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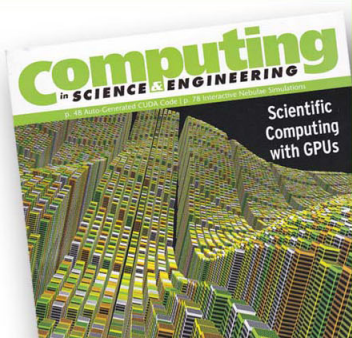
The Free Energy of Iodine and Hydrogen Iodide from Spectroscopic Data

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Partition functions have been calculated for HI, I_2 and I atom between 298.1 and 1500°K from spectroscopic data and the results have been fitted to a free energy equation of the usual thermodynamic form which may be differentiated and integrated to give change of heat content, specific heat and entropy for chemical reactions involving HI, I_2, I and H_2. The experimentally determined equilibrium constants for the reactions $I_2 \rightarrow 2I$ and $HI \rightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2$ have been compared with the theoretical equilibrium constants. For the latter reaction, it is shown that the results of Bodenstein may be in error due to incorrect temperatures. Reliable values have been given for the heat of dissociation of iodine and hydrogen iodide at 25°C.

CALCULATION of thermodynamic functions from spectroscopic data may be made with complete confidence since the statistical weights of the degenerate energy levels are now well understood. Moreover, the measurements of molecular spectroscopy are so exact that in most cases these calculated functions will far exceed the experimental ones in precision. The requisite partition functions have now been summed and discussed for a large number of molecules[1] including Cl_2 and HCl,[2] Br_2 and HBr[3] but the corresponding data for I_2 and HI[4] have not been given in detail.

In connection with experiments now completed in this laboratory on the rate of decomposition of deuterium iodide, it became necessary to calculate the equilibrium concentration of DI at various temperatures and we have therefore obtained the partition functions for I_2, HI and I atom and determined the free energy decrease and other thermodynamic functions for the reaction

$$HI \rightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2 \qquad (1)$$
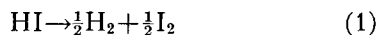
and the corresponding deuterium reaction. This paper is concerned with the hydrogen case while the corresponding data for DI as well as a discussion of the rates of the two reactions will appear later.

The method of calculating thermodynamic functions from spectroscopic data is well known and reference may be made to the reviews cited above for complete details. The partition functions are given by $Q = \Sigma p \exp(-E/kT)$, where p is the statistical weight of the energy level and summation is made over the required number of electronic, vibrational and rotational states. The energy, as obtained from spectroscopic data is a complicated function of v and $J(J+1)$, the vibrational and rotational quantum numbers, respectively. Once the Q functions and their derivatives are known the free energy, entropy and other properties follow by the well-known methods of statistical mechanics and thermodynamics. The laborious task of summing over all the energy levels has been simplified by several methods. We have found the procedure of Kassel[5] useful, especially for such a molecule as I_2 where a large number of vibrational levels must be summed.

The molecular constants for I_2 were taken from Jevons[6] and may be found in Table I along with those for HI, which were recalculated from the recent experiments of Nielsen and Nielsen,[7] who measured the fundamental and first harmonic

[1] For reviews of the subject, see Giauque, J. Am. Chem. Soc. **52**, 4808 (1930); Zeise, Zeits. f. Elektrochemie **39**, 758, 895 (1933); **40**, 662, 885 (1934). The latter author has compiled the available data for both diatomic and polyatomic molecules.
[2] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).
[3] Gordon and Barnes, J. Chem. Phys. **1**, 692 (1933).
[4] The free energy function for HI at a few temperatures has been given by Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933). Zeise (reference 1) has given the same functions for I_2 but has not discussed the experimental data critically as we do here.

TABLE I.

