (6)$$

Investigation of the other integrals which are substituted for summations in Equation 4 shows that no appreciable error is introduced by this procedure. For example, it may be shown that

$$\sum 2m^5 e^{-Bhcm^2/kT} = \int_0^\infty 2m^5 e^{-Bhcm^2/kT} dm + \frac{31}{4032} + = \frac{2}{B^3} \left(\frac{kT}{hc} \right)^3 + \frac{31}{4032} + \quad (7)$$

in which the correction term may be shown to be negligible.

² Mulholland, *Proc. Camb. Philos. Soc.*, **24**, 280 (1928).

³ Sutherland, *ibid.*, **26**, 402 (1930).

The effect of the correction $(B/12)(hc/kT)$ is small compared to the effect of molecular stretching. Applying the above correction to Equation 5a we obtain

$$Qe^{-\epsilon_{hc}/kT} = \frac{kT}{Bhc} \left[1 + \frac{B}{12} \left(\frac{hc}{kT} \right) - 2! \frac{D}{B^2} \left(\frac{kT}{hc} \right) - 3! \frac{F}{B^3} \left(\frac{kT}{hc} \right)^2 + \frac{4! D^2}{2! B^4} \left(\frac{kT}{hc} \right)^2 + 5! \frac{DF}{B^5} \left(\frac{kT}{hc} \right)^3 \dots \right] \quad (5b)$$

This equation leads to values of Q which are more accurate than our requirement of 0.001 calorie per degree per mole in F/T . Equation 5a may be used to obtain the first and second derivatives of Q which are required for the calculation of energy and entropy and for heat capacity, respectively.

Sutherland used Q and its derivative, from Equation 6, to compute the entropy of nitric oxide by a formula which will be mentioned later. His calculation, which was made only for the boiling point temperature where the assumption of rigidity is a fair approximation, gave a result different by 0.03 E. U. from that obtained by Johnston and Giauque,⁴ who used the more accurate summation method. Since we could see no reason why Sutherland's method should not be accurate, a recalculation was made using his method and assumption and we find agreement with the value of Johnston and Giauque.

A comparison of the results of actual summations, which had previously been made, and values from the application of Equation 5a to hydrogen chloride is given in Table I, which also shows the relative importance of the corrections.

TABLE I

COMPARISON OF Q VALUES FOR HCl^{35} BY SUMMATION AND APPROXIMATION METHODS

T	$\frac{hc\epsilon_m = 1/2}{e^{kT}}$	$\times \frac{kT}{Bhc}$	$\times \left(1 + \frac{Bhc}{12kT} - \frac{D}{B^2} \frac{kT}{hc} - \text{etc.} \right)$	$Q \text{ approx.}$ $n = 1/2$	$Q \Sigma$ $n = 1/2$
1000	1.00374	\times	66.825 $(1 + 0.00125 + 0.00684)$	= 67.618	67.618
2000	1.00187	\times	133.651 $(1 + 0.00062 + 0.01386)$	= 135.84	135.85

Before proceeding to the calculation of the free energy it is necessary to consider the manner in which such calculations are affected by the existence of isotopic molecules. It has long been recognized that the thermodynamic consequences of isotopes affect the reactants and products concerned in a chemical reaction at or above ordinary temperature in such a way as virtually to cancel the free energy effect. Nevertheless, it has seemed worth while to present figures showing the actual magnitude of such effects. Usually, accurate band spectra data apply to the predominant isotopic molecule. However, this is sufficient since the corresponding levels for the others may be easily and accurately calculated from those of the predominant one. The method of making this calcula-

⁴ Johnston and Giauque, *THIS JOURNAL*, 51, 3194 (1929).

tion has been carefully considered by Mulliken.⁵ Since the law of force binding the molecule is independent of the particular isotope considered, it may be shown that the constant B in Equation 2 is inversely proportional to the reduced mass μ where $\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$. D varies as μ^{-2} and F as μ^{-3} . In the case of vibrational levels where

$$\epsilon_v = (v + 1/2)\omega_e + (v + 1/2)^2 \chi_e \omega_e + (v + 1/2)^3 y_e \omega_e \quad (8)$$

$\mu^{-1/2}$ occurs in each term to the same power as $(v + 1/2)$. Thus the first term varies as $\mu^{-1/2}$, the second as μ^{-1} , etc.

The Free Energy of Diatomic Chlorine.—For the Cl_2 molecule the calculation of the Q function was made for the Cl_2^{35-35} molecule and the values for the Q 's of Cl_2^{35-37} and Cl_2^{37-37} were then obtained by the application of correction factors based on the above equations. We shall not give the details of the above calculation as it should not be necessary to duplicate it for other cases when the negligible extent to which isotopic differences affect the distribution of atoms is made apparent.

