

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, THE STATE UNIVERSITY OF IOWA]

THE FREE ENERGY OF DILUTION AND THE ACTIVITY OF THE IONS OF HYDROGEN IODIDE IN AQUEOUS SOLUTION¹

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RECEIVED AUGUST 16, 1923

The free-energy decrease accompanying the transfer of one mole of salt from any concentration c_2 to concentration c_1 is most conveniently determined by the electromotive-force method. The free-energy decrease ($-\Delta F$) and the electromotive force E are related to the activities of the ions by the well-known thermodynamic expression, $(-\Delta F) = e.m.f. = RT \log \frac{a_2^+ \cdot a_2^-}{a_1^+ \cdot a_1^-}$, where a_2^+ , a_2^- and a_1^+ , a_1^- represent the activities of the cation and anion in concentrations c_2 and c_1 , respectively. The other symbols have their usual significance. If we now choose one solution so dilute, that we may assume the activity product, $a_1^+ \cdot a_1^-$, equal to the product of the concentrations of the ions as measured by conductance, then it is possible to calculate the product of the activities of the ions, $a_2^+ \cdot a_2^-$, at any other concentration c_2 from purely electromotive-force data. If we assume with MacInnes² the hypothesis of the independent activity of the ions and also that in any solution of potassium chloride the activities of the potassium and chloride ions are equal, the expression $\sqrt{a_K^+ \cdot a_{Cl}^-}$ gives us directly the activity of either of these ions. Likewise, having determined by electromotive force the activity product of the ions for a given concentration for any other binary electrolyte containing either a potassium or a chloride ion, the ratios, $(a_M^+ \cdot a_{Cl}^-)/a_{Cl}^-$ or $(a_K^+ \cdot a_X^-)/a_K^+$ give immediately the activities, a_M^+ or a_X^- , respectively.

Adopting this procedure, Pearce and Hart³ have found that the activities of the chloride and bromide ions are equal for equal concentrations of their binary salts. It should be said in passing that we are not unmindful of the excellent work of Lewis and Randall.⁴ These men have calculated the same results for these ions from freezing-point and vapor-pressure data. For the sake of brevity, however, the discussion of their work as well as that of others will be omitted at this time. The present paper deals with a study of the free energy of dilution and the activities of the ions in aqueous solutions of hydrogen iodide.

Apparatus and Materials

The cell used was similar to that described by Linhart.⁵ The platinum wire anode

¹ This paper contains the essential parts of a dissertation by Dr. A. R. Fortsch.

² MacInnes, *THIS JOURNAL*, **41**, 1086 (1919).

³ Pearce and Hart, *ibid.*, **43**, 2483 (1921).

⁴ Lewis and Randall, *ibid.*, **43**, 1112 (1921).

⁵ Linhart, *ibid.*, **41**, 1175 (1919).

was tightly packed with fine, electrolytically deposited crystals of metallic silver and then covered with a layer of silver iodide. The silver iodide was prepared by precipitation from carefully recrystallized silver nitrate and potassium iodide; it was then washed with conductivity water until the washings gave no test for iodides and finally stored under conductivity water. Every possible care was taken throughout the work to exclude light, and in no experiment did the precipitate darken perceptibly. Two hydrogen electrodes were placed in each cell. These consisted of large pieces of platinum gauze heavily coated with platinum black. The hydrogen iodide was made by passing hydrogen sulfide through an aqueous suspension of pure resublimed iodine. The solution was boiled to remove the last traces of hydrogen sulfide and then fractionally distilled. The fraction of constant boiling point was stored over a small quantity of red phosphorus and was freshly distilled in a current of pure hydrogen when needed.