	I_2	HI
B_0	3.73×10^{-2}	6.4576
D_0	-4.536×10^{-9}	-2.1013×10^{-4}
α	1.2×10^{-4}	1.725×10^{-1}
β	1.63×10^{-11}	—
ω_e	214.26	2309.55
$x_e\omega_e$	0.592	39.735

[5] Kassel, J. Chem. Phys. **1**, 576 (1933); Phys. Rev. **43**, 364 (1933).
[6] Jevons, *Report on Band-Spectra of Diatomic Molecules* (University Press, Cambridge, 1932).
[7] Nielsen and Nielsen, Phys. Rev. **47**, 585 (1935).

TABLE II.

T	Q	$-(F°-E_0°)/T$
	I₂	
298.1	4,375.64	54.193
500	10,356.64	58.474
800	24,109.80	62.487
1000	36,595.51	64.425
1500	79,854.51	67.988
	HI	
298.1	32.6307	42.418
500	54.6738	46.012
800	89.0072	49.315
1000	114.0486	50.916
1500	187.4235	53.916
	I	
298.1	4	38.225
500	4	40.794
800	4	43.128
1000	4	44.237
1500	4	46.250

absorption bands of HI in the infrared. Their results are in agreement with the work of Czerny,[8] Salant and Sandow[9] and Kirkpatrick.[10] In accordance with the practice of Giauque and co-workers, we have used the natural constants given in the *International Critical Tables*.[11] The partition functions were calculated for both HI and I₂ at 298.1, 500, 800, 1000 and 1500°K and are given in Table II. Many intermediate values were also summed in order to test the interpolation formula which is described below. For the iodine atom, the normal state is an inverted ^2P level, with a doublet separation[12] of 7600 cm^{-1} and the contribution from this level is negligible up to several thousand degrees. The partition function for I atom is therefore independent of temperature in this range and is $Q=4$.

From the Q functions, the free energy for the molecule or atom may be obtained from the expression

$$-(F°-E_0°)/T=(3/2)R \ln M+(5/2)R \ln T +R \ln Q-7.267, \quad (2)$$

where M is the molecular or atomic weight and $E_0°$ is the energy at the absolute zero. Following the usual custom, which is valid for temperatures above 25°C, the nuclear spin contributions have been excluded but for the homo-nuclear molecule,

[8] Czerny, Zeits. f. Physik **44**, 235 (1927).
[9] Salant and Sandow, Phys. Rev. **37**, 373 (1931).
[10] Kirkpatrick, Phys. Rev. **49**, 104 (1936).
[11] Int. Crit. Tab., Vol. I, p. 16. The numerical constant of the free energy equation was taken as 7.267; $R=1.9869$; $hc/k=1.4324$.
[12] Turner, Phys. Rev. **27**, 397 (1926).

I₂, the Q function as calculated must be divided by two which has been done for the results given in Table II. The atomic weights for hydrogen and iodine were taken as 1.00778 and 126.932, respectively.[13]

Since interpolation for other temperatures is fairly laborious, the free energy functions obtained at the five temperatures mentioned above were fitted to an equation of the form

$$-(F°-E_0°)/T=a/T+b \log T+cT+dT^2+i, \quad (3)$$

which is suggested by thermodynamic considerations.[14] The constants in this equation are given for HI, I₂ and I atom as well as for H₂, the latter being taken from the free energy functions of Giauque[15] at the same five temperatures as for the other molecules. The results will be found in Table III. It is probably not safe to extrapolate these equations beyond 298.1 or 1500°K but over this entire range, the free energy function (3) is reproduced to within ±0.001 cal./mole as tested by calculation and comparison with about 15 points within this temperature range.

If the value of $\Delta E_0°$ is known for any particular reaction, it may be combined with equations of the form (3) for the individual reactants to obtain an equation of the same form, representing the free energy change of the reaction

$$-\Delta F°/T= -\Delta(F°-E_0°)/T-\Delta E_0°/T$$
$$=R \ln K, \quad (4)$$

where K is the equilibrium constant at unit pressure. In accordance with the thermodynamic

TABLE III.