The molecular constants of the chlorine molecule are given in Table II. They were taken from the work of Elliott.⁶

B_v and D_v may be represented by the expressions

$$\begin{aligned} B_v &= B_e + \alpha(v + 1/2) \\ D_v &= D_e + \beta(v + 1/2) \end{aligned}$$

In computing the isotope effect α varies as $\mu^{-3/2}$ and β varies as $\mu^{-5/2}$.

TABLE II

CONSTANTS IN THE ENERGY EQUATION OF THE CHLORINE 35-35 MOLECULE IN CM.^{-1}

Normal State:

$$\begin{aligned} \epsilon_v &= 564.9(v + 1/2) - 4.0(v + 1/2)^2 \\ B_v &= 0.2438 - 1.7 \times 10^{-3}(v + 1/2) \\ D_v &= -1.815 \times 10^{-7} - 3.1 \times 10^{-9}(v + 1/2) \\ F_0 &= -9.4 \times 10^{-14} \end{aligned}$$

First Electronic Level:

$$\begin{aligned} \epsilon_0 &= 17657.7 \\ \epsilon_v &= 261.1(v + 1/2) - 5.42(v + 1/2)^2 \end{aligned}$$

v	Bv	v	Bv	v	Bv
0	0.1625	5	0.1470	10	0.1297
1	.1594	6	.1437	11	.1254
2	.1563	7	.1408	12	.1209
3	.1532	8	.1375	13	.1166
4	.1501	9	.1341		

The values given in heavy type have been observed; the others were calculated.

The electronic level at 17657.7 cm.^{-1} has been classified as a ${}^3\pi$ level by Mulliken.⁷

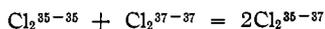
With λ type doubling there are six electronic series of rotation-vibration

⁵ Mulliken, *Phys. Rev.*, **25**, 119 (1925).

⁶ Elliott, *Proc. Roy. Soc. (London)*, [A] **127**, 638 (1930).

⁷ Mulliken, *Phys. Rev.*, **36**, 699, 1440 (1930); **37**, 1412 (1931).

levels. Some small doubt remains concerning the $^3\pi$ classification but the matter is of almost negligible importance in the present calculations since at 3000°K. the total contribution to $(F^\circ - E_0^\circ)/T$ is only 0.010 and is but 0.002 calorie per degree per mole at 2500°K. In considering the isotope effect we will make use of the reaction



From Equation 8 the zero point vibrational energy for each of the three molecules can be calculated. They were found to be 800.46, 778.56 and 789.60 cm.^{-1} , respectively. While the absolute accuracy of these values is not as great as the figures indicate, the relative accuracy is significant and thus the value of $\Delta E_0^\circ = 0.18 \text{ cm.}^{-1}$ is reliable. Similarly, in obtaining the value of $(F^\circ - E_0^\circ)/T$ particular attention was paid to relative accuracy, thus giving a more reliable value of $\Delta(F^\circ - F_0^\circ)/T$ than can be obtained from our tables, to be given later.

The value of $\Delta(F^\circ - E_0^\circ)/T$ for 298.1°K. is -2.7549 . Combining this with $\Delta E_0^\circ/T$ we find

$$K = \frac{[\text{Cl}_2^{35-37}]^2}{[\text{Cl}_2^{35-35}][\text{Cl}_2^{37-37}]}$$

from the equation $\Delta F^\circ/T = -R \ln K = -2.7549 + 0.0006$, $K_{298.1} = 3.9997$. If the isotopes of chlorine were without preference as to the type of diatomic molecule formed, the value of K would be exactly 4. It may be of interest to note that at the absolute zero all of the chlorine atoms would be combined into molecules of Cl_2^{35-35} and Cl_2^{37-37} type since $R \ln K = -\Delta E_0^\circ/O = -\infty$ for the above reaction. By the methods given above one could readily compute the manner in which the equilibrium would shift with decreasing temperature to approach this interesting condition. However, a knowledge of the nuclear spin of Cl^{37} would be necessary.

Since the calculated value of K agrees with 4 within the limits of accuracy of our tables it is evident that we need not consider the effect further.

In making the above calculation the effect of nuclear spin has been neglected since it has been proved by Gibson and Heitler⁸ that cancellation of this effect occurs in such cases.

