THE HEAT OF FORMATION OF HYDROGEN CHLORIDE AND SOME RELATED THERMODYNAMIC DATA

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ABSTRACT

The calorimetric experiments of the present investigation give for the change in heat content associated with the formation of gaseous hydrogen chloride from its elements, at a constant pressure of 1 atmosphere, $\Delta H°_{298.1} = -92.30 \pm 0.05$ international kilojoules mole^{-1}, or $-22,063 \pm 12$ g-cal.$_{15}$ mole^{-1}.

The existing data on the free energy and entropy of formation of gaseous hydrogen chloride are shown to be in accord, within the limits of uncertainty, with the above result. This correlation consists in bringing together (1) data on the emf of certain cells, (2) data on the vapor pressure of hydrogen chloride over its aqueous solution and the activity of aqueous hydrogen chloride, and (3) values of entropy which have been calculated from the data of spectroscopy.

Values of the apparent and partial molal heat capacity, and heat content, for hydrogen chloride, and of the partial molal heat capacity, and heat content, for water, in aqueous solution of hydrogen chloride at 25° C., are given for the entire range of concentration.

The change in heat content associated with the solution of 1 mole of gaseous hydrogen chloride in an infinite amount of water is calculated to be $\Delta H°_{298.1} = -17,880 \pm 40$ g-cal.$_{15}$ mole^{-1}.

The change in heat content for the formation of silver chloride from its elements is given by: $\Delta H°_{298.1} = -30,304 \pm 40$ g-cal.$_{15}$ mole^{-1}. For mercurous chloride the corresponding value is $\Delta H°_{298.1} = -31,580 \pm 45$ g-cal.$_{15}$ mole^{-1}.

The change in heat content for the formation, from its elements, of aqueous hydrogen chloride at infinite dilution is given by: $\Delta H°_{298.1} = -39,943 \pm 40$ g-cal.$_{15}$ mole^{-1}.

The free energy of formation of gaseous hydrogen chloride is calculated to be $\Delta F°_{298.1} = -22,775 \pm 12$ g-cal.$_{15}$ mole^{-1}.

The entropy of aqueous hydrogen chloride, in a hypothetical 1 molal solution, is calculated to be: $S°_{298.1} = 13.40 \pm 0.15$ g-cal.$_{15}$ mole^{-1} °C.$^{-1}$.

CONTENTS

I. INTRODUCTION

It has seemed desirable for a number of years that a new measurement be made of the heat of formation of hydrogen chloride, a fundamentally important chemical substance because it is one of the components of a number of chemical reactions having industrial and scientific importance, and because the value of its heat of formation is used in computing the heats of formation of practically all the metallic chlorides and of numerous other compounds.

The usually accepted value for the heat of formation of gaseous hydrogen chloride is based upon the work of Thomsen [1] in 1873. The pioneer work of Abria,[2] and of Favre and Silbermann,[3] gave values that are now obviously too high. The work of Berthelot [4] is difficult to appraise because of the lack of information concerning his experiments.

In effect, then, there is only one calorimetric investigation of the heat of formation of hydrogen chloride whose detailed data are available for appraisal and recalculation, and that work was performed 60 years ago.

An accurate calorimetric value of the change in heat content, ΔH, for the reaction

$$\tfrac{1}{2}H_2 \text{ (gas)} + \tfrac{1}{2}Cl_2 \text{ (gas)} = HCl \text{ (gas)} \tag{1}$$

is unusually interesting because of the opportunity it affords for correlating the thermodynamic data on this reaction by means of the relation [5]

$$\Delta H° = \Delta F° + T\Delta S° \tag{2}$$

where $\Delta F°$ and $\Delta S°$ are, respectively, the free energy and entropy of formation. The value of $\Delta S°$ is accurately known from the data of spectroscopy; [6] and the value of $\Delta F°$ is obtained by combining data on the emf of cells and the vapor pressure of hydrogen chloride over its aqueous solution.[7] Thus there is the interesting situation where the values of $\Delta H°$, $\Delta F°$, and $\Delta S°$ for the same reaction are obtained from totally independent sources:

    $\Delta H°$, from calorimetric measurements;

    $\Delta S°$, from spectroscopic data; and

    $\Delta F°$, from emf and vapor-pressure data.

[1] Thomsen, J., Pogg. Ann., vol. 148, p. 177, 1873.
[2] Abria, Compt. rend., vol. 22, p. 372, 1846.
[3] Favre, P. A., and Silbermann, J. T., Ann. chim. phys., vol. 34, p. 357, 1852.
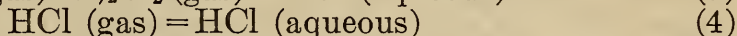[4] Berthelot, M., Thermochimie (Gauthier-Villars, Paris), 1897.
[5] The thermodynamic symbols used in this paper will follow the nomenclature of Lewis and Randall, Thermodynamics and the Free Energy of Chemical Substances (McGraw-Hill Book Co., New York), 1923.
[6] Giauque, W. F., and Overstreet, R., J. Am. Chem. Soc., vol. 54, p. 1741, 1932.
[7] Randall, M., and Young, L. E., J. Am. Chem. Soc., vol. 50, p. 989, 1928.

These data should all agree, according to equation (2), within the limits of uncertainty of the weakest link in the chain.

Another interesting correlation can be made on the change in heat content for reaction (1) and the following:

$$\tfrac{1}{2}H_2 \text{ (gas)} + \tfrac{1}{2}Cl_2 \text{ (gas)} = HCl \text{ (aqueous)} \qquad (3)$$
$$HCl \text{ (gas)} = HCl \text{ (aqueous)} \qquad (4)$$

For reaction (3) $\Delta H°$ can be computed from data on the temperature coefficient of the emf of cells, and for reaction (4) it is known from direct calorimetric measurements. The sum of the changes in heat content for reactions (1) and (4) should agree, within the limits of uncertainty, with the value of $\Delta H°$ for reaction (3). For this correlation there are required values of the apparent and partial molal heat content of hydrogen chloride in aqueous solution to infinite dilution, and the heats of formation of silver chloride and mercurous chloride.

With accurate values available for $\Delta H°$ and $\Delta F°$ it becomes possible to compute $\Delta S°$ for reaction (3), and consequently to obtain an accurate value of the entropy of aqueous hydrogen chloride in its standard state of a hypothetical 1 molal solution. This quantity serves as a basis for the calculation of the entropies of aqueous ions according to the methods used by Latimer and his coworkers.[8]

II. UNITS, FACTORS, ATOMIC WEIGHTS, ETC.

The fundamental unit of energy employed in the present calorimetric experiments is the international joule based upon standards of emf and resistance maintained at this bureau.[9]

The conversion factors used throughout this paper are:

1 international joule $= 1.0004$ absolute joules
1 g-cal.$_{15}$ $= 4.185$ absolute joules
R (gas constant) $= 1.9869$ g-cal.$_{15}$ °C^{-1}
F (Faraday constant) $= 23{,}067$ g-cal.$_{15}$ (international volt-equivalent)$^{-1}$

The atomic weights of hydrogen and chlorine are taken from the 1932 report of the International Committee on Atomic Weights:[10] H, 1.0078; Cl, 35.457.