	HI	H₂
a	−108.672	114.572
b	14.6592	16.7648
c	$7.649×10^{-4}$	$-5.410×10^{-4}$
d	$-4.0 ×10^{-10}$	$1.67 ×10^{-7}$
i	6.2820	−17.2832
	I₂	I
a	180.778	−28.052
b	19.8028	11.1292
c	$4.442×10^{-4}$	$1.907×10^{-4}$
d	$-6.87 ×10^{-8}$	$-4.09 ×10^{-8}$
i	4.4605	10.7277

[13] Aston, *Mass-Spectra and Isotopes* (Longmans, Green and Co., New York, 1933).
[14] See, for example, Lewis and Randall, *Thermodynamics* (McGraw-Hill Book Co., New York, 1932), particularly Chapter XV.
[15] Giauque, J. Am. Chem. Soc. **52**, 4816 (1932).

notation, we write Eq. (4) in the form

$$\Delta F^\circ/T = \Delta H_0/T - \Delta\Gamma_0 \ln T - \tfrac{1}{2}\Delta\Gamma_1 T - \tfrac{1}{6}\Delta\Gamma_2 T^2 + I. \quad (5)$$

This equation, except for the uncertainty in the quantity, ΔE_0° will give the correct free energy change of the reaction to ± 0.001 cal./mole over the entire temperature range from 298.1 to 1500°K. It may also be differentiated and integrated to give changes in heat content, specific heat and entropy

$$\Delta H = \Delta H_0 + \Delta\Gamma_0 T + \tfrac{1}{2}\Delta\Gamma_1 T^2 + \tfrac{1}{3}\Delta\Gamma_2 T^3 + \cdots, \quad (6)$$

$$\Delta C_p = \Delta\Gamma_0 + \Delta\Gamma_1 T + \Delta\Gamma_2 T^2 + \cdots, \quad (7)$$

$$\Delta S = \Delta\Gamma_0(\ln T + 1) + \Delta\Gamma_1 T + \tfrac{1}{2}\Delta\Gamma_2 T^2 - I. \quad (8)$$

We have not investigated the precision of any of these expressions by direct summation except the entropy equation which we discuss later but it seems likely that they will all give results of sufficient precision for most applications, although they are not as exact as the free energy equation. Their chief advantage lies in the avoidance of the tedious process of summation which is required for determining the entropy and other quantities from spectroscopic data.

THE DISSOCIATION OF IODINE MOLECULE

The decomposition of molecular iodine into atoms has been studied by Starck and Bodenstein,[16] Braune and Ramstetter[17] and DeVries and Rodebush.[18] Gibson and Heitler[19] have shown that the experimental results of Starck and Bodenstein are in agreement with the statistical calculations. They assumed the iodine molecule to be a rigid rotator and a simple harmonic oscillator and added a slight correction term to account for anharmonicity but the exact partition functions as calculated here do not change their results by a very large amount. The value of ΔE_0° for this reaction has been given by Brown[20] from extrapolation of spectroscopic data as 1.535 ± 0.001 ev or $35,395 \pm 23$ cal./mole.[21] This result when substituted into

Eq. (4) is definitely inconsistent with the equilibrium data. Gibson and Heitler have rejected a similar result of 1.532 ev given by Kuhn[22] as too small and have preferred to take 1.544 ± 0.003 ev by extrapolation of the bands of Mecke.[23] Because of this uncertainty, we have used Eq. (4) and the experimental equilibrium constants to determine ΔE_0°, giving a result of $35,795 \pm 100$ cal./mole. While this is definitely higher than any of the previous values it seems necessary if all of the experimental data are to be given equal weight. Combining this value of ΔE_0° with the proper constants from Table III and using Eq. (5) we obtain values for the coefficients of that equation as given in Table IV. A plot of $\log K$ against $1/T$ for all the

TABLE IV.

