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Citation: *J. Chem. Phys.* **5**, 637 (1937); doi: 10.1063/1.1750090

View online: <http://dx.doi.org/10.1063/1.1750090>

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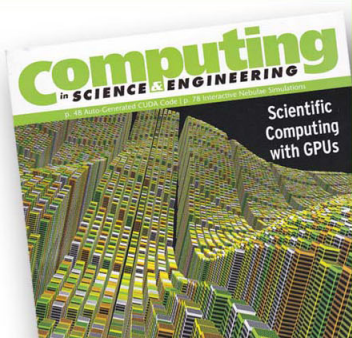
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the molecular beam in the electron diffraction camera showed approximately 50 percent phosphorus tetroxide and 50 percent phosphorus pentoxide. They will later describe the method of preparation used. Electron diffraction photographs obtained from this mixture gave an interference pattern almost identical to that found for P_4O_{10} . Values of $(1/\lambda) \sin \frac{1}{2}\theta$ for the interference maxima Nos. 2, 3, 5 and 6 agreed with the data given for P_4O_{10} in Table II above to within less than 1 percent. The first maximum appeared to be slightly weaker than the similar

one found for P_4O_{10} but it had approximately the same position. Both first and second minima differed by less than 2 percent in position from the corresponding minima for P_4O_{10} . It was possible to see an additional weak maximum for the mixture at $(1/\lambda) \sin \frac{1}{2}\theta = 0.87$ which was previously too weak for measurement in the case of P_4O_{10} .

Since the resultant diffraction pattern of this mixture is practically the same as for a pure sample of P_4O_{10} it is thus concluded that the true interference pattern of P_4O_8 must be approximately the same as found for P_4O_{10} .

AUGUST, 1937

JOURNAL OF CHEMICAL PHYSICS

VOLUME 5

The Temperature Variation of Some Thermodynamic Quantities*

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(Received June 15, 1937)

The quantity, $(F^0 - E_0^0)/T$, calculated from spectroscopic data has been fitted to a five constant equation in T for 19 molecules. It may be differentiated and integrated to give values of S^0 , E^0 , H^0 and C_p^0 between 298.1 and 3000°K and is sufficiently exact for most purposes. The equilibrium constant for exchange reactions involving isotopes has been calculated and in each case, maxima exist and in one case a minimum also. This effect probably occurs at some temperature for all reactions involving isotopic molecules although not for other equilibria. An optimum temperature therefore exists for separation of isotopes by exchange reactions.

THE calculation of thermodynamic quantities from spectroscopic data has usually resulted in numerical values of these functions at a series of temperatures, 100° or so apart.¹ Since most experiments are performed at some odd temperature, interpolation in these tables is necessary in order to make comparison with the calculations. This may be done graphically from a large scale plot or by some method of numerical interpolation, either of which may be rather tedious. It is obvious that an analytical expression to represent these quantities as a function of the temperature would be useful. This has been done for the heat capacity of a number of molecules by Spencer and Justice² but a suitable expression for the variation of the free energy with temperature appears more satisfactory as this may be differentiated and integrated to give other thermodynamic quantities without the

involved summation necessary to obtain them directly from the spectroscopic data.

The constants for a satisfactory analytical equation have been given recently³ for H_2 , D_2 , HI and DI and it is the purpose of this paper to give the constants for other molecules and to apply the results in calculating the variation with temperature of the equilibrium constant of certain exchange reactions.

If we represent the free energy function by the equation⁴

$$-(F^{0*} - E_0^0)/T = a/T + b \log T + cT + dT^2 + \dots + i, \quad (1)$$

the well-known methods of thermodynamics⁵ lead immediately to expressions for the additional quantities:

$$S^{0*} = -dF^0/dT = -b\{\log e + \log T\} + 2cT + 3dT^2 + \dots + i, \quad (2)$$

* Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Chapel Hill, N. C., April 14, 1937.

¹ For a review of the methods of calculation and references to molecules for which calculations have been made, see Kassel, *Chem. Rev.* **18**, 277 (1936).

² Spencer and Justice, *J. Am. Chem. Soc.* **56**, 2311 (1934).

³ Murphy, *J. Chem. Phys.* **4**, 344 (1936); Blagg and Murphy, *ibid.* **4**, 631 (1936).

⁴ For the meaning of the symbols used here, see Giauque, *J. Am. Chem. Soc.* **52**, 4808 (1930).

⁵ See any text-book on thermodynamics, as Lewis and Randall, *Thermodynamics* (McGraw-Hill Book Co., New York, 1923).