In making the solutions of hydrogen iodide, approximately the required volume of the constant-boiling acid was added to a given volume of cooled, previously boiled conductivity water. The cell and contents were repeatedly rinsed with the solution and then filled to the proper volume, the electrodes were inserted and the cell was placed in a large constant-temperature oil-bath. Hydrogen, obtained by the electrolysis of a strong solution of sodium hydroxide, was first passed through a strong alkaline solution of pyrogallol, then through concd. sulfuric acid and, finally, through saturator bulbs, containing an acid of the cell concentration into the cell. In preliminary experiments it was found that the rate of bubbling may be varied between 30 and 250 bubbles per minute without affecting the constancy of the voltage readings. The rate of flow was limited in every experiment to about 60 bubbles per minute. The time required for the cell to attain equilibrium under the precautions necessary varied from 4 to 8 days, depending on the concentration. The exact molal concentration of the hydrogen iodide was determined gravimetrically as silver iodide after the cell potentials had been read.

Accuracy of Method

All electromotive-force data given in the following tables are the mean values for at least two different arrangements of the cell. Readings were taken on the two hydrogen electrodes independently and unless the variation between the two was less than 0.04 mv. the process of preparation was repeated. All potential readings were corrected by applying the usual formula: $E = \frac{0.0001983T}{2} \log \frac{760}{x}$, where E is the correction voltage, T the absolute temperature and x the partial pressure of the hydrogen above the solution. All barometer readings were from a standard precision barometer and were corrected for latitude, altitude and temperature. The electromotive forces were read at 25°, 30° and 35°, in the order named, and then to ascertain whether any changes had occurred within the cell during the experiment the temperature was lowered to 25° and the readings were again taken. In only one cell (0.24608 M) did the initial and final readings at 25° differ by more than a few tenths of a millivolt.

In the preliminary work it was observed that the potential readings begin to vary considerably when the electrodes were allowed to remain in the solution for more than 60 hours. Upon removing the electrodes, allowing them to stand in nitric acid for an hour or more and then replatinizing them,

readings could be duplicated indefinitely to within 0.10 mv. At 0.12972 *M* a slight opalescence was observed on adding a soluble chloride to the nitric acid wash water. At concentrations greater than 0.24608 *M* the amount of silver deposited on the electrodes became considerable and no consistent readings were obtainable.

The potential readings were made on a standard potentiometer, the reference standard being a certified Weston cadmium cell (1.01871 volts at 23°). The temperatures were accurately controlled to $\pm 0.03^\circ$.

Experimental Part

Table I gives the final values for the electromotive forces of the cells at various concentrations and at 25°, 30° and 35°.

TABLE I
ELECTROMOTIVE FORCES OF THE CELLS
H₂ | HI, AgI | Ag

<i>c</i> 1000 g.	<i>E</i> ₂₅ volts	<i>E</i> ₃₀ volts	<i>E</i> ₃₅ volts
0.24608	-0.06905	-0.06864	-0.06829
.12972	-.03615	-.03556	-.03531
(.10000)	-.02273	-.02202	-.02162
.07914	-.01210	-.01128	-.01073
.05049	+.01006	+.01128	+.01235
.01981	+.05735	+.05931	+.06083
.01045	+.08825	+.09060	+.09262
.00505	+.12417	+.12707	+.12964
(.00500)	+.12453	+.12744	+.13991

The values of *E* (in parentheses) for the concentration 0.005 *M* were obtained by assuming *E* as a quadratic function of *c*, using the three concentrations 0.01981, 0.01045 and 0.00505. Those for the 0.10 *M* were obtained in a similar way by using the concentrations 0.24608, 0.12972 and 0.07914. It will be noted that a change of sign occurs between the concentrations 0.07914 *M* and 0.05049 *M*. This is due doubtless to the fact that silver iodide is extremely insoluble; a small concentration of hydrogen iodide is sufficient by reason of the common ion effect to reduce the concentration of the silver ion to such an extent that the potential of the cell is reversed.

The free-energy decrease ($-\Delta F$) accompanying the cell reaction was obtained by multiplying the electromotive force of the cell by 96494. These values have been calculated for the various cells at the three temperatures, and from them we have calculated the temperature coefficients of free energy, α and β . The decrease in heat content ($-\Delta H$)₂₅ was computed by means of the relation: ($-\Delta H$)₂₅ = ($-\Delta F$)₂₅(1 - 298.09 α). This is obtained by substituting the expression for ($-\Delta F$) as a function of the temperature in the fundamental thermodynamic equation, $\frac{d}{dT}\left(\frac{-\Delta F}{T}\right) =$

$\frac{-\Delta H}{T^2}$, performing the differentiation indicated and rearranging terms. The data thus assembled are collected in Table II.