	$I_2 \rightarrow 2I$	$HI \rightarrow \tfrac{1}{2}H_2 + \tfrac{1}{2}I_2$
ΔH_0	36.032	715.48
$\Delta\Gamma_0$	1.0664	1.5741
$\Delta\Gamma_1$	-1.256×10^{-4}	-1.6266×10^{-3}
$\Delta\Gamma_2$	-7.86×10^{-8}	2.973×10^{-7}
I	-16.9949	12.6934

experimental data is given in Fig. 1, which is seen to be a straight line. A more certain value of ΔE_0° will only result in a shift of the whole curve parallel to itself in either direction. The equilibrium constant is given by

$$K_p = 4\alpha^2 P/(1-\alpha^2), \quad (9)$$

where α is the degree of dissociation of iodine and P is the pressure in atmospheres.

Using Eq. (6), we obtain for the heat of dissociation of iodine into atoms at 298.1°K

$$\Delta H_{298.1} = 36,343 \pm 100 \text{ cal./mole}$$

and from Eq. (8)

$$\Delta S_{298.1} = 24.097 \text{ cal./degree per mole.}$$

By direct summation at this temperature, we have obtained $S_{298.1}(I_2) = 62.29$; $S_{298.1}(I) = 43.19$; $\Delta S_{298.1} = 24.09$ in satisfactory agreement with Eq. (8). The value for I_2 is in exact agreement with the calculations of Giauque,[24] who used an approximate method for determining the partition functions.

[16] Starck and Bodenstein, Zeits. f. Elektrochemie 16, 961 (1910); 22, 327 (1916).
[17] Braune and Ramstetter, Zeits. f. physik. Chemie 102, 480 (1922).
[18] DeVries and Rodebush, J. Am. Chem. Soc. 49, 656 (1927).
[19] Gibson and Heitler, Zeits. f. Physik 49, 465 (1928).
[20] Brown, Phys. Rev. 38, 709 (1931).
[21] We take 1 ev = 23,085.5 cal./mole.

[22] Kuhn, Zeits. f. Physik 39, 77 (1926).
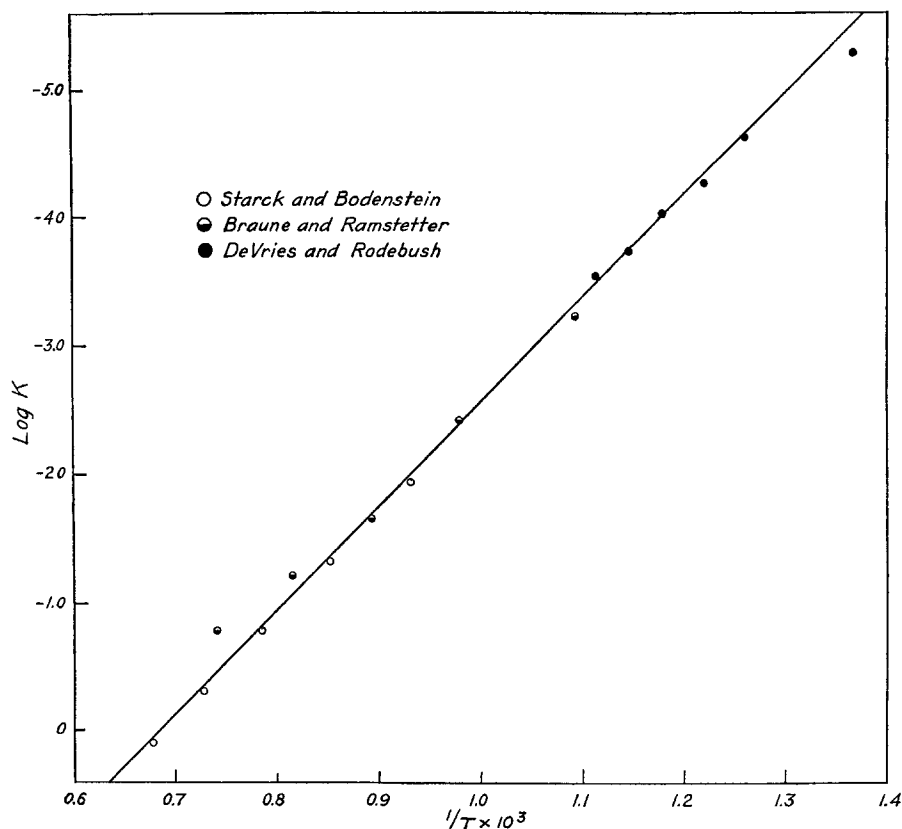[23] Mecke, Ann. d. Physik 71, 103 (1923).
[24] Giauque, J. Am. Chem. Soc. 53, 507 (1931).