TABLE I.

	<i>a</i>	<i>b</i>	<i>c</i> × 10 ⁴	<i>d</i> × 10 ⁸	<i>i</i>	REFERENCE
H ₂	3.1414	15.5999	1.245	3.72	-14.2131	1
HD	-12.5833	15.4831	2.200	3.04	-10.7961	2
D ₂	-46.0643	15.0859	4.972	25.70	-9.5419	2
HCl	-153.6940	14.3834	7.836	-3.73	2.4254	3
DCI	-120.3214	14.4026	10.286	-6.13	3.5836	4
HBr	-122.2812	14.5503	7.748	-2.72	4.7350	5
DBr	-93.8502	14.4317	11.945	-8.77	6.1790	6
HI	-108.6720	14.6592	7.649	-4.00	6.2820	7
DI	-365.5120	11.1051	36.420	-67.80	16.5063	8
Cl ₂	358.5050	19.2272	3.635	-2.07	-2.9302	3
Br ₂	212.7441	19.1883	6.703	-10.76	2.4832	5
I ₂	180.7780	19.8028	4.444	-6.87	4.4605	7
N ₂	-212.7056	13.9765	11.719	-8.60	5.0589	9
O ₂	-25.0666	14.8456	12.108	-9.47	5.0869	10
CO	-178.0274	13.9435	12.068	-9.13	6.1073	11
H ₂ O	-218.0344	15.5972	16.472	-4.64	-1.1745	12
H ₂ S	-189.4691	15.1434	25.565	-15.22	3.5973	13
CO ₂	727.1367	20.1610	25.200	-1.592	-9.4306	14
SO ₂	253.4268	18.8812	34.804	-36.78	1.9950	15

1. Giauque, J. Am. Chem. Soc. **52**, 4816 (1930); Davis and Johnston, *ibid.* **56**, 1045 (1934).
2. Johnston and Long, J. Chem. Phys. **2**, 389 (1934).
3. Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).
4. Calculated for this paper. The spectroscopic constants for DCI were obtained from those of HCl (see reference 3) by well-known methods.
5. Gordon and Barnes, J. Chem. Phys. **1**, 692 (1933). Valid only to 1600°K.
6. Calculated for this paper by Mr. T. Ivan Taylor, Department of Chemistry, Columbia University. The spectroscopic constants for DBr were obtained from those of HBr (see reference 5) by well-known methods.
7. Murphy, J. Chem. Phys. **4**, 344 (1936). Valid only to 1500°K.
8. Blagg and Murphy, J. Chem. Phys. **4**, 631 (1936). Valid only to 1500°K.
9. Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933); Johnston and Davis, *ibid.* **56**, 271 (1934).
10. Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933); **57**, 682 (1935).
11. Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932); **55**, 5071 (1933); Kassel, J. Chem. Phys. **1**, 576 (1933); Johnston and Davis (see reference 9).
12. Gordon, J. Chem. Phys. **2**, 65 (1934).
13. Cross, J. Chem. Phys. **3**, 168 (1935). Valid only to 1800°K.
14. Kassel, J. Am. Chem. Soc. **56**, 1838 (1934).
15. Gordon, J. Chem. Phys. **3**, 336 (1935). Valid only to 2800°K.

$$H^0 = F^0 + TS^0 = (E_0^0 - a) + bT \log e + cT^2 + 2dT^3 + \dots, \quad (3)$$

$$E^0 = H^0 - RT, \quad (4)$$

$$C_p^0 = dH^0/dT = b \log e + 2cT + 6dT^2 + \dots \quad (5)$$

In all of these equations and in Table I, the nuclear spin contributions have *not* been included. If absolute values of $(F^0 - E_0^0)/T$ or S^0 are desired, it is necessary to add a constant term to the quantity i which appears in Eqs. (1) and (2). For details as to the magnitude of this constant, reference 1 may be consulted.

Consideration of Eqs. (1) to (5) shows that a knowledge of the five constants for Eq. (1) is sufficient to determine the other quantities as shown in Eqs. (2) to (5). The five constants have been determined for a number of diatomic and polyatomic molecules and appear in Table I. The data required have been taken from various places in the literature or computed by well-known methods,¹ the source of the data for each molecule being given in footnotes to Table I.