III. CALORIMETRIC DETERMINATION OF THE HEAT OF FORMATION OF HYDROGEN CHLORIDE

1. METHOD AND APPARATUS

The same calorimetric method and apparatus as were employed in determining the heat of formation of water were used in the present investigation,[11] with the exception that an automatic photo-electric regulator was used to maintain the temperature of the jacket constant

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[8] Latimer, W. M., and Ahlberg, J. A., J. Am. Chem. Soc., vol. 54, p. 1900, 1932. References to the earlier publications are given in this paper.
[9] For a report on the international comparison of electrical standards, see Vinal, G. W., B. S. Jour. Research, vol. 8, p. 448, 1932.
[10] J. Am. Chem. Soc., vol. 54, p. 1269, 1932.
[11] Rossini, F. D., B. S. Jour. Research, vol. 6, p. 1, 1931; vol. 7, p. 329, 1931. The flow meters were removed from their previous positions and placed in the waste lines.
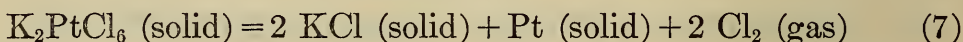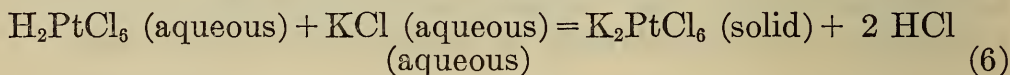
to $\pm 0.001°$ C.[12] A platinum resistance thermometer, placed under the stirrer and heater in the water of the calorimeter jacket, served as one arm of a Wheatstone bridge whose unbalancing caused a shifting of a beam of light (reflected from a galvanometer mirror) on or off the photo-electric cell, which resulted in actuation of the relay and consequent stopping or starting of the regulatory flow of electrical current through the heater of the calorimeter jacket.

The calorimetric method is substantially the same as that of Thomsen. Chlorine is burned in an atmosphere of hydrogen, and the amount of reaction is determined from the mass of hydrogen chloride formed.

2. CHEMICAL PROCEDURE

(a) CHLORINE

Pure chlorine was obtained by decomposing potassium chloroplatinate which was carefully prepared from pure platinum, potassium chloride, and hydrochloric acid according to the procedure recommended by Noyes and Weber [13] in their work on the atomic weight of chlorine. The following reactions indicate the nature of the process used in the present investigation:

$$\text{Pt (solid)} + 6 \text{ HCl (aqueous)} = \text{H}_2\text{PtCl}_6 \text{ (aqueous)} + 2 \text{ H}_2 \text{ (gas)} \quad (5)$$

$$\text{H}_2\text{PtCl}_6 \text{ (aqueous)} + \text{KCl (aqueous)} = \text{K}_2\text{PtCl}_6 \text{ (solid)} + 2 \text{ HCl} \\ \text{(aqueous)} \quad (6)$$

$$\text{K}_2\text{PtCl}_6 \text{ (solid)} = 2 \text{ KCl (solid)} + \text{Pt (solid)} + 2 \text{ Cl}_2 \text{ (gas)} \quad (7)$$

Each of the above reactions is practically complete and not complicated by any side reaction. The required reagents, platinum, potassium chloride, and hydrochloric acid, are obtainable in a very pure state.

Pure platinum was obtained from the platinum metals section of this bureau. It had been prepared according to the methods described by Wichers, Gilchrist, and Swanger.[14]

The potassium chloride was made by recrystallizing twice the best "reagent quality" potassium chloride. The most probable impurity in this material would be bromine, and tests indicated that this was present to the extent of 1 mole in 50,000 moles of potassium chloride.[15]

Aqueous hydrogen chloride was obtained by treating the best "reagent quality" hydrochloric acid with chlorine (made by the action of hydrogen chloride upon potassium permanganate) and then boiling off the dissolved chlorine. Tests of this aqueous hydrogen chloride indicated that the bromine present must have been less than 1 mole in 100,000 moles of hydrogen chloride.

The preparation of the chloroplatinic acid was carried out in the electrolytic cell of Weber, according to his directions, except that a current of 6 to 7 amperes instead of 10 was used.[16]

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[12] This regulator was of the type that has been described quite frequently in the past few years (see for example (a) Southard, J. C., and Andrews, D. H., J. Frank. Inst., vol. 207, p. 323, 1929; (b) Scott, R. B., and Brickwedde, F. G., B. S. Jour. Research, vol. 6, p. 401, 1931; (c) Beattie, J. A., Rev. Sci. Inst., vol. 2, p. 458, 1931). The author is indebted to E. N. Bunting for assembling the circuit of vacuum tubes, photoelectric cell, and relay.

[13] (a) Noyes, W. A., and Weber, H. C. P., J. Am. Chem. Soc., vol. 30, p. 13, 1908; B. S. Bull., vol. 4, p. 345, 1907–8. (b) Weber, H. C. P., J. Am. Chem. Soc., vol. 30, p. 29, 1908; B. S. Bull., vol. 4, p. 365, 1907–8.

[14] Wichers, E., Gilchrist, R., and Swanger, W. H., Trans. Am. Inst. Mining Met. Eng., vol. 76, p. 602, 1928.

[15] The tests for bromine were made according to Noyes, A. A., Qualitative Chemical Analysis (Macmillan Co., New York, N. Y.), 1925.

[16] The construction of the electrolytic cell had been improved by Edward Wichers, and the author is greatly indebted to him for his advice with regard to the preparation of the chlorine used in the present investigation.

The potassium chloroplatinate was made according to reaction (6), following the directions of Noyes and Weber except that the salt was washed with water only. The potassium chloroplatinate was then placed in an oven at 110° C. for several days to remove most of the moisture.

For carrying out reaction (7) the apparatus shown in Figure 1 was used. *A* is the furnace with electrical resistance heater; *B* is a silica flask containing the potassium chloroplatinate; *C* is a silica to Pyrex-glass seal; *D* is a trap for catching any potassium or platinum chlorides which might be volatilized; *E* is a condensing tube for collecting the chlorine; *G* is a connection to the vacuum system, which consists of a mercury vapor pump (properly trapped with liquid air) backed by an oil vacuum pump; *K* is a vacuum-tight Pyrex glass-to-copper
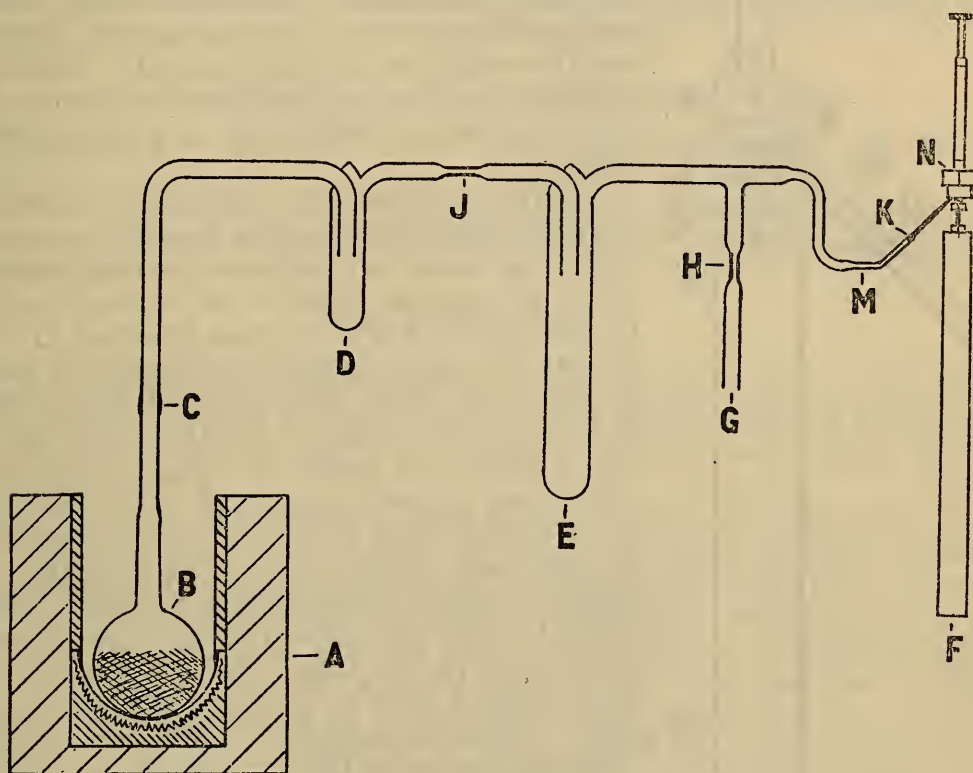

FIGURE 1.—*Apparatus for preparing pure chlorine*
The description is given in the text

seal; *F* is the Monel-metal container, having a Monel-metal dia-phragm valve, in which the chlorine was finally stored.