FIG. 1. The equilibrium constant for the reaction: I₂→2I. Theoretical curve from Eq. (5) and Table IV; experimental points from various authors.

THE DISSOCIATION OF HYDROGEN IODIDE

The thermal equilibrium between hydrogen, iodine and hydrogen iodide has been studied by Bodenstein[25] and is generally considered to be the most carefully investigated gaseous equilibrium to be found in the literature. In addition to the earlier experiments of Hautefeuille[26] and Lemoine,[27] the equilibrium has also been studied at 1022 and 1217°C by von Falckenstein[28] and near room temperatures by Stegmüller,[29] using an electromotive force method. More recently, Urey and Rittenberg[30] have studied the equilibrium with mixtures of hydrogen and deuterium

and have shown that the constants obtained from the spectroscopic data for the reaction

$$H_2+2DI \rightarrow D_2+2HI \qquad (10)$$
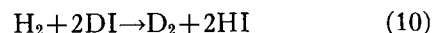
are in agreement with the experimentally determined ones. The latter authors have also given two measurements with hydrogen iodide alone.

For this reaction, the value of $\Delta E_0°$ is still more uncertain than for the iodine decomposition. We have therefore followed the same procedure as above to determine this quantity although we have used only the data of Bodenstein and the two points of Rittenberg and Urey. Following a suggestion of Haber,[31] however, we first correct the measured equilibrium constants for the dissociation of iodine molecules into atoms which is not very great but should not be neglected at the highest temperatures. If ξ is the concentration of hydrogen or iodine at

[25] Bodenstein, Zeits. f. physik. Chemie 13, 56 (1894); 22, 1 (1897); 29, 295 (1899); Habilitationsschrift, Heidelberg, 11–36, W. Engelmann, Leipzig, 1899.
[26] Hautefeuille, Comptes rendus 64, 608 (1867).
[27] Lemoine, Ann. chim. phys. (5) 12, 145 (1877).
[28] von Falckenstein, Zeits. f. physik. Chemie 68, 270 (1909); 72, 113 (1910).
[29] Stegmüller, Zeits. f. Elektrochemie 16, 85 (1910).
[30] Rittenberg and Urey, J. Am. Chem. Soc. 56, 1885 (1934).

[31] Haber, Thermodynamics of Technical Gas-Reactions (Longmans, Green and Co., New York, 1908).

equilibrium and α is the percentage decomposition of iodine into atoms, the corrected equilibrium constant for the reaction (1) is given by

$$K' = \xi(1-\alpha)^{\frac{1}{2}}/2(1-\xi) = K(1-\alpha)^{\frac{1}{2}}, \quad (11)$$

where K is Bodenstein's constant.