The constants were determined in some cases by least squares, all of the temperatures for which $(F^0 - E_0^0)/T$ had been summed, being used. However, it was found that sufficiently precise values could be obtained using the method of averages,⁶ by which 15 or more equations of the form of (1) were reduced to five simultaneous equations which were then solved for the constants. In solving the five simultaneous equations, the constants involved must be eliminated in a particular order if any precision is obtained. Reference to Table I shows that the numerical value of the constants is approximately in the order $a > b > i > c > d$. They should thus be eliminated in the reverse order so that the final pair of equations should be solved for a . If this is not done, the cumulative errors involved give constants of an entirely different order of magnitude and will not reproduce the values of $(F^0 - E_0^0)/T$.⁷

The minimum temperature for which the constants of Table I are valid is 298.1°K. The maximum temperature is in most cases 3000°K, the exceptions being given in Table I. Any extrapolation beyond these limits is not reliable. Extension beyond these temperatures in either direction, however, may easily be made by redetermining the constants with values of $(F^0 - E_0^0)/T$ at higher and lower temperatures. If necessary, coefficients of higher powers of T may be added to Eq. (1).

The errors in reproducing the values of the thermodynamic functions as calculated from spectroscopic data with the constants of Table I and Eqs. (1) to (5) vary somewhat from one molecule to another. The average and maximum deviations for H₂ are shown in Table II. This

TABLE II. Deviations from the thermodynamic functions of H₂ as calculated from Eqs. (1) to (5) and the constants of Table I and those calculated from the spectroscopic data.

	$-(F^0 - E_0^0)/T^a$	S^0 ^a	C_p ^{0b}	$E^0 - E_0^0$ ^b
Average deviation	0.003 cal. 0.01%	0.014 cal. 0.04%	0.032 cal. 0.5%	8.25 cal. 1.2%
Maximum deviation	0.006 cal. 0.02%	0.085 cal. 0.2%	0.067 cal. 1%	36.6 cal. 5%

^a Upper temperature limit of 3000°K.

^b Upper temperature limit of 2000°K.

⁶ Scarborough, *Numerical Mathematical Analysis* (The Johns Hopkins Press, Baltimore, 1930), p. 357.

⁷ This is undoubtedly a general procedure in solving a set of simultaneous equations, although no statement of this fact could be found in books on numerical calculations.

may be considered as a good example as the deviations for other molecules are of about the same order of magnitude. The values of C_p^0 and E^0 begin to deviate rather badly toward the upper limit of the temperature range and for these functions, it is best to confine the calculations to something lower than 2000°K. Reference to Table II indicates that the precision of calculation with these empirical equations is probably as good as the experimental data in most cases. For molecules other than H_2 , the errors will in general not exceed those in Table II and in some cases will be somewhat less. The ease in using these functions should make them useful in comparing experimental results with the corresponding quantities calculated from spectroscopic data.

TEMPERATURE VARIATION OF THE EQUILIBRIUM CONSTANT

For a chemical equilibrium, the equilibrium constant is given by

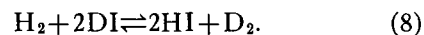
$$\frac{-\Delta F^0}{T} = -\Delta \left\{ \frac{F^0 - E_0^0}{T} \right\} - \frac{\Delta E_0^0}{T} = R \ln K. \quad (6)$$

All molecules taking part in the equilibrium are assumed to be in their standard states and hence at unit activity and since gases are sufficiently ideal at moderate pressures to substitute partial pressure for activity, Eq. (6) refers to unit pressure of 1 atmosphere. By using the Gibbs-Helmholtz equation it is easy to show that

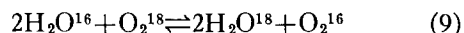
$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2}, \quad (7)$$

and upon the assumption that ΔH^0 is independent of the temperature or that it varies only very slowly with the temperature, Eq. (7) may be integrated between two temperatures, this being valid if the temperature range is not large. The integrated form of Eq. (7) shows that a plot of $\log K$ against $1/T$ should give a straight line from the slope of which ΔH^0 may be determined. This procedure is very commonly followed but it will be shown below that this may lead to erroneous results in some cases. Eq. (3) shows how H^0 actually varies with the temperature and it is commonly supposed that the absolute value of

ΔH^0 increases monotonically with the temperature. Under these conditions the equilibrium constant of a homogeneous gaseous reaction should increase (or decrease) monotonically with the temperature although the plot of $\log K$ against $1/T$ need not be a straight line. The possibility of a maximum or a minimum in the equilibrium constant should not be overlooked. As a matter of fact, a maximum in the ionization constant is actually observed in certain homogeneous liquid systems.⁸ An indication of this effect is also noticeable in the calculations of Urey and Rittenberg⁹ for the gaseous exchange reaction