The potassium chloroplatinate was heated to about 300° C. and the system kept evacuated to 0.0001 mm mercury for about three days. This was done to remove the last traces of water and hydrogen chloride from the solid. Then the constriction at *H* was sealed off. The flask *B* was heated to about 750° C. and liquid air placed around the condensing tube *E* where chlorine slowly began to collect as a solid. When chlorine no longer came over, the constriction at *J* was sealed off. The solid chlorine in *E* was liquefied and then distilled into the container *F*, the lower end of which was cooled with liquid air. When all but a small amount of the chlorine was collected in *F*, the valve *N* was closed and the glass system was broken at *M*. The chlorine container *F* was then sealed to the glass line leading to the calorimeter.
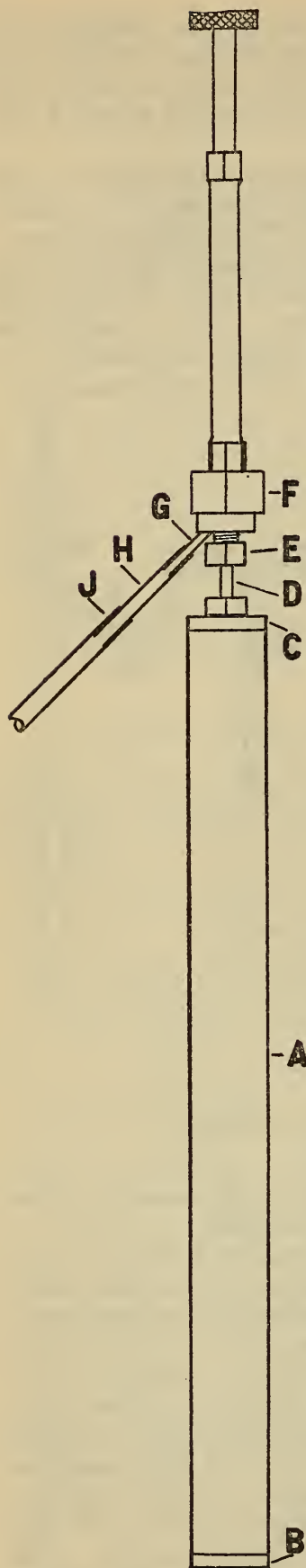
A sketch of the chlorine container and valve is shown in Figure 2. *A* is the cylindrical body of the container. The end plugs *B* and *C* are screwed and silver soldered in place. The connecting tube *D* is screwed and silver soldered to the plug *C* and tightly connected to the valve *F* by means of the metal-to-metal connection at *E*. The valve *F*, which has a silver diaphragm and in which closures are made with Monel metal to silver seats, is one of the type used in the calorimetric researches on steam by Osborne, Stimson, and Fiock.[17] *G* is the exit tube which is lead soldered to the body of the valve. The parts *A, B, C, D, F,* and *G* are all made of Monel metal. The short copper tube *H* is lead soldered to the tube *G*.[18] At *J* is a vacuum-tight seal of Pyrex glass to copper.

In order to select the material of which the container and valve were to be made, an experiment was made to determine the relative reactivity of gaseous chlorine to various metals. In one end of a Pyrex glass inverted **U** tube (about 12 by 12 inches) were placed pieces of platinum, silver, Monel metal, steel, brass, and phosphor bronze. To the other end of the **U** tube was sealed a small quartz tube containing a small amount of potassium chloroplatinate. The entire tube was evacuated to a pressure of about 2 mm of mercury, and the potassium chloroplatinate was then decomposed to give a pressure of 1 to 2 atmospheres of chlorine in the tube (which probably contained also a very small amount of water vapor). After a period of about six months, visual inspection of the tube, which had been at room temperature, showed that the platinum and Monel metal were apparently unaffected by the chlorine, the silver and brass were very slightly coated with chloride, and the phosphor bronze and steel showed considerable evidence of reaction. When at the end of the first series of reaction experiments, which are to be described later, the Monel-metal valve was taken apart, the silver diaphragm and seat, as well as the Monel-metal surface of the interior of the valve, were found to have been unaffected by the chlorine.

FIGURE 2.—*Chlorine container with diaphragm valve*

The description is given in the text.

(b) HYDROGEN

The hydrogen used in the present investigation was taken from a cylinder of commercial electrolytic hydrogen. Oxygen was removed from this gas by passage through a tube containing asbestos, impregnated with palladium, and quartz, impregnated with platinum, at about 500° C. Before entering the calorimeter, the gas then passed successively through "Ascarite" (a sodium-hydroxide asbestos mixture), "Dehydrite" ($Mg(ClO_4)_2 \cdot 3H_2O$), and phosphorus pentoxide.

Analyses of the hydrogen gas as it would enter the reaction chamber were made by the gas chemistry section. That part of the gas which was noncombustible with oxygen was found to be 0.0 ± 0.1 per cent. A test for the presence of carbon compounds in the hydrogen was made by burning it with a special sample of oxygen [19]] and testing the exit gases for carbon dioxide. None was found.

(c) DETERMINATION OF THE AMOUNT OF REACTION

The amount of reaction in each combustion experiment was determined by absorbing the hydrogen chloride in "Ascarite."

With the absorber filled with hydrogen at 1 atmosphere and 25° C., and with brass weights in air, the true mass [20] of hydrogen chloride absorbed is

$$m_{(HCl)} = 0.99991 \Delta m \tag{8}$$

where Δm is the observed increase in weight of the absorber, corrected for the small amount of unburned chlorine which was also absorbed. The determination of this latter quantity is described on page 686 of this paper.

In its passage from the container to the reaction chamber, the chlorine traversed one 2-way stopcock, which served to permit wasting immediately before the ignition and after the extinction of the flame, and two small ground-glass joints. Phosphoric acid was used to lubricate the stopcock and the two ground joints, the latter being lubricated anew for each experiment. With hydrogen gas flowing through the stopcock and ground joints so lubricated, a carefully weighed absorber connected to the exit end of the reaction chamber showed constancy of weight (± 0.1 mg per experiment, which is 1 part in 50,000).

The two ground joints on the exit side of the reaction chamber were lubricated with the same lubricant as previously used for nonreactive gases. In order to make sure that the lubricant on these two small ground joints would take up no appreciable amount of hydrogen chloride, the lubricant, spread over a large area, was exposed to hydrogen-chloride gas for the time of a calorimetric reaction experiment, and its change in weight determined. It was calculated that under the conditions of a calorimetric reaction experiment, the amount of hydrogen chloride taken up by the lubricant on the two ground joints was about 0.03 mg, or 1 part in 200,000.

Several experiments were made to determine the completeness of the removal, by the "Ascarite," of hydrogen chloride from the gas leaving the reaction vessel. In one experiment a concentrated aqueous solution of silver nitrate was placed beyond the absorber.

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[19] See footnote 11, p. 681.
[20] See footnote 11, p. 681.

In another experiment a second absorber, carefully weighed, was placed in series with the first absorber. In both these experiments no hydrogen chloride passed the first absorber with the gas flowing at three or four times the rate actually used in the calorimetric experiments.