A more serious difficulty is the uncertainty of Bodenstein's temperatures. His experiments cover the temperature range between 283 and 508°C and several thermostats were used. A number of temperatures were obtained with a sulfur vapor bath, the temperature being varied by boiling the sulfur under reduced pressures. The temperature was determined by measuring the vapor pressure of the sulfur with a manometer, the pressure-temperature curve for sulfur having been previously determined by means of calibrated mercury thermometers. Comparison with the present vapor pressure curve[32] of sulfur shows some divergence from the temperatures as given by Bodenstein and since he gave the observed pressure in each case, it is possible to make corrections. The present vapor pressure curve of sulfur may be in error by as much as 3° at the lowest temperature but since Bodenstein's temperature differs at this point by 10°, the corrected temperatures as given in Table V seem more nearly correct than those given by Bodenstein. The boiling point of mercury was used for another temperature and this is apparently correct while PS_5 was used in another thermostat and we have changed this temperature from 508° to 514°C in accordance with the *International Critical Tables*, although this is more uncertain than the sulfur points. All of his other temperatures were measured with a mercury thermometer and naturally nothing can be said of their errors, if any. The two points of Urey and Rittenberg mentioned above are apparently correct since the temperatures were directly measured with a thermocouple. The corrected temperatures and equilibrium constants corrected in accordance with Eq. (11) for the dissociation of iodine are given in Table V.

Using these corrected temperatures only, we have then used Eq. (4) to calculate $\Delta E_0{}^\circ$ as before. The value obtained is

$$\Delta E_0{}^\circ = 971.83 \pm 13.65 \text{ cal./mole.}$$

[32] Int. Crit. Tab., Vol. III, p. 201.

TABLE V.

$T_{Bod.}$	$T_{corr.}$	log K' (exp.)	log K' (calc.)
781	787	−0.8002	−0.8121
760	—	−0.8163	−0.8268
—	*741	−0.8328	−0.8377
716	717	−0.8513	−0.8523
700	700	−0.8618	−0.8630
683	684	−0.8765	−0.8736
—	*671	−0.8840	−0.8826
666	671	−0.8876	−0.8826
647	657	−0.9004	−0.8925
629	—	−0.9179	−0.9179
601	—	−0.9350	−0.9361
575	—	−0.9552	−0.9588
556	—	−0.9639	−0.9765

$T_{Bod.}$ are Bodenstein's experimentally determined temperatures in °K. $T_{corr.}$ are the temperatures which could be corrected as explained above.
* Data of Rittenberg and Urey.

This constant has then been used in Eq. (5) to give the free energy decrease of the reaction, the constants in the equation being found in Table IV. The same remarks that were made above as to precision apply also in this case.

Using Eq. (6) we obtain

$$\Delta H_{298.1} = 1113 \pm 15 \text{ cal./mole.}$$

If we take the heat of sublimation of iodine as 7438 cal./mole as given by Giauque,[24] we obtain -6325 ± 15 cal./mole for the heat of dissociation of HI into hydrogen and solid iodine. This may be compared with the calorimetric determinations of Thomsen and Berthelot[33] who found 6000 and 6300 cal./mole, respectively. A recent calorimetric determination by Günther and Wekua[34] for the reaction

$$HI(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(g) + \tfrac{1}{2}I_2(s) \quad (12)$$

gave $\Delta H = 27,966 \pm 50$ cal./mole at room temperature. Assuming the latter to be 25°C and combining with the heat of formation of HCl, given by Giauque and Overstreet[2] as $22,028 \pm 10$ cal./mole gives 5942 ± 50 cal./mole for the heat of decomposition of HI. This value cannot be combined with the spectroscopic data to give agreement with the experimental equilibrium constants[35] and it seems evident that some unsuspected source