In preparing the tables to be given below we have therefore not included in the free energy the effect due to the mixing of isotopes nor the effect due to the nuclear spins which the isotopes may possess. Before proceeding further there is a point which will need special discussion. The Cl_2^{35-37} molecules have twice as many states as the Cl_2^{35-35} or Cl_2^{37-37} molecules and in considering the reaction $\text{Cl}_2^{35-35} + \text{Cl}_2^{37-37} = 2\text{Cl}_2^{35-37}$ we have recognized this fact in computing the $\Delta F/T$ given above. However, in calculating the equilibrium constant we have taken the standard state of each of the three kinds of molecules as that of unit fugacity. While

⁸ Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

this was desirable for our investigation of the isotope effect, we wish to place the final calculations on the basis of a standard state which consists of the existing mixture of isotopic chlorine molecules in the ideal gas state at a total pressure of one atmosphere. This is in order to be consistent with ordinary thermodynamic procedure. In other words, we are going to agree to ignore the existence of isotopic molecules. Having done this we have imposed the requirement that we must not use any molecular quantum states which owe their origin to the presence of isotopes. We have in mind the fact mentioned above, that Cl_2^{35-37} has twice the number of rotational states possessed by the homopolar chlorine molecules. The Q obtained by summing over all states of the Cl_2^{35-37} molecule must be divided by 2 before computing the contribution which this molecule makes to the total Q of the mixture.

The necessity of the above procedure may be made clearer by considering the reactions



Neglecting the small effects due to the different masses it is evident that the equilibrium constant $K_a = K_c = 2 K_b$, due to the double statistical weight of Cl_2^{35-37} . In this calculation the standard state of each gas is the ideal gas at unit pressure. However, although K_b is but one-half of K_a or K_c , it may be seen that the three chlorine molecules will dissociate to the same extent. If we consider a total pressure of Cl atoms amounting to one atmosphere in each case, the partial pressures of Cl^{35} and Cl^{37} in case b will be one-half atmosphere each. This factor of two just balances the double statistical weight of the Cl_2^{35-37} molecules. In other words, the increased entropy due to the double number of states in Cl_2^{35-37} , namely, $R \ln 2$, is just balanced by the entropy of mixing of the two different species of atoms resulting from its dissociation. Thus if the existence of the isotopic mixture is to be ignored, it is evident that the double weight of Cl_2^{35-37} must also be ignored. Similar consideration shows that in molecules which have a number of equivalent positions occupied by a given element, all statistical weight should be neglected which is created by the presence of two or more isotopes occupying otherwise equivalent positions.

It seems necessary to compare the self-consistent results of the above procedure with those obtained in the ordinary application of the third law of thermodynamics. We may state at once that they are consistent and may be combined with them. In fact, the above method of calculation is practically dictated by this consideration of convenience. As an example let us consider the Cl_2^{35-37} molecule in the solid state. The figure axis of the molecule will point in some direction specified by the crystal structure. However, the crystal will show no appreciable prefer-

ence as to which isotope is on a given end of the figure axis. This factor of two which is ignored by heat capacity measurements to the lowest available temperatures is just that which is concerned in the double statistical weight of the gas molecule which is to be ignored in our calculations. It has previously been pointed out⁹ that in accordance with the third law, the positions of the various isotopes in the crystal become ordered so as to remove the uncertainty referred to above as the absolute zero is approached under equilibrium conditions. However, while this point is of theoretical interest in connection with the exact truth of the third law, it was also pointed out that the required conditions of sufficiently low temperature and attainment of equilibrium are not present in the ordinary application of this law.

The above considerations may be applied with the same results to more complicated molecules in the solid state.

There are, however, two respects in which we shall not ignore the isotope effect. First, the several isotopic molecules have slightly different molecular constants and the value of a given thermodynamic property for the substance as a whole will be obtained by adding the contributions of the several molecules, each in proportion to its abundance. Second, the double statistical weight of the Cl_2^{35-37} molecule is considered in obtaining the relative abundance of these molecules for computing the above average.

In this connection it is very interesting to compare the ordinary method of calculating abundance which assumes that each atom has equal chance with the method of observing the number of molecular states in determining the statistical weight of each kind of molecule. The chance of withdrawing two Cl^{35} atoms in succession from a mixture of the isotopic atoms is equal to $N_{\text{Cl}^{35}}^2$, where $N_{\text{Cl}^{35}}$ is its mole fraction. The chance of obtaining a Cl^{35} and a Cl^{37} atom in two successive draws is $2 \times N_{\text{Cl}^{35}}N_{\text{Cl}^{37}}$ since there is equal chance for each order of drawing Cl^{35} , Cl^{37} or Cl^{37} , Cl^{35} . When the statistical weight is calculated from the number of observed states of the molecules it is seen that the double weight of the Cl_2^{35-37} molecule compared to Cl_2^{35-35} is given by the double number of rotational states. Were it not for the fact that the nuclear spin of chlorine causes all of the energy levels to have some representatives, the Cl_2^{35-35} bands would have only one-half as many lines as the Cl_2^{35-37} bands. This phenomenon has been observed in the case of O_2^{16-16} and O_2^{16-18} .