3. CALORIMETRIC PROCEDURE

(a) ELECTRICAL ENERGY EXPERIMENTS

These experiments were performed, as nearly as possible, over the same temperature range and with the same rate of temperature rise as the combustion experiments. The description of the procedure for the electrical energy experiments has already been given.[21]

The results of the electrical energy experiments are given in Table 1. The "error," computed [22] as

$$\pm 2\sqrt{\frac{\overline{(x-\overline{x})^2}}{n(n-1)}}, \text{ is } \pm 0.014 \text{ per cent}$$

TABLE 1.—*Calorimetric results of the electrical energy experiments for hydrogen chloride*

Experiment No.	ΔR	k	u	K	U	Δt corr.	Average temperature	Electrical energy [1]	Mass of calorimeter water	Electrical equivalent of calorimeter system [2]	Deviation from mean
	ohm	min.$^{-1}$	min.$^{-1}$	ohm	ohm	° C.	° C.	Int. joules	g	Int. joules ° C.$^{-1}$	joules ° C.$^{-1}$
1	0.100338	0.001970	−0.0000084	0.002819	−0.000235	0.97044	30.00	14,988.3	3,620.53	15,359.1	2.7
2	.099976	.001945	−.0000035	.002810	−.000098	.96557	30.00	14,884.0	3,614.38	15,354.7	−1.7
3	.101019	.001934	.0000024	.002783	.000067	.97455	30.00	15,009.2	3,611.53	15,353.1	−3.3
4	.099545	.001947	.0000015	.002577	.000039	.96225	29.99	14,832.4	3,614.38	15,354.3	−1.9
5	.099308	.001966	−.0000032	.002617	−.000083	.96071	29.99	14,841.5	3,621.98	15,356.8	.6
6	.099320	.001968	.0000003	.002635	.000008	.95975	29.99	14,811.1	3,617.38	15,359.7	3.5
Mean										15,356.3	±2.3

[1] The time of electrical energy input was 1,320.00 seconds in experiments 1, 2, and 3, and 1,200.00 seconds in experiments 4, 5, and 6.
[2] Corrected to 3,600.00 g of water and an average temperature of 30.00° C.

(b) FIRST SERIES OF REACTION EXPERIMENTS

The amount of chlorine unburned during the time of ignition and extinction of the flame, was determined in "correction" experiments which consisted in ignition, burning for one or two seconds, and then extinction of the flame. The following data were required: (1) The increase in mass of the absorber, (2) the total energy imparted to the calorimeter by the reaction and the sparking operation (determined from the corrected temperature rise of the calorimeter and its electrical energy equivalent), and (3) the "spark" energy.

The "spark" energy was determined in two separate experiments to be 10.3 ± 0.1 joules for each sparking time of five seconds. From the energy imparted to the calorimeter by the reaction, which was the total energy less the "spark" energy and the "gas" energy,[23] the amount of hydrogen chloride formed was calculated. The differ-

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[21] See footnote 11, p. 681.   [22] See footnote 11, p. 681.   [23] See footnote 11, p. 681.

ence between the mass actually taken up by the absorber and the mass of hydrogen chloride formed gave m_{Cl}, the mass of unburned chloride.

In the first series of reaction experiments the chlorine which was in the burner tube at the time the flow of chlorine was cut off was not burned out, and consequently the value of m_{Cl} for these experiments is relatively large, being about one-half per cent of the total mass absorbed. The results of the "correction" experiments of the first series to determine the value of m_{Cl} are given in Table 2.

TABLE 2.—*Calorimetric results of the correction experiments for hydrogen chloride, first series*

Experiment No.	Number of ignitions and extinctions of flame	Total mass absorbed	Total energy	"Spark" energy	"Gas" energy	Mass of HCl	m_{Cl} per experiment
		g	*int. joules*	*joules*	*joules*	*g*	*g*
a	8	0.3749	473.1	82.4	−2.0	0.1551	0.0275
b	3	.1308	134.3	30.9	.3	.0411	.0299
c	3	.1408	156.5	30.9	.4	.0498	.0303
Mean							.0292

The calorimetric results of the first series of reaction experiments are given in Table 3. All the symbols are defined and explained in an earlier paper.[24] The only change from previous procedure was that the chlorine gas coming from the Monel metal container passed through a coil (about 9 feet long) of glass tubing immersed in a water bath maintained at the temperature of the room.

TABLE 3.—*Calorimetric results of the reaction experiments for hydrogen chloride, first series*

Experiment No.	ΔR	k	u	K	U	$\Delta t_{corr.}$	Average temperature
	ohm	*min⁻¹*	*ohm min⁻¹*	*ohm*	*ohm*	*° C.*	*° C.*
A	0.094404	0.001963	0.0000038	0.002473	0.000106	0.91157	30.00
B	.093969	.001923	−.0000040	.002461	−.000112	.90954	30.00
C	.095208	.001957	.0000001	.002422	.000003	.92109	30.00
Mean							

Experiment No.	Electrical equivalent of calorimeter system	Total energy	"Gas" energy	"Spark" energy	Mass of HCl formed	$Q_{30°C.}$, 1 atmosphere	Deviation from mean
	Int. joules ° C.⁻¹	*Int. joules*	*joules*	*joules*	*mole*	*Int. joules mole⁻¹*	*joules mole⁻¹*
A	15,418.2	14,054.8	39.2	10.3	0.152679	92,243	−143
B	15,494.4	14,092.8	40.4	10.3	.152770	92,445	59
C	15,432.0	14,214.3	43.8	10.3	.154078	92,471	85
Mean						92,386	±96

[24] See footnote 11, p. 681.

(c) SECOND SERIES OF REACTION EXPERIMENTS

In the second series of reaction experiments the chlorine remaining in the burner tube was all burned out by mixing hydrogen with the chlorine stream before the latter was cut off. This mixing was accomplished by opening the tube connecting the hydrogen and chlorine lines at their entrance into the calorimeter. Because of this improvement in the procedure, the value of m_{Cl} for the second series of reaction experiments was only about one-sixth of that for the first series, or about 0.08 per cent of the total mass absorbed; and a much greater precision was obtained in these experiments.

The results of the "correction" experiments of the second series are given in Table 4.

TABLE 4.—*Calorimetric results of the correction experiments for hydrogen chloride, second series*

Experiment No.	Number of ignitions and extinctions of flame	Total mass absorbed	Total energy	"Spark" energy	"Gas" energy	Mass of hydrogen chloride	m_{Cl} per experiment
		g	*Int. joules*	*joules*	*joules*	*g*	*g*
a	3	0.1652	412.1	30.9	−0.5	0.1508	0.0048
b	3	.1694	423.0	30.9	−0.7	.1552	.0047

The calorimetric results of the reaction experiments of the second series are given in Table 5.

TABLE 5.—*Calorimetric results of the reaction experiments for hydrogen chloride, second series*

Experiment No.	ΔR	k	u	K	U	Δt_{corr}	Average temperature
	Ohm	*Min^{-1}*	*Ohm Min^{-1}*	*Ohm*	*Ohm*	*° C.*	*° C.*
D	0.098361	0.001946	−0.0000012	0.002665	−0.000034	0.95034	30.00
E	.098986	.001968	−.0000030	.001771	−.000066	.96575	30.03
F	.089307	.002035	.0000022	.002792	.000062	.85825	30.00
G	.067365	.001927	.0000018	.002756	.000043	.64095	29.85
Mean							

Experiment No.	Electrical equivalent of calorimeter system	Total energy	"Gas" energy	"Spark" energy	Mass of HCl formed	$Q_{30° C.}$, 1 atmosphere	Deviation from mean
	Int. joules ° C.$^{-1}$	*Int. joules*	*Joules*	*Joules*	*Mole*	*Int. joules mole^{-1}*	*Joules mole^{-1}*
D	15,415.3	14,649.8	38.5	10.3	0.159049	92,286	−22
E	15,433.8	14,905.2	19.7	10.3	.161479	92,363	+55
F	15,381.0	13,200.7	16.7	10.3	.143083	92,304	−4
G	15,406.4	9,874.8	16.8	10.3	.107079	92,280	−28
Mean						92,308	±27

4. RESULTS OF THE PRESENT INVESTIGATION

The results of the experiments of the present investigation are shown in Figure 3. This plot indicates clearly the increased precision obtained in the second series of reaction experiments and the relation of each result to the average value from the second series.

For the second series of reaction experiments the "error"

$$\pm 2\sqrt{\frac{(x-\bar{x})^2}{n(n-1)}}$$

is computed to be ± 0.039 per cent. Combination [25] of this with the "error" of the electrical energy experiments gives a resultant error of 0.041 per cent, or ± 38 joules per mole.