TABLE II
THE FREE-ENERGY DECREASE AND THE HEAT-CONTENT DECREASE ACCOMPANYING THE
CELL REACTION AT 25°

c 1000 g.	$(-\Delta F)_{25}$ joules	$\alpha \cdot 10^6$	$\beta \cdot 10^7$	$(\Delta H)_{25}$ joules
0.24608	- 6663	- 1277	+ 177	-9199
.12972	- 3488	- 4211	+1886	-7867
(.10000)	- 2193	- 7609	+2726	-7168
.07914	- 1167	-16151	+4453	-6789
.05049	+ 970	+25909	-3092	-6524
.01981	+ 5534	+ 7608	-1539	-7016 ?
.01045	+ 8515	+ 5699	- 748	-5953
.00505	+11982	+ 4950	- 531	-5699
(.00500)	+12016	+ 4950	- 549	-5715

It will be noted that the values of α and β change sign between the concentrations 0.05049 M and 0.07914 M . At some concentration between these the electromotive force and hence the free-energy decrease are zero. Thus, the values of α must change from a small negative number to an infinitely large negative number on the one hand, and from an infinitely large positive to a small positive number on the other hand. In other words, the coefficient α changes sign by passing through infinity. The negative values of $(-\Delta H)_{25}$ decrease regularly with increasing dilution.

The decrease in free energy attending the transfer of one mole of hydrogen iodide from any concentration c to one exactly 0.005 M was obtained by the algebraic addition of the $-\Delta F_{25}$ values given in Table II. By substituting these values in the expression, $-\Delta F_{25} = RT \ln \frac{c_2^2 (\alpha_2^+ \alpha_2^-)}{c_1^2 (\alpha_1^+ \alpha_1^-)}$, and assuming that the value of $(a_1^+ \cdot a_1^-)$ for 0.005 M hydrogen iodide is the same as that determined by Noyes and MacInnes⁶ for the same concentration of hydrogen chloride, namely, 0.9312, we have calculated the product of the activity coefficients of the two ions at the remaining concentrations. Lewis and Randall⁴ have used as the basis of their values for hydrochloric acid a method of extrapolation described by Linhart.⁵ The value of the product of the activity coefficients for a 0.005 M solution is 0.8968. We have calculated the product of the activity coefficients using both values; the results are assembled in Table III.

From the data of Noyes and MacInnes⁶ on hydrochloric acid it may be noted that there is a minimum value for the activity-coefficient product at about 0.5 M . From this investigation we are led to the conclusion that the same type of variation is exhibited by the activity coefficients of hydro-

⁶ Noyes and MacInnes, THIS JOURNAL, 42, 239 (1920).

TABLE III

THE FREE-ENERGY DECREASE ATTENDING THE TRANSFER OF ONE MOLE OF HYDROGEN IODIDE FROM CONCENTRATION c TO 0.005 M , AND THE PRODUCTS OF THE ACTIVITY COEFFICIENTS OF THE IONS

c 1000 g.	$-\Delta F_{25}$ joules	$\alpha_{\text{H}^+}^+ \alpha_{\text{I}^-}^-$ (N—M)	$\alpha_{\text{H}^+}^+ \alpha_{\text{I}^-}^-$ (L—R)
0.2408	18679	0.7201	0.6857
.12972	15504	.7199	.6856
(.10000)	14209	.7185	...
.07914	13184	.7585	.7223
.05049	11046	.7865	.7491
.01981	6482	.8111	.7724
.01045	3501	.8751	.8331
.00500	0000	.9312	.8968

odic acid, but that the minimum occurs at a lower concentration, about 0.11 M . We next plotted the activity-coefficient products against the concentrations on a large scale and read from the smooth curve the activity products at round concentrations. The geometric mean activity coefficients of the ions have been calculated and are tabulated for comparison along with the corresponding coefficients of the ions of hydrochloric acid as calculated on the assumptions of Noyes and MacInnes and of Lewis and Randall in Table IV.