Their equilibrium constants are 1.212, 1.234, 1.222 at 400°, 575° and 700°K, respectively, indicating a maximum at some temperature higher than 575°K. A more detailed calculation³ of this equilibrium shows in fact a maximum near this temperature and a minimum near 1250°K. The exchange reaction¹⁰



seems to have a minimum around 1500°K. Since this same effect would probably appear in other equilibria, a consideration of its cause seemed indicated. From Eq. (7) excluding the case where $T=0$ or ∞ , it is obvious that the equilibrium constant will have a maximum, a minimum or a point of inflection if $\Delta H^0=0$. Correspondingly, if $\Delta C_p \geq 0$ the equilibrium constant possesses a minimum, a maximum or a point of inflection, respectively. It may easily be shown that

$$H^0 = E_0^0 + \frac{5}{2}RT + RT^2 \frac{d \ln Q}{dT}, \quad (10)$$

where the partition function, $Q = \sum p e^{-E/kT}$, summation is made over the required number of electronic, vibrational and rotational states and p is the statistical weight of the individual energy level. The partition function may be further written

$$Q = (\mu kT/hcB_0)(1-z)^{-1}f, \quad (11)$$

⁸ See, for example, Harned and Embree, J. Am. Chem. Soc. **56**, 1050 (1934).

⁹ Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).

¹⁰ Jones and Hall, J. Am. Chem. Soc. **59**, 259 (1937).

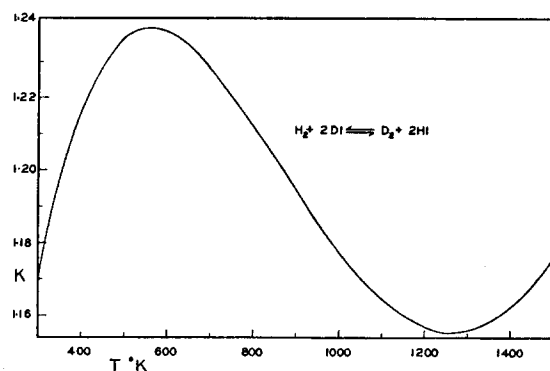


FIG. 1.

where $z = e^{-hc\omega_0/kT}$, the contribution from a linear harmonic oscillator of frequency, $c\omega_0$; the first term that from a rigid rotator with moment of inertia $h/8\pi^2cB_0$; the constant μ represents nuclear spin or symmetry contributions and the factor f which may be developed in a power series in T , all contributions from stretching, anharmonicity and other interaction terms. Substitution of Eq. (11) in Eq. (10) results in:

$$H^0 = E_0^0 + \frac{5}{2}RT + RT + \frac{zhc\omega_0 R}{(1-z)k} + \{\alpha + \beta T + \gamma T^2 + \delta T^3 + \dots\}, \quad (12)$$

where the first term is the zero-point energy and the next terms in order are translational, rotational, vibrational and anharmonic contributions to the heat content and may be indicated for convenience by H_t , H_r , H_v and H_a , respectively. For reactions of the type of (10) where there is no change in the number of moles, it is obvious that neither H_t nor H_r can cause a maximum or a minimum as these quantities will both cancel in forming ΔH^0 . However, either H_v or H_a may vary with temperature in such a way that ΔH^0 may change sign from positive to negative and thus go through a maximum or minimum. A similar argument applies to ΔC_p , since

$$C_p^0 = \frac{5R}{2} + R + \left\{ R \left(\frac{hc\omega_0}{kT} \right)^2 \left[\frac{z}{(1-z)^2} \right] \right\} + \{\alpha' + \beta' T + \gamma' T^2 + \dots\}, \quad (13)$$

where the terms are, respectively, C_t , C_r , C_v and C_a . If ΔH^0 were set equal to zero after substitution of equations of the form of (12) for the

reactants and the reaction products and if this were solved for T , the results would be T_{\max} or T_{\min} . Unfortunately it is not an easy matter to solve these equations due to the presence of the exponential terms in T . Several attempts to solve them were made without success for even if the anharmonic terms are neglected, the resulting equation is rather difficult to handle and series approximations fail. A qualitative explanation, however, seems to be as follows. With increasing temperature H_t and H_r cause ΔH^0 to increase (or decrease) regularly. At a given temp. H_v for one molecule will begin to contribute to ΔH^0 and depending on whether one of the reactants or one of the reaction products begins to vibrate first, ΔH^0 will either decrease (or increase) giving a maximum or a minimum. At some higher temperature, a molecule on the other side of the equilibrium equation will begin to vibrate and ΔH^0 will again change sign.