The total uncertainty in the average value of the second series is estimated to be not more than ± 50 joules per mole.

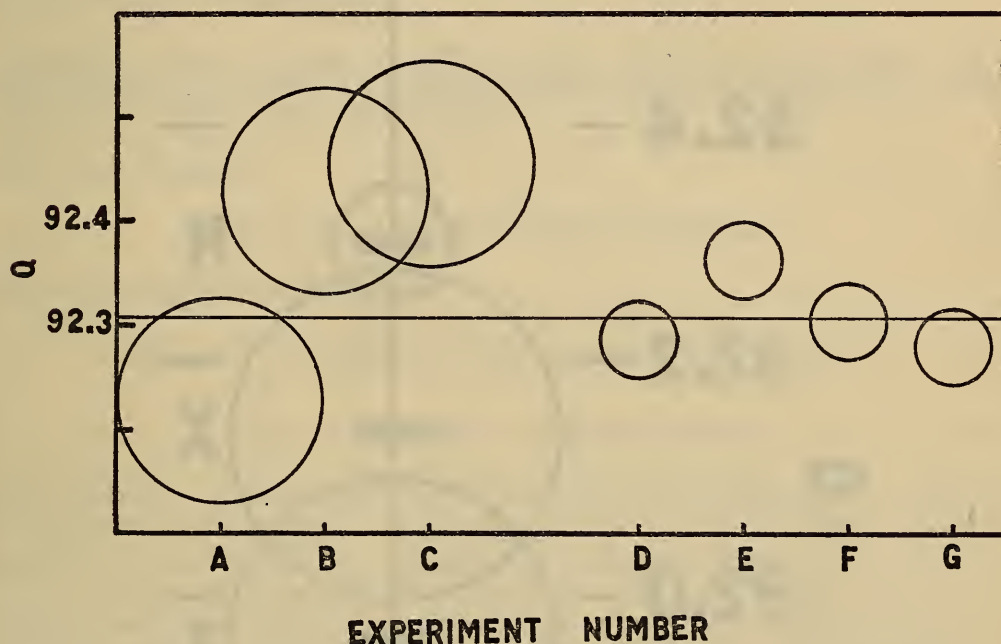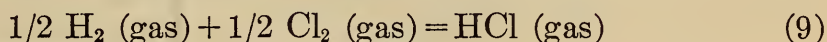The present experiments give, then, for the heat evolved in the reaction

$$1/2\ H_2\ (gas) + 1/2\ Cl_2\ (gas) = HCl\ (gas) \tag{9}$$

EXPERIMENT   NUMBER

FIGURE 3.—*Plot of the experimental results for the heat of formation of gaseous HCl, from the present investigation*

The scale of ordinates gives Q, the heat of formation of gaseous HCl from its elements, at 30° C. and a constant pressure of 1 atmosphere, in international kilojoules mole^{-1}.

On the scale of abscissae are shown the individual values: A, B, C, the first series; and D, E, F, G, the second series. The circles indicate the relative precision for the two series, and the horizontal line, at 92.308, gives the average value from the second series.

at 30° C. and a constant pressure of 1 atmosphere

$$Q_{30°C.} = 92,308 \pm 50\ \text{international joules mole}^{-1} \tag{10}$$

Since $\Delta C_p = -\dfrac{dQ}{dT} = -1.7$ joules mole^{-1} °C.$^{-1}$, the value for 25° C. and 1 atmosphere becomes

$$Q_{25°C.} = 92,300 \pm 50\ \text{international joules mole}^{-1} \tag{11}$$

Using the factor 1.0004/4.185, this is equivalent to

$$Q_{25°C.} = 22,063 \pm 12\ \text{g-cal.}_{15}\ \text{mole}^{-1}. \tag{12}$$

5. THE RESULTS OF EARLIER INVESTIGATIONS

As has already been noted, calorimetric determinations of the heat of formation of hydrogen chloride have been made by Abria,[26] Favre and Silbermann,[27] Berthelot,[28] and Thomsen.[29] The results obtained

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[25] See footnote 11, p. 681.   [27] See footnote 3, p. 680.   [29] See footnote 1, p. 680.
[26] See footnote 2, p. 680.   [28] See footnote 4, p. 680.

by Abria, and by Favre and Silbermann are, respectively, about 10 and 8 per cent higher than the values obtained by the later investigators, and may be disregarded in view of the more concordant work of later investigators who had the advantage of purer materials and better calorimetric technic.   There are no details of Berthelot's experiments, though his value is practically identical with that of Thomsen.

Thomsen published complete details of his four experiments on hydrogen chloride.   The writer has recomputed Thomsen's data in
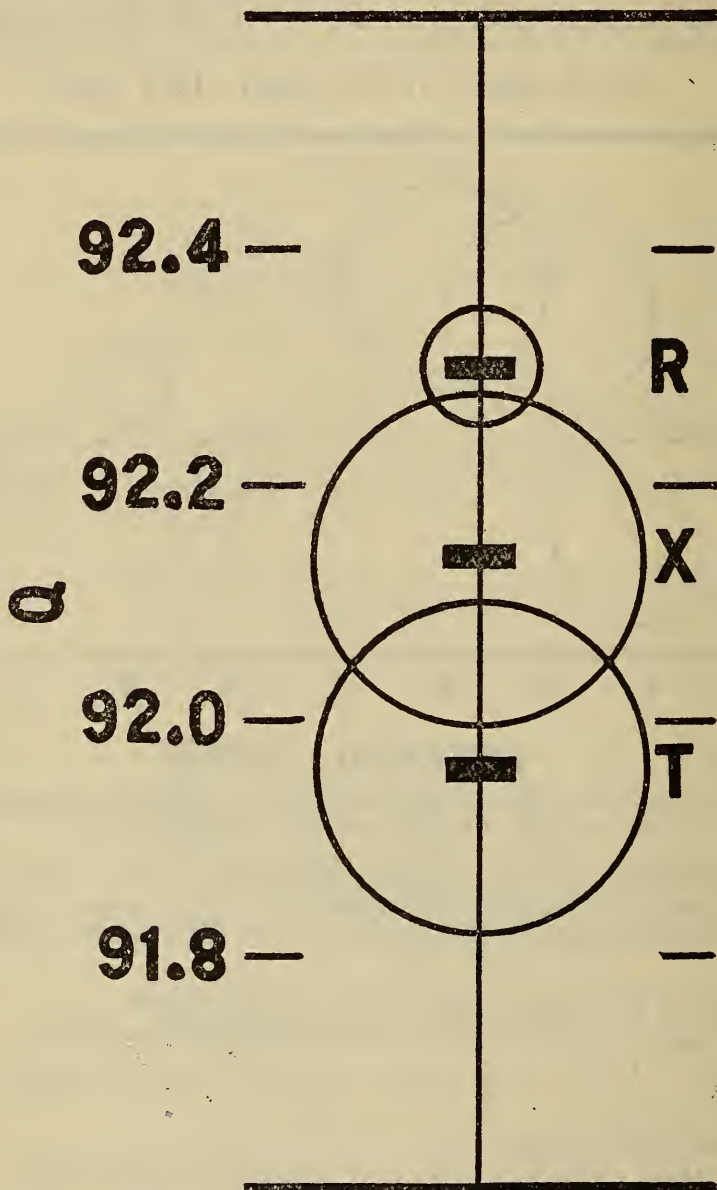

FIGURE 4.—*Plot of the various values for the heat of formation of* HCl

The scale of ordinates gives Q, the heat evolved in the formation of 1 mole of gaseous HCl from its elements, at 25° C. and a constant pressure of 1 atmosphere, in international kilojoules mole $^{-1}$.