[33] Lewis and Randall, reference 14, page 525.
[34] Günther and Wekua, Zeits. f. physik. Chemie A154, 193 (1931).
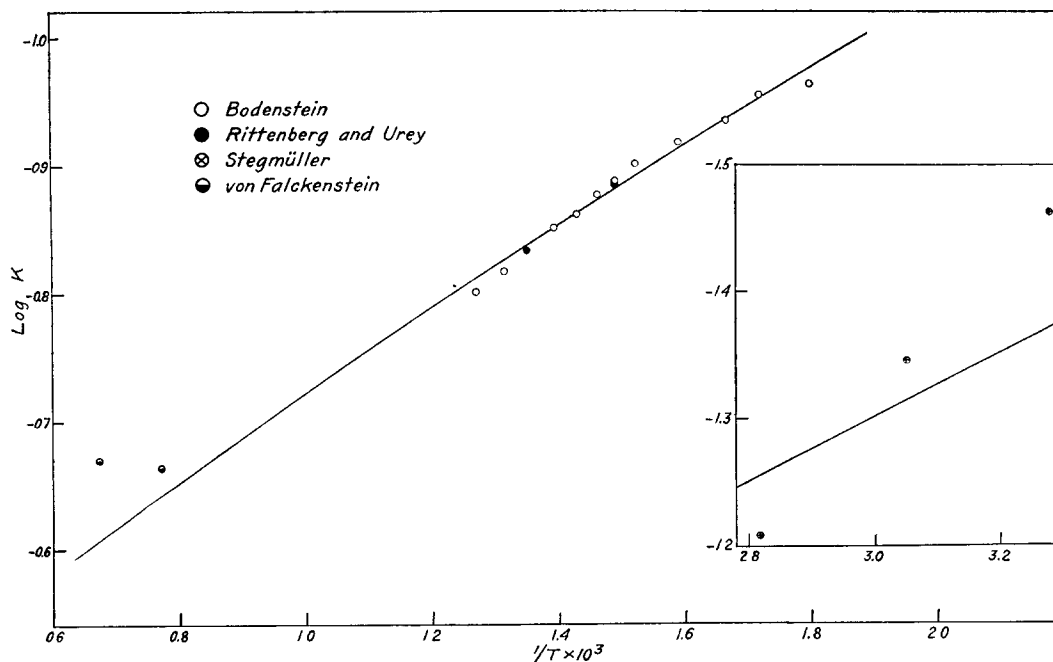[35] Zeise, reference 1, has also reached a similar conclusion.

FIG. 2. The equilibrium constant for the reaction: HI→½H$_2$+½I$_2$. Theoretical curve from Eq. (5) and Table IV; experimental points from various authors.

of error was present in these calorimetric determinations.

Using Eq. (8) we find

$$\Delta S_{298.1} = -2.623 \text{ cal./degree per mole.}$$

Summation gives for HI at the same temperature the value -49.36 and combining with $S(H_2) = 31.23$ from Giauque[15] and the entropy of I$_2$ as given above, we obtain $\Delta S_{298.1} = -2.60$, in satisfactory agreement with our interpolation formula (8). Giauque[24] using a rigid molecule for HI, obtained $S(HI) = 49.8$ and since he used the same values as above for H$_2$ and I$_2$, he finds $\Delta S = -3.04$. The difference is due entirely to his value for HI. Experimentally, Giauque and Wiebe,[36] find $S_{298.1}(HI) = 49.5$.

The equilibrium constants as calculated by Eq. (4) and the constants given in Table IV will be found in Table V and a plot of log K against $1/T$ in Fig. 2. We have also included there the results of von Falckenstein and Stegmüller. The former were apparently incorrectly

changed by the author for the decomposition of I$_2$ and the possibility of a reaction between Pt and I$_2$ was not considered as pointed out by Jellinek and Uloth,[37] which undoubtedly accounts for the divergence from the calculated curve, although the values of K' as plotted here do not help the agreement very much. The results of Stegmüller are probably in error because of neglect of liquid junction potentials as stated by Lewis and Randall.[33] On the other hand, the points of Bodenstein and Rittenberg and Urey are in good agreement with the theoretical curve. Consideration of the errors involved shows that an error of 0.5 percent in the analysis would account for the divergence of the point which lies furthest from our theoretical curve. However, if one drew the best curve through all of the experimental points, the slope of the line would be quite different from the one we have chosen from the statistical calculations. Although Fig. 2 has a slight curvature and is not a straight line like Fig. 1, the spectroscopic data can certainly not be so adjusted to give the

[36] Giauque and Wiebe, J. Am. Chem. Soc. **51**, 1441 (1929).