In the case of chlorine the relative percentages of isotopes 35 and 37 are 75.9 and 24.1%, respectively. These values are obtained from the atomic weight 35.457 combined with the values 34.975 and 36.972 for the individual isotopes. These latter values were obtained from the work of Aston and are corrected on the basis of Mecke and Childs'¹⁰ determination

⁹ Giaque and Johnston, *THIS JOURNAL*, 50, 3221 (1928).

¹⁰ Mecke and Childs, *Z. Physik*, 68, 362 (1931).

of the relative abundance of the oxygen isotopes. From the above figures it is found that chlorine gas is 57.6% Cl_2^{35-35} , 36.6% Cl_2^{35-37} and 5.8% Cl_2^{37-37} .

The values of $(F^\circ - E_0^\circ)/T$ are given in Table IV. As mentioned above, the value of $Q_{\text{Cl}_2^{35-37}}$ has been reduced by a factor of two.

The Free Energy of Hydrogen Chloride

The free energy of hydrogen chloride was calculated in the manner used for chlorine except that the summation method was used to 2000°K. This was done only for comparing the two methods of calculation as previously discussed.

The constants used for hydrogen chloride are those given by Kemble.¹¹ These have been expressed in terms of the more recent nomenclature and are collected in Table III.

TABLE III
CONSTANTS IN THE ENERGY EQUATION OF HCl^{85} IN Cm.^{-1}

$$B_v = 10.6080 - 0.3281(v + 1/2) + 0.01195(v + 1/2)^2$$

$$D_v = -0.000533 + 0.0000121(v + 1/2)$$

$$F_e = 1.46 \times 10^{-8}$$

$$\epsilon_v = 2994.33(v + 1/2) - 53.58(v + 1/2)^2$$

From the above data the free energy values for hydrogen chloride were calculated. As in the case of chlorine the effects of nuclear spin and isotopic mixing have been neglected but the free energies of the two isotopic molecules were calculated and have been given their proportionate weight in obtaining the final values. The free energy values for the two kinds of hydrogen chloride and the mixture are given in Table IV.

The Reaction $1/2 \text{H}_2 + 1/2 \text{Cl}_2 = \text{HCl}$.—We are now prepared to consider the reaction $1/2 \text{H}_2 + 1/2 \text{Cl}_2 = \text{HCl}$. Combining the free energy values for chlorine and hydrogen chloride given in Table IV with the free energy of hydrogen^{1b} the $\Delta(F^\circ - E_0^\circ)/T$ for the above reaction is found. The $(F^\circ - E_0^\circ)/T$ values used for hydrogen are those obtained when the nuclear spin is ignored since this has also been done in the preparation of the present tables.

In Table V the values of $\Delta(F^\circ - E_0^\circ)/T$ are given along with values of $\Delta F^\circ/T$ and their resulting equilibrium constants.

In making these calculations the ΔE_0° used was obtained by combining the free energy of the reaction at 25° with the value of $\Delta(F^\circ - E_0^\circ)/T$ at this temperature. This free energy has been given by Randall and Young¹² as $\Delta F_{298.1} = -22,741$ calories. Since this value has been obtained from electromotive force measurements, the resulting value of $\Delta E_0^\circ = -21,984$ calories per mole is very reliable.

¹¹ Kemble, *J. Opt. Soc. Am.*, **12**, 1 (1926).

¹² Randall and Young, *THIS JOURNAL*, **50**, 989 (1928).

The equilibrium constants given in Table V are not sufficient to give the extent to which hydrogen chloride will dissociate at high temperatures where the reaction is complicated by the dissociation of chlorine and of hydrogen. The dissociation constant for hydrogen has been previously given^{1b} while that of chlorine may be calculated. For this we shall need the free energy of atomic chlorine which we shall now obtain.

The Free Energy of Atomic Chlorine.—The only electronic levels of the chlorine atom which need be considered for the present calculation are the $^2P_{1/2}$, zero state and the $^2P_{3/2}$ level which Kiess and DeBruin¹⁸ have found to be 881 cm.^{-1} above.