TABLE IV

THE GEOMETRIC MEAN ACTIVITY COEFFICIENTS AT ROUND CONCENTRATIONS

c 1000 g.	HI (exp.)	HCl (N—M)	HI (exp.)	HCl (L—R)
0.005	0.965	0.965	0.947	0.947
.010	.937	.932	.920	.924
.020	.901	.899	.886	.894
.030	.893	.880	.877	..
.050	.884	.855	.868	.860
.100	.862	.847	.846	.814
.200	.849	.796	.834	.783

It is evident from the data here given that the activity coefficients and the activities of the iodide and chloride ions are equal for any concentration of their acids up to 0.05 M . It is interesting to note that the activity coefficients, based on the assumption that the activity coefficient of 0.005 M hydrochloric acid is 0.965, agree closely with the fractional ionization of uni-univalent salts of the type KCl as calculated by Randall.⁷ In regard to the different values of the activity coefficients obtained by using different values for the coefficient of the dilute solution arbitrarily chosen for reference, it is apparent that the difference lies mainly in the value of the reference chosen. Any error in either standard would influence the entire series of activity coefficients.

⁷ Randall, THIS JOURNAL, 38, 790 (1916).

Summary

1. The electromotive forces of cells of the type, $H_2 | HI (c), AgI | Ag$, have been measured at 25° for various concentrations of hydrogen iodide.
2. The free-energy decrease and the heat-content decrease attending the cell reaction have been calculated.
3. The free-energy decrease accompanying the transfer of one mole of hydrogen iodide from the various concentrations to a concentration exactly $0.005 M$ has been computed. From these values we have calculated the geometric mean activity coefficients of the ions of hydrogen iodide, and we have found that for concentrations up to $0.05 M$ these coefficients are practically equal to the corresponding coefficients for hydrogen chloride at the same concentrations. Obviously, the activities of the iodide and chloride ions are equal when in equivalent concentrations of their salts.

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THE DIFFUSION OF HYDROGEN THROUGH METALS¹

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RECEIVED AUGUST 29, 1923

Deville and Troost,² Graham,³ Sieverts,⁴ and Charpy and Bonnerot⁵ have studied the diffusion of hydrogen through platinum, iron, palladium, copper and nickel. The rate of diffusion, found to be very different for different metals, was shown to increase rapidly with increasing temperature, but the results obtained were hardly more than qualitative, and were not expressed in terms that may be compared with recent work. More accurate data have been obtained by Schmidt⁶ and by Holt⁷ on palladium, by Richardson and coworkers⁸ on platinum, and by Edwards and Pickering⁹ on rubber, the rate of diffusion of hydrogen through these substances at different temperatures being shown graphically. In the work described in the present paper a method has been developed that permits the rate of diffusion of gases through metals to be determined under more precisely controlled conditions than has previously been possible; and preliminary

¹ Abstract of a thesis presented by B. Clifford Hendricks to the Graduate College of the University of Nebraska in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

² Deville and Troost, *Compt. rend.*, **56**, 977 (1865); **57**, 965 (1866).

³ Graham, *Phil. Mag.*, [4] **32**, 503 (1866).

⁴ Sieverts, *Z. physik. Chem.*, **60**, 129 (1907).

⁵ Charpy and Bonnerot, *Compt. rend.*, **156**, 394 (1913).

⁶ Schmidt, *Ann. Physik*, [IV] **13**, 767 (1904).

⁷ Holt, *Proc. Roy. Soc.*, **91A**, 148 (1915).

⁸ Richardson and others, *Phil. Mag.*, [6] **8**, 1 (1904).

⁹ Edwards and Pickering, *Bur. Standards Sci. Paper*, **387**, 346 (1920).