The circles give the estimated uncertainties for values from the following sources: T, calorimetric experiments of Thomsen.   X, calculation by way of the free energy and entropy of formation of gaseous HCl. R, calorimetric experiments of the present investigation.

the light of modern atomic weights and units of energy, and obtains as the average value

$$Q_{25°C.} = 91.96 \pm 0.14 \text{ international kilojoules mole}^{-1} \qquad (13)$$

The "error" is estimated from the consistency of Thomsen's data, together with the assumption of a calibration error of 0.10 per cent. There still remains the possibility of there being an unknown systematic error in the above value.

The values from the various investigations are as follows, in international kilojoules per mole at 25° C. and 1 atmosphere:

Abria_____ 101
Favre and Silbermann_____ 99
Berthelot_____ 92
Thomsen_____ 91. 96 ± 0. 14
Present investigation_____ 92. 30 ± 0. 05

In Figure 4, the value from Thomsen's data is shown in relation to the result obtained in the present investigation. The circles show the estimated uncertainties.

6. CORRELATION OF THE PRESENT DATA ON HEAT CONTENT WITH EXISTING DATA ON THE FREE ENERGY AND ENTROPY OF FORMATION OF HYDROGEN CHLORIDE

For the reaction

$$1/2 \ H_2 \ (gas) + 1/2 \ Cl_2 \ (gas) = HCl \ (gas) \tag{14}$$
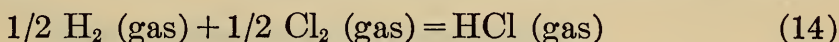
the present investigation gives

$$\Delta H_{298.1} = -92,300 \pm 50 \text{ international joules mole}^{-1} \tag{15}$$

or

$$\Delta H_{298.1} = -22,063 \pm 12 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{16}$$

The reference or standard state [30] used in calculating the values of entropy and free energy of a gas is that of an "ideal" gas where the fugacity is 1 atmosphere. In this state the heat content is the same as that of the real gas at zero pressure. A knowledge of the p-v-T relations suffices to permit computation of ΔH for the above reaction with the gases in their standard states by means of the relation

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \tag{17}$$

But the necessary P-V-T data for chlorine and hydrogen chloride are not available. A calculation employing the Berthelot equation of state, which requires only a knowledge of the critical temperature and pressure for each gas, shows that, although appreciable for chlorine and hydrogen chloride separately, the change in ΔH for reaction (14) from a pressure of 1 atmosphere to a fugacity of 1 atmosphere is only about 0.01 per cent of the value of ΔH. Without additional information this correction can for the present be neglected, as it is less than the uncertainty in the value of ΔH, and one can write

$$\Delta H°_{298.1} = -22,063 \pm 12 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{18}$$

The values of the entropies of hydrogen, chlorine, and hydrogen chloride (less the entropy of nuclear spin) have been calculated very accurately from the data of spectroscopy by Giauque,[31] and Giauque
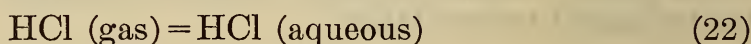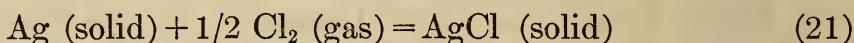
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[30] See footnote 5, p. 680.   [31] Giauque, W. F., J. Am. Chem. Soc., vol. 52, p. 4816, 1930.

and Overstreet.[32]   The values of $S°_{298.1}$, in g-cal.$_{15}$ mole^{-1} °C. $^{-1}$, are: H_2, 31.225; Cl_2, 53.310; HCl, 44.658.   Then for reaction (14)

$$\Delta S°_{298.1} = 2.390 \text{ g-cal.}_{15} \text{ mole}^{-1} \text{ °C}^{-1} \tag{19}$$

For the present calculations the uncertainty in this value is negligible.
The value of $\Delta F°$ for reaction (14) is best obtained [33] by combining the data for the following reactions:

$$1/2 \text{ H}_2 \text{ (gas)} + \text{AgCl (solid)} = \text{HCl (aqueous)} + \text{Ag (solid)} \tag{20}$$

$$\text{Ag (solid)} + 1/2 \text{ Cl}_2 \text{ (gas)} = \text{AgCl (solid)} \tag{21}$$

$$\text{HCl (gas)} = \text{HCl (aqueous)} \tag{22}$$

The value for the free energy change in reaction (20) is obtained from the standard emf of the cell in which reaction (20) occurs.   The best values are: [34] Randall and Young, 0.2221; Harned and Ehlers, 0.2224; Carmody, 0.2223; Spencer, 0.2222.   These give

$$E°_{298.1} = 0.2222 \text{ international volt} \tag{23}$$

The uncertainty in this value is about 0.0002 volt.   Then, for reaction (20)

$$\Delta F°_{298.1} = -5,125 \pm 5 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{24}$$

Randall and Young [35] conclude that the best value for the emf of the cell in which reaction (21) occurs is that given by Gerke [36] who finds, with chlorine at a pressure of 1 atmosphere,

$$E°_{298.1} = 1.1362 \text{ international volts} \tag{25}$$

Correcting the chlorine to a fugacity of 1 atmosphere,[37] one finds

$$E°_{298.1} = 1.1363 \text{ international volts} \tag{26}$$

The uncertainty in this value can be taken as 0.0004 volt.   Therefore, for reaction (21)

$$\Delta F°_{298.1} = -26,211 \pm 9 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{27}$$

The value of $\Delta F°$ for reaction (22) can be calculated from the ratio of p_2, the vapor pressure of hydrogen chloride over its aqueous solution, to a_2, the activity of hydrogen chloride in that solution:

$$\Delta F° = -RTln\frac{p_2}{a_2} \tag{28}$$

Lewis and Randall [38] reviewed the data on the vapor pressure of

[32] Giauque, W. F., and Overstreet, R., J. Am. Chem. Soc., vol. 54, p. 1731, 1932.
[33] See footnote 7, p. 680.
[34] (a) See footnote 7, p. 680; (b) Harned, H. S., and Ehlers, R. W., J. Am. Chem. Soc., vol. 54, p. 1350, 1932; (c) Carmody, W. R., J. Am. Chem. Soc., vol. 54, p. 188, 1932; (d) Spencer, H. M., J. Am. Chem. Soc., vol. 54, p. 3647, 1932.
[35] See footnote 7, p. 680.
[36] Gerke, R. H., J. Am. Chem. Soc., vol. 44, p. 1684, 1922.
[37] See p. 499 of the reference given in footnote 5, p. 680.
[38] See p. 503 of the reference given in footnote 5, p. 680.

hydrogen chloride over its aqueous solution, and the activity of aqueous hydrogen chloride, and concluded that

$$\frac{p_2}{a_2} = 4.41 \times 10^{-7} \tag{29}$$

Later, Randall and Young [39] recomputed this value, having available some few new data on vapor pressure and better values for a_2, and found

$$\frac{p_2}{a_2} = 4.97 \times 10^{-7} \tag{30}$$

This value is 13 per cent higher than the previous one. Assuming the uncertainty in the latest value to be about 5 per cent, then, for reaction (22)

$$\Delta F^{\circ}_{298.1} = 8,598 \pm 30 \text{ g-cal. }_{15} \text{ mole}^{-1} \tag{31}$$

Combination of ΔF° for reactions (20), (21), and (22), gives for reaction (14)

$$\Delta F^{\circ}_{298.1} = -22,738 \pm 33 \text{ g-cal. }_{15} \text{ mole}^{-1} \tag{32}$$

Then from equations (2), (19), and (32) one finds for reaction (14)

$$\Delta H^{\circ}_{298.1} = -22,026 \pm 33 \text{ g-cal. }_{15} \text{ mole}^{-1} \tag{33}$$

or

$$\Delta H^{\circ}_{298.1} = -92.14 \pm 0.14 \text{ international kilojoules mole}^{-1} \tag{34}$$

which agrees, within the limits of uncertainty, with the value obtained from the present calorimetric experiments

$$\Delta H^{\circ}_{298.1} = -92.30 \pm 0.05 \text{ international kilojoules mole}^{-1} \tag{35}$$

The values are shown together in Figure 4.