In Table V the values of $(F^\circ - E_0^\circ)/T$ are given for the isotopic mixture of atomic chlorine gas. As in the case of molecular chlorine and hydrogen chloride these values do not include the effect of nuclear spin or of isotopic mixing.

The Dissociation of Chlorine.—From the data in Table IV the $\Delta(F^\circ - E_0^\circ)/T$'s for the reaction $\text{Cl}_2 = 2\text{Cl}$ are obtained and given in Table V. These values, when combined with $\Delta E_0^\circ/T$, give $\Delta F^\circ/T$, which is also given in Table V.

The value of ΔE_0° has been taken from Elliott's⁹ revision of Kuhn's¹⁴ determination of this quantity from the band spectrum of chlorine. The value 56,900 calories per mole is in good agreement with the value 57,000 given by Wohl and Kadow¹⁵ on the basis of explosion experiments.

If the accepted value $\Delta E_0^\circ = 56,900$ calories per mole is altered by further investigation a very simple calculation will permit revision of the values given for $\Delta F^\circ/T$ and K in Table V.

Löwenstein¹⁶ has measured the dissociation of hydrogen chloride by passing this gas through a platinum tube and observing the equilibrium pressure of hydrogen which diffused through the wall. His one observation at 1810°K. gave 0.274% dissociation. However, this value was calculated without making a correction for the dissociation of chlorine or of hydrogen. Löwenstein found an equilibrium pressure of 1.03 mm. of hydrogen when the total pressure was 751.2 mm. At 1810°K. and a total pressure of 1.03 mm. of hydrogen, the pressure of diatomic hydrogen is 1.018 mm. and that of atomic hydrogen 0.0115 mm., a very small correction. However, the error made by neglecting the dissociation of chlorine is more serious. Instead of 1.03 mm. pressure of Cl_2 , calculation shows this pressure to be 0.044 mm. and the pressure of monatomic chlorine to be 1.96 mm.

From the above corrections to Löwenstein's values we calculate $K_{1810^\circ} = [\text{HCl}]/[\text{H}_2]^{1/2} [\text{Cl}_2]^{1/2} = 3.54 \times 10^3$, whereas by interpolation in Table IV

¹⁸ Kiess and DeBruin, *Bur. Standards J. Res.*, **2**, 1117 (1929).

¹⁴ Kuhn, *Z. Physik*, **39**, 77 (1926).

¹⁵ Wohl and Kadow, *Z. physik. Chem.*, **118**, 460 (1925).

¹⁶ Löwenstein, *ibid.*, **54**, 715 (1906).

TABLE IV
 $(F^\circ - E_0^\circ)/T$ FOR CHLORINE AND HYDROGEN CHLORIDE GASES

T, °K.	$-(F^\circ - E_0^\circ)/T$ calories per degree per mole							
	Cl_2^{35-35}	Cl_2^{35-37} Cl_2^{35-35}	Cl_2^{37-37} Cl_2^{35-35}	Cl_2 equil. mixture	HCl^{35}	HCl^{37} HCl^{35}	HCl mixture	Cl mixture
250	44.598	0.141	0.282	44.666	36.447	0.164	36.487	33.555
298.1	45.881	.144	.288	45.951	37.695	.164	37.734	34.437
300	45.928	.144	.288	45.997	37.738	.164	37.778	34.468
350	47.072	.146	.291	47.141	38.806	.164	38.847	35.246
400	48.078	.147	.294	48.148	39.732	.164	39.771	35.924
450	48.978	.148	.297	49.049	40.549	.164	40.589	36.527
500	49.793	.150	.299	49.865	41.281	.164	41.321	37.070
550	50.538	.150	.301	50.611	41.943	.164	41.983	37.563
600	51.225	.151	.303	51.298	42.548	.164	42.588	38.015
650	51.863	.152	.305	51.936	43.106	.164	43.146	38.432
700	52.458	.153	.306	52.531	43.623	.164	43.663	38.820
750	53.016	.153	.308	53.089	44.106	.164	44.145	39.182
800	53.540	.154	.309	53.614	44.557	.164	44.597	39.521
850	54.036	.155	.310	54.110	44.983	.164	45.023	39.840
900	54.506	.155	.311	54.580	45.385	.164	45.425	40.141
950	54.953	.156	.312	55.027	45.767	.164	45.807	40.426
1000	55.378	.156	.313	55.453	46.131	.164	46.171	40.687
1050	55.784	.157	.314	55.859	46.477	.164	46.517	40.955
1100	56.173	.157	.314	56.248	46.809	.164	46.849	41.201
1150	56.546	.157	.315	56.621	47.127	.164	47.167	41.435
1200	56.904	.158	.316	56.979	47.432	.164	47.472	41.659
1250	57.249	.158	.316	57.324	47.727	.164	47.766	41.875
1300	57.581	.158	.317	57.656	48.011	.164	48.051	42.082
1400	58.210	.159	.318	58.286	48.550	.164	48.590	42.473
1500	58.800	.159	.319	58.876	49.056	.164	49.096	42.836
1600	59.353	.160	.320	59.430	49.532	.164	49.572	43.175
1700	59.875	.160	.321	59.952	49.983	.164	50.023	43.494
1800	60.369	.161	.321	60.446	50.411	.164	50.451	43.794
1900	60.839	.161	.322	60.916	50.819	.164	50.859	44.078
2000	61.285	.161	.322	61.363	51.208	.164	51.248	44.346
2100	61.711	.161	.323	61.789	51.580	.164	51.619	44.601
2200	62.119	.162	.323	62.196	51.936	.165	51.976	44.844
2300	62.510	.162	.324	62.587	52.279	.165	52.319	45.076
2400	62.885	.162	.324	62.962	52.609	.165	52.649	45.298
2500	63.246	.162	.324	63.324	52.928	.165	52.968	45.510
2600	63.594	.162	.325	63.672	53.238	.165	53.276	45.714
2700	63.930	.162	.325	64.009	53.534	.165	53.573	45.910
2800	64.256	.163	.325	64.334	53.820	.165	53.860	46.098
2900	64.571	.163	.326	64.649	54.096	.165	54.137	46.280
3000	64.878	.163	.326	64.956	54.364	.165	54.404	46.456