It now remains to be seen whether this behavior is to be expected for every reaction. The condition given above may be written

$$\Delta H^0 = (\Delta H^0 - \Delta H_0^0) + \Delta H_0^0 = 0; \quad (14)$$

the quantity ΔH_0^0 is, of course, independent of temperature and is of the order of 1000–10,000 calories for an ordinary chemical reaction. It does not seem likely that at any reasonable temperature, $\Delta(H^0 - H_0^0)$ will vary enough to cause ΔH^0 to change sign. On the other hand, for exchange reactions, ΔH_0^0 is of the order of only a few hundred calories and thus $\Delta(H^0 - H_0^0)$ may easily cause ΔH^0 to change sign.

The exchange between the hydrogen halides and deuterium are convenient equilibria to apply to these calculations. The equilibrium constants may be obtained from Table I and by using Eqs. (8) and (1) are seen to be given by

$$-R \ln K = \Delta a/T + \Delta b \log T + \Delta cT + \Delta dT^2 + \dots + \Delta i + \Delta E_0^0/T. \quad (15)$$

TABLE III. Zero-point energies in calories per mole.

H ₂	6180.46
HD	5364.85
D ₂	4391.11
HCl	4222.96
DCI	3036.70
HBr	3730.92
DBr	2662.36
HI	3258.33
DI	2319.98

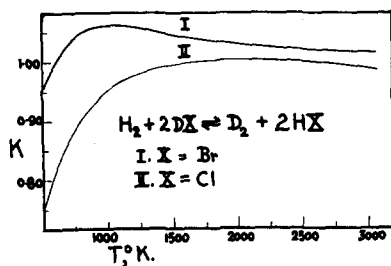
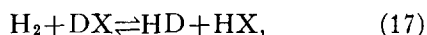


FIG. 2.

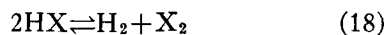
The quantity ΔE_0^0 in the case of these isotopic exchange reactions¹¹ is very simply obtained from the spectroscopic data, since

$$E_0^0 = hc \left\{ \frac{1}{2} \omega_e - \frac{1}{4} x_e \omega_e + \dots \right\}. \quad (16)$$

Values of E_0^0 are given in Table III for a few molecules. The corresponding variation of K with temperature for some exchange reactions is found in Figs. 1 and 2. Each is found to have a maximum and for the HI-DI reaction, a minimum as well. Presumably at higher temperatures, the others would also show a minimum. Unfortunately, none of these equilibria have yet been investigated experimentally over a wide enough temperature range to show the effect. The equilibria



where $X = \text{Cl}, \text{Br}, \text{I}$ have been studied by Wirtz¹² but slightly higher temperatures are necessary to reach the maximum in K . Equilibria of the type shown in Figs. 1 and 2 could probably be studied most simply experimentally from the individual equilibria



¹¹ In the case of reactions which do not involve isotopic exchanges, ΔE_0^0 must be obtained in other ways, see, for example, reference 4.

¹² Wirtz, Zeits. f. physik. Chemie, **B31**, 309 (1936).

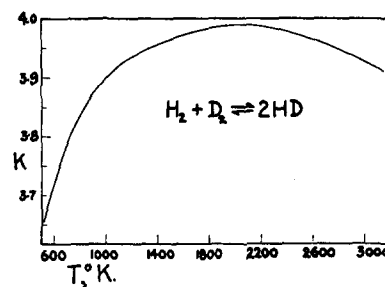
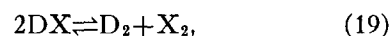
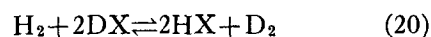


FIG. 3.

and the corresponding one



and the constant for



would then be the ratio of the individual constants of (18) and (19).

A similar maximum is found in the case



and shown in Fig. 3. A minimum may also be found at considerable higher temperature. An attempt to find a similar effect at very low temperatures due to changes in the rotational heat content were unsuccessful and probably do not exist for any reaction since H_r is too small compared with H_0^0 , although there is a point of inflection in the curve below 100°K.¹³

No doubt other exchange reactions may be found showing maxima or minima and they may prove useful in the separation of isotopes since it is obvious that some one temperature offers the best opportunity of concentrating an isotope by exchange.

¹³ The values of $(F^0 - E_0^0)/T$ and $(E^0 - E_0^0)$ for D_2 and HD may be found in reference 2, but the values for HD at 150° are in error and should be 26.462 and 259.92, respectively.