IV. CALCULATION OF SOME RELATED THERMODYNAMIC DATA

1. THE APPARENT AND PARTIAL MOLAL HEAT CAPACITY OF HYDROGEN CHLORIDE AND THE PARTIAL MOLAL HEAT CAPACITY OF WATER IN AQUEOUS SOLUTION OF HYDROGEN CHLORIDE

In order to calculate the temperature coefficient of reactions involving aqueous hydrogen chloride, it is necessary to know the apparent and partial molal heat capacities. The apparent molal heat capacity, Φ_c, is calculated from the experimental data on the heat capacity of hydrogen chloride solutions by the methods already described.[40]

When Φ_c has been determined as a function of $m^{1/2}$, the square root of the molality,[41] then $\overline{C}_{p_2}$, the partial molal heat capacity of hydrogen chloride, and $\overline{C}_{p_1}$, the partial molal heat capacity of water, are derived from the relations:

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[39] See footnote 7, p. 680.
[40] (a) Randall, M., and Rossini, F. D., J. Am. Chem. Soc., vol. 51, p. 323, 1929. (b) Rossini, F. D., B. S. Jour. Research, vol. 4, p. 313, 1930; (c) vol. 7, p. 47, 1931.
[41] m is the number of moles of solute per 1,000 g water.

$$\overline{C}_{p_2} = \Phi_c + 1/2 m^{1/2} \frac{d\Phi_c}{dm^{1/2}} \qquad (36)$$

$$\overline{C}_{p_1} - \overline{C}_{p_1} = -\frac{m}{55.508}\left(1/2 m^{1/2}\frac{d\Phi_c}{dm^{1/2}}\right) \qquad (37)$$

$$\Phi^\circ{}_c = \overline{C}_{p_2}{}^\circ \qquad (38)$$

For the present compilation of the thermal data on aqueous hydrogen chloride, it is desired to obtain values of Φ_c over as large a range of concentration as possible. In a previous paper,[42] the present author reviewed the existing data from the dilute region of concentration to about 2 molal. To these data can be added the values for the more concentrated solutions and some new data for the dilute region.
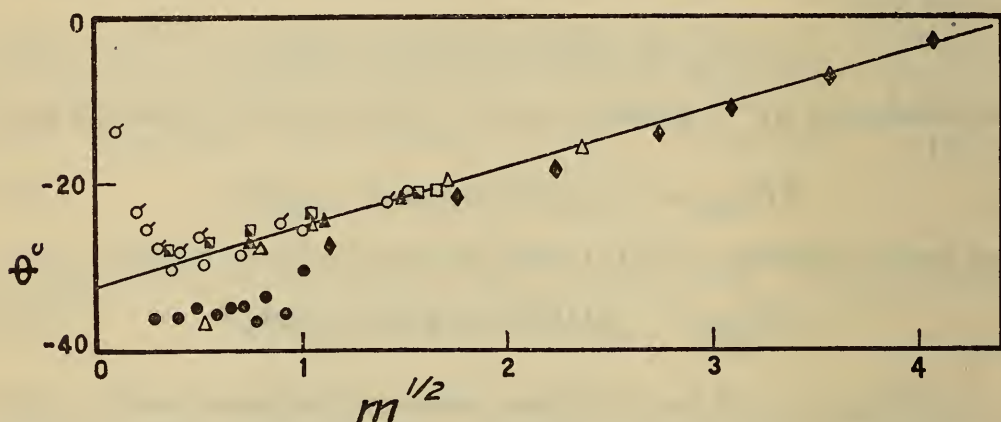

FIGURE 5.—*The apparent molal heat capacity of HCl in aqueous solution of HCl at 25° C.*

The scale of abscissae gives the square root of the molality.
The scale of ordinates gives Φ_c, the apparent molal heat capacity, for HCl in aqueous solution of HCl at 25° C., in g-cal. per mole.
The points designate values (corrected to 25° C.) from the data of the following investigators: ○Richards and Rowe; ⬓Richards, Mair, and Hall; △Thomsen; □Thorvaldson, Brown, and Peaker; ◆Wrewsky and Savaritzky; ▲Marignac; ●Randall and Ramage; and, ◁Gucker and Schminke.

In Figure 5 are plotted values of Φ_c for aqueous hydrogen chloride at 25° C. calculated from the data of the following investigators: Thomsen [43] at 18° C.; Marignac [44] at 22° C.; Richards and Rowe [45] at 18° C.; Wrewsky and Kaigorodoff [46] at 20.5° C.; Randall and Ramage [47] at 25° C.; Richards, Mair, and Hall [48] at 18° C.; Thorvaldson, Brown, and Peaker [49] at 18° C.; Gucker and Schminke [50] at 25° C. The last-named investigators reported directly values of Φ_c. Where the data of the above experimenters were obtained at temperatures other than 25° C., they were corrected to 25° C., by means of the temperature coefficient of Φ_c previously given by the present author.[51]

The heavy black line in Figure 5 represents the linear relation between Φ_c and $m^{1/2}$ previously reported by the present author for aqueous hydrogen chloride at 25° C., for the range from infinite dilution to about 2 molal. Inspection of the plot shows that this relation

[42] See footnote 40 (c), p. 693.
[43] Thomsen, J., Ann. Physik, vol. 142, p. 337, 1871.
[44] Marignac, C., Ann. chim. phys., vol. 8, p. 410, 1876.
[45] Richards, T. W., and Rowe, A. S., J. Am. Chem. Soc., vol. 42, p. 162, 1920.
[46] Wrewsky, M., and Kaigorodoff, A., Z. physik, Chem., vol. 112, p. 83, 1924.
[47] Randall, M., and Ramage, L. E., J. Am. Chem. Soc., vol. 49, p. 93, 1927.
[48] Richards, T. W., Mair, B. J., and Hall, L. P., J. Am. Chem. Soc., vol. 51, p. 727, 1929.
[49] Thorvaldson, T., Brown, W. G., and Peaker, C. R., J. Am. Chem. Soc., vol. 52, p. 3927, 1930.
[50] Gucker, F. T., and Schminke, K. H., J. Am. Chem. Soc., vol. 54, p. 1358, 1932.
[51] See footnote 40 (c), p. 693.

represents the data very well over the entire range of concentration, though there is apparently some question as to the extrapolation to infinite dilution.[52]

Then for acqueous hydrogen chloride at 25°C.

$$\Phi_c = -32.5 + 7.2\ m^{1/2} \text{g-cal. mole}^{-1}\ °C.^{-1} \tag{39}$$

$$\overline{C}_{p_2} = -32.5 + 10.8\ m^{1/2} \text{g-cal. mole}^{-1}\ °C.^{-1} \tag{40}$$

$$\overline{C}_{p_1} - \overline{C}_{p_1}° = -0.065\ m^{3/2} \text{g-cal. mole}^{-1}\ °C.^{-1} \tag{41}$$

The temperature coefficients of the above quantities can be taken as

$$\frac{d\Phi_c}{dT} = \frac{d\overline{C}_{p_2}}{dT} = \frac{2.0}{7} \text{ g-cal. mole}^{-1}\ °C.^{-2} \tag{42}$$

$$\frac{d(\overline{C}_{p_1} - \overline{C}_{p_1}°)}{dT} = 0 \tag{43}$$

Equations (42) and (43) are approximations for the temperature range 10° to 35° C.

2. THE APPARENT AND PARTIAL MOLAL HEAT CONTENT OF HYDROGEN CHLORIDE AND THE PARTIAL MOLAL HEAT CONTENT OF WATER IN AQUEOUS SOLUTION OF HYDROGEN CHLORIDE AT 25° C.