The values given in heavy type are calculated by means of Equations 1 and 5b. The others were obtained by interpolating differences between the directly calculated $(F^\circ - E_0^\circ)/T$'s and approximate values calculated by assuming a constant moment of inertia and harmonic oscillation. The values obtained by combination of the interpolated differences with approximate values calculated for the intermediate temperatures gave results of practically the same reliability as those calculated directly.

TABLE V

FREE ENERGY CHANGES IN THE REACTION $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 = \text{HCl}$ AND THE DISSOCIATION OF CHLORINE

$T, ^\circ\text{K.}$	$\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 = \text{HCl}$ $-\Delta(F^\circ - E_0^\circ)/T$	$-\Delta(F^\circ/T)$	$K = \frac{[\text{HCl}]}{[\text{H}_2]^{1/2} [\text{Cl}_2]^{1/2}}$	$-\Delta(F^\circ - E_0^\circ)/T$	$\text{Cl}_2 = 2\text{Cl}$ $\Delta F^\circ/T$	$K = [\text{Cl}]^2/\text{Cl}_2$
250	2.532	90.468		22.444	205.156	
298.1	2.541	76.288	4.730×10^{16}	22.923	167.953	1.95×10^{-37}
300	2.539	75.819		22.939	166.728	
350	2.511	65.322		23.351	139.220	
400	2.478	57.438		23.700	118.550	
450	2.442	51.295		24.005	102.439	
500	2.405	46.373	1.368×10^{10}	24.275	89.525	2.70×10^{-20}
550	2.367	42.338		24.515	78.940	
600	2.330	38.970		24.732	70.101	
650	2.293	36.115		24.928	62.610	
700	2.257	33.663		25.109	56.177	
750	2.221	31.533		25.275	50.592	
800	2.188	29.668		25.428	45.697	
850	2.156	28.020		25.570	41.371	
900	2.125	26.552		25.702	37.520	
950	2.095	25.236		25.825	34.070	
1000	2.068	24.052	1.808×10^5	25.941	30.959	1.71×10^{-7}
1050	2.041	22.978		26.051	28.139	
1100	2.016	22.001		26.154	25.573	
1150	1.992	21.109		26.249	23.229	
1200	1.968	20.288		26.339	21.078	
1250	1.947	19.534		26.426	19.094	
1300	1.928	18.839		26.508	17.261	
1400	1.890	17.593		26.660	13.983	
1500	1.855	16.511	4.064×10^3	26.796	11.137	3.68×10^{-3}
1600	1.822	15.562		26.920	8.643	
1700	1.792	14.724		27.036	6.435	
1800	1.766	13.979		27.142	4.469	
1900	1.744	13.315		27.240	2.707	
2000	1.723	12.715	6.015×10^2	27.329	1.121	5.69×10^{-1}
2100	1.704	12.173		27.413	-0.318	
2200	1.687	11.680		27.492	-1.628	
2300	1.668	11.226		27.565	-2.826	
2400	1.651	10.811		27.634	-3.926	
2500	1.633	10.427	1.902×10^3	27.696	-4.936	11.99
2600	1.616	10.071		27.756	-5.871	
2700	1.598	9.740		27.811	-6.737	
2800	1.582	9.433		27.862	-7.541	
2900	1.564	9.145		27.911	-8.290	
3000	1.546	8.874	8.702×10	27.956	-8.989	92.21

we find the reliable value 1.099×10^3 . The disagreement of the two values is very surprising. In order to bring agreement it would be necessary to assume a value for the heat of dissociation of chlorine which is about 15,000 cal./mole greater than the reliable one which we have used above.