[37] Jellinek and Uloth, Zeits. f. anorg. Chemie **151**, 161 (1926).

extreme curvature required by the experimental points but can only be shifted parallel to itself because of the uncertainty in $\Delta E_0°$. The slight curvature in Fig. 2, mentioned above is probably due to the anharmonic terms and the rotational stretching terms in the energy expression for HI which also explains why Fig. 1 is a straight line since these quantities are nearly negligible for a heavy molecule like iodine.

Note added in proof: Further consideration shows that the attempted correction of Bodenstein's temperatures may not be justified as his experimental temperatures with the sulfur baths fit the theoretical curve as well as the corrected ones. However, this does not affect any of the calculations made above since either set of temperatures will give the same $\Delta E_0°$ within the probable error stated. The doubtful points are thus the ones at the lowest and highest temperatures which may be explained by errors in analysis or what is more likely some further uncertainty in the experiments.

The Isotope Effect in the Evaporation of Lithium, Potassium and Rubidium Ions

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Abundance ratio measurements are necessarily complicated by the possibility of an isotope effect at the source. In the emission of positive thermions of lithium, potassium and rubidium the extent to which the ion ratio represents the atom ratio within the source can be estimated by observing the change in the abundance ratio as a function of the percent of alkali evaporated. In the case of lithium an initial ratio of $Li^7/Li^6 = 11.60$ was observed; the abundance ratio followed the computed ratio for ideal evaporation until the lithium was 40 percent exhausted, beyond which it fell below the ideal value. The abundance ratios of $K^{39}/K^{41} = 14.22$ and $Rb^{85}/Rb^{87} = 2.59$ remained almost unchanged during the process of exhaustion. It is apparent therefore that a correction factor needs to be applied to the ion abundance ratio for lithium, but is unnecessary for potassium and for rubidium. The atomic weights computed from the abundance ratios are $Li = 6.939$, $K = 39.094$ and $Rb = 85.46$.

A N accurate estimation of isotope abundance ratios from mass-spectrographic measurements necessarily involves the question of an isotope effect at the positive ion source. The extent to which the ion ratio represents the true abundance ratio is amenable to a comparatively simple test in the case where positive thermions are used as the ion source.

In the mass spectrograph which was described recently,[1] heated platinum disks impregnated with alkali were used as the source of positive ions. These ion emitters were prepared by coating the platinum with a water paste made from the salt to be tested. These coated disks can be used directly as positive ion emitters, although platinum impregnated with alkali is in general the more satisfactory source. This impregnation is readily accomplished by heating the disk to dull redness in contact with the adhering coating for about half an hour; the coating is then removed by scraping and washing with distilled water.

During the heating process the platinum dissolves sufficient alkali to become an excellent emitter of positive ions.

The test for a preferential isotope effect in the emission of alkali ions was made by observing the changes in the abundance ratio as a function of the fraction of the alkali evaporated. This fraction was obtained from a determination of the time and current necessary for the complete exhaustion of the less abundant isotope; the abundance ratio was measured at regular intervals during the exhaustion period.

RESULTS

The procedure just described yields the abundance ratio as a function of the less abundant isotope evaporated from the platinum. Curve A, Fig. 1 shows a representative run obtained with lithium. The initial abundance ratio, $Li^7/Li^6 = 11.6$, is the same as that reported previously.[2] During the exhaustion period it was necessary

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[1] A. Keith Brewer, J. Am. Chem. Soc. **58**, 365 (1936).

[2] A. Keith Brewer, Phys. Rev. **47**, 571 (1935).