It appears necessary to conclude that Löwenstein's single observation was subject to some very large error.

The Heat of Formation of Hydrogen Chloride.—From the equation^{1a}

$$\Delta H^\circ = \Delta E_0^\circ + \Delta \left[\frac{5}{2} RT + RT^2 \frac{d \ln Q}{dT} \right] = \Delta E_0^\circ + \Delta \left[\frac{5}{2} RT + N \frac{\sum e^{\epsilon/kT}}{\sum p e^{-\epsilon/kT}} \right] \quad (9)$$

A very reliable value for the heat of formation of gaseous hydrogen chloride from hydrogen and chlorine may be obtained. This calculation could be made for any temperature but we shall obtain only the value for $\Delta H_{298.1}^\circ$ which seems of the greatest utility.

For the equilibrium mixture of ortho and para hydrogen the value of $\frac{5}{2} RT + RT^2 \frac{d \ln Q}{dT}$ is^{1b} 2023.20 calories per mole at 298.1°K. For chlorine the value of $\frac{5}{2} RT + RT^2 \frac{d \ln Q}{dT} = 2193.69$ calories per mole at 298.1°K. This value was obtained by properly weighting the individual contributions of the three isotopic molecules as mentioned above. The effect of ortho and para states could be ignored in this calculation due to the essential establishment of the high temperature limiting equilibrium even at temperatures far below 298.1°K. The corresponding effect in hydrogen^{1b} was only 0.01 calorie per mole at 298.1°K. For hydrogen chloride

$$\frac{5}{2} RT + RT^2 \frac{d \ln Q}{dT} = 2064.30$$

Thus for the reaction $\frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2 = \text{HCl}$, $\Delta H = -21,984 - 44 = -22,028$ calories per mole. The only appreciable inaccuracy in this value is the same as that in the free energy change given by Randall and Young.¹² This is probably reliable to ≈ 10 calories per mole.

It is of interest to note that both Thomsen and Berthelot found $\Delta H = -22,000$ calories per mole for the above reaction.

The Entropy of Hydrogen Chloride and of Chlorine.—From the equation

$$S = \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R \ln P - 2.300 + R \ln Q + RT \frac{d \ln Q}{dT} \quad (10)$$

the entropies of HCl^{35} and HCl^{37} were calculated.

At 298.1°K. and a pressure of one atmosphere HCl^{35} , $S_{298.1} = 44.619$ calories per degree per mole. HCl^{37} , $S_{298.1} = 44.783$ E. U. Thus for the existing mixture HCl , $S_{298.1} = 44.658$ E. U. This value does not include the entropy of isotopic mixing nor that due to nuclear spin. The value obtained for $S_{298.1}$, HCl from low temperature heat capacity measurements¹⁷ is 44.5 E. U.

For chlorine Cl_2^{35-35} , $S_{298.1} = 53.235$ E. U.; Cl_2^{35-37} , $S_{298.1} = 53.389$ E. U. (one-half of states used on account of isotope effect); Cl_2^{37-37} , $S_{298.1} = 53.543$ E. U. Thus Cl_2 , $S_{298.1} = 53.310$ E. U. This value may be compared with

¹⁷ Giauque and Wiebe, *THIS JOURNAL*, 50, 101 (1928).

one calculated by combining the temperature coefficient of the cell $\text{Ag} + \frac{1}{2}\text{Cl}_2 = \text{AgCl}$, determined by Gerke¹⁸ with the entropies of silver chloride and silver obtained from the third law of thermodynamics. A very accurate value of the entropy of silver chloride has recently been made available through the work of Eastman and Milner¹⁹ soon to be published. AgCl , $S_{298.1} = 22.97 \pm 0.07$ E. U. Combining this with a preliminary determination of the entropy of silver by P. F. Meads and one of us, that is, Ag , $S_{298.1} = 10.01$ E. U. and $\Delta S = -13.73$ E. U., $S_{298.1}$, Cl_2 is found to be 53.38 E. U., which compares very well with the spectroscopic value of 53.310 E. U.

In the above calculations we have gone into considerable detail in investigating the isotope effect. We have had in mind from the beginning that while the presentation of such an example was desirable, the main object was to eliminate the necessity of such detail in future calculations.

It is therefore suggested that in considering the thermodynamic properties of substances which consist of two or more isotopic molecules, the following procedure be adopted. Instead of using the several energy levels of the various isotopic molecules an average set of energy levels may be constructed by giving the proper weight to each isotopic molecule present. When the levels can be represented by equations, the above procedure requires only the computation of an average set of constants.

This procedure assumes that the isotopes have reached their limiting high temperature equilibrium. That this is reached with sufficient accuracy for calculations to 0.001 calorie per degree per mole, far below ordinary temperatures, has been demonstrated above.

Summary

An approximation method which permits the calculation of free energy from the energy levels of diatomic molecules without the necessity of summing the Boltzmann factors for the individual rotational energy levels has been given. The method considers the effects of molecular distortion due to rotation of the non-rigid molecules, without loss in accuracy.

The manner in which the presence of various isotopic molecules affects such calculations is discussed. It is shown that equilibrium in the reaction $\text{Cl}_2^{35-35} + \text{Cl}_2^{37-37} = 2\text{Cl}_2^{35-37}$ is entirely to the left at 0°K.

The values of $(F^\circ - E_0^\circ)/T$ for Cl_2^{35-35} , Cl_2^{35-37} , Cl_2^{37-37} and the equilibrium mixture have been tabulated for ready interpolation from 250°K. to 3000°K.

Similar tables have been prepared for HCl^{35} , HCl^{37} and for Cl^{35} , Cl^{37} and their respective existing mixtures.

The values of $\Delta F^\circ/T$ for the reaction $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 = \text{HCl}$ have been

¹⁸ Gerke, *THIS JOURNAL*, **44**, 1684 (1922).

¹⁹ Personal communication.

presented so that values over the range 250 to 3000°K. may be easily obtained by interpolation.

The $\Delta F^\circ/T$ for $\text{Cl}_2 = 2\text{Cl}$ has been tabulated to 3000°K.

The change in heat content for the reaction $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 = \text{HCl}$ has been accurately determined from the electromotive force of the hydrogen-chlorine cell and spectroscopic data. The value found was $\Delta H_{298.1} = -22,028$ calories per mole.

The entropies of hydrogen chloride and of chlorine have been calculated.

$$\text{HCl}^{35}, S_{298.1} = 44.619 \text{ E. U.}$$

$$\text{HCl}^{37}, S_{298.1} = 44.783 \text{ E. U.}$$

$$\text{HCl}(\text{mixture}), S_{298.1} = 44.658 \text{ E. U.}$$

$$\text{Cl}_2^{35-35}, S_{298.1} = 53.235 \text{ E. U.}$$

$$\text{Cl}_2^{35-37}, S_{298.1} = 53.389 \text{ E. U.}$$

$$\text{Cl}_2^{37-37}, S_{298.1} = 53.543 \text{ E. U.}$$

$$\text{Cl}_2 (\text{equilibrium mixture}), S_{298.1} = 53.310 \text{ E. U.}$$

The entropy effect of nuclear spin (unknown for Cl^{37}) has purposely been omitted from the above values so that they may be used in combination with those obtained from low temperature heat capacity measurements. The entropy of mixing in the isotopic solutions and the entropy due to the presence of two isotopes in the same molecule have been eliminated for the same reason.

It is suggested that thermodynamic properties of substances which consist of two or more isotopic molecules be based on an average set of energy levels, computed by weighting the several values in proportion to the abundance of the respective molecules. The effect of the reduction in the number of levels by molecular symmetry on the above method has been discussed.

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THE RATE OF SOLUTION OF ZINC IN ACIDS

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RECEIVED NOVEMBER 10, 1931

PUBLISHED MAY 7, 1932

The classical theory for the rate of solution of solids in aqueous solutions, developed by Noyes and Whitney,¹ Nernst² and Brunner,³ postulates that the rate of chemical reaction in such cases is very high compared to the rate at which the active component of the solution can reach the solid surface by diffusion; hence the observed rate of dissolution will be that of diffusion to the surface through the products as they diffuse away.

¹ Noyes and Whitney, *Z. physik. Chem.*, **23**, 689 (1897).

² Nernst, *ibid.*, **47**, 52 (1904).

³ Brunner, *ibid.*, **47**, 56 (1904).