In order to correlate the existing data on the heat of solution of hydrogen chloride and the heat of formation of aqueous hydrogen chloride with the present data on the heat of formation of gaseous hydrogen chloride, it is necessary to have values of $\Phi_h - \Phi_h°$, the relative apparent molal heat content, for aqueous hydrogen chloride. These values can be easily determined from data on heat of dilution by the procedure previously employed by the present author.[53] The method consists simply in plotting the values of the measured heats of dilution as ordinates with the square root of the molality as the scale of abscissas. The intercept at $m^{1/2} = 0$ is made the zero for the scale of ordinates and the curve is then that of $\Phi_h - \Phi_h°$ against $m^{1/2}$. Then the relative partial molal heat content of hydrogen chloride is obtained by means of the relation

$$\overline{H}_2 - \overline{H}_2° = (\Phi_h - \Phi_h°) + 1/2\ m^{1/2} \frac{d(\Phi_h - \Phi_h°)}{dm^{1/2}} \tag{44}$$

and the relative partial molal heat content of water is given by

$$\overline{H}_1 - \overline{H}_1° = -\frac{m}{55.508}\ 1/2\ m^{1/2} \frac{d(\Phi_h - \Phi_h°)}{dm^{1/2}} \tag{45}$$

The existing data on heats of dilution (with the exception of many data for the dilute region of concentration which appeared in the paper already referred to [54]) are shown in Figure 6, where the ordi-

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[52] Gucker, F. T., and Schminke, K. H. (see footnote 50, p. 694), found that, for aqueous hydrogen chloride and potassium hydroxide, the values of Φ_c at about 0.04 molal undergo an abrupt change, apparently increasing to very high values at infinite dilution. However, pending the confirmation of this behavior, which Gucker and Schminke found peculiar to hydrogen chloride and potassium hydroxide but not to lithium chloride, one can continue to use the linear extrapolation to infinite dilution.

[53] Rossini, F. D., B. S. Jour. Research, vol. 6, p. 791, 1931.

[54] See footnote 53, p. 695.

nate scale has already been shifted to make the plot one of $\Phi_h - \Phi_h^\circ$ against $m^{1/2}$. The values plotted in Figure 6 are from the data of Thomsen [55] at 18° C., Berthelot [56] at 18° C., and Wrewsky and Savaritzky [57] at 21.5° C. These data have been corrected to 25° C., using the appropriate values for heat capacity. The curve in the region from $m^{1/2} = 0$ to $m^{1/2} = 1.4$ represents values of $\Phi_h - \Phi_h^\circ$ for 25° C., calculated from those for $\Phi_h - \Phi_h^\circ$ at 18° C. which have already been compiled by the present author.[58]

In the above manner the values given in Tables 6 and 7 have been derived. Table 6 gives $\Phi_h - \Phi_h^\circ$ for aqueous hydrogen chloride
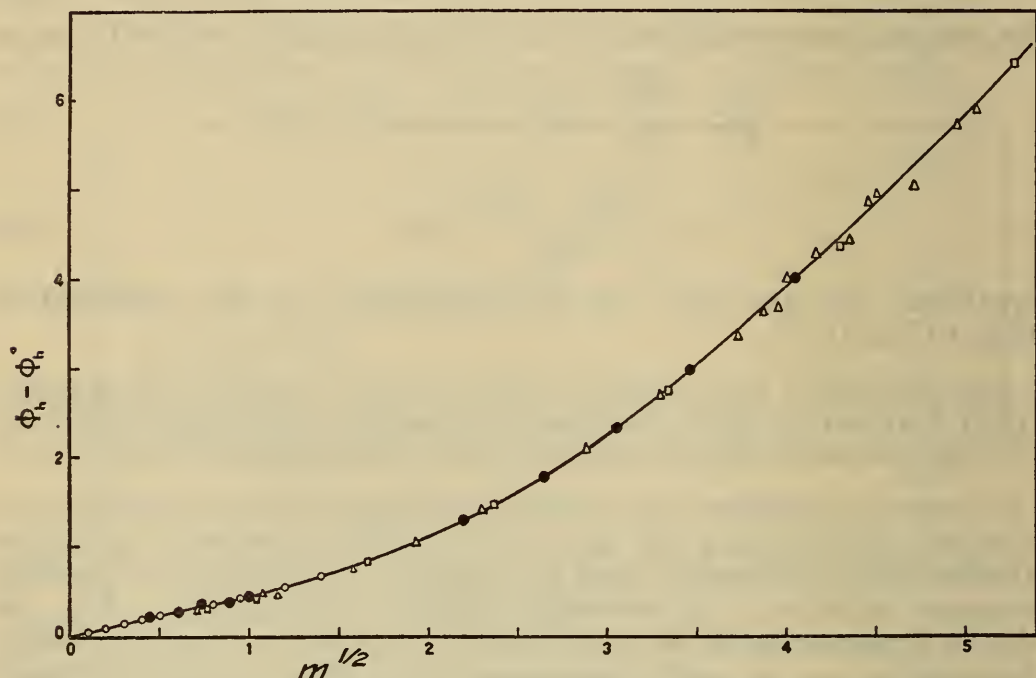

FIGURE 6.—*The relative apparent molal heat content of HCl in aqueous solution of HCl at 25° C.*

The scale of abscissas gives the square root of the molality.
The scale of ordinates gives $\Phi_h - \Phi_h^\circ$, the relative apparent molal heat content, for HCl in aqueous solution of HCl at 25° C., in kg-cal.15 per mole.
The points designate the experimental values (corrected to 25° C.) of the following investigators: ●, Wrewsky and Savaritzky; △, Berthelot; and □, Thomsen.
The points marked ○ are values (corrected to 25° C.) obtained from those for 18° C. previously given by the present author.

at 25° C., with the composition of the solution expressed in terms of the number of moles of water associated with 1 mole of hydrogen chloride. Table 7 gives values for $\Phi_h - \Phi_h^\circ$, $\overline{H}_2 - \overline{H}_2^\circ$, and $\overline{H}_1 - \overline{H}_1^\circ$, at 25° C., for selected values of $m^{1/2}$.

[55] Thomsen, J., Thermochemische Untersuchungen, vol. 2, Barth, Leipzig, 1886.
[56] Berthelot, M., Ann. chim. phys., vol. 4, p. 467, 1875.
[57] Wrewsky, M., and Savaritzky, N., Z. physik. Chem., vol. 112, p. 90, 1924.
[58] See footnote 53, p. 695.

TABLE 6.—*Relative apparent molal heat content of HCl in aqueous solution of HCl, at 25° C.*

[The composition of the solution is given in terms of the number of moles of H_2O associated with 1 mole of HCl]

Solution	$\Phi_h - \Phi_h°$	Solution	$\Phi_h - \Phi_h°$
	g-cal per mole of HCl		g-cal per mole of HCl
$HCl.\infty H_2O$	0	$HCl.18H_2O$	920
$HCl.6400H_2O$	46	$HCl.15H_2O$	1,050
$HCl.3200H_2O$	65	$HCl.12H_2O$	1,250
$HCl.1600H_2O$	90	$HCl.10H_2O$	1,460
$HCl.800H_2O$	128	$HCl.8H_2O$	1,760
$HCl.400H_2O$	181	$HCl.6H_2O$	2,320
$HCl.200H_2O$	249	$HCl.5H_2O$	2,760
$HCl.100H_2O$	343	$HCl.4H_2O$	3,440
$HCl.50H_2O$	483	$HCl.3H_2O$	4,480
$HCl.25H_2O$	730	$HCl.2H_2O$	6,400
$HCl.20H_2O$	850	$HCl.1H_2O$	11,800

TABLE 7.—*Apparent and partial molal heat content of HCl and partial molal heat content of H_2O in aqueous solution of HCl, at 25° C.*

$m^{1/2}$	m moles of HCl per 1,000 g H_2O	$\Phi_h - \Phi_h°$ g-cal. per mole of HCl	$\overline{H_2} - \overline{H_2}°$ g-cal. per mole of HCl	$\overline{H_1} - \overline{H_1}°$ g-cal. per mole of H_2O
0	0	0	0	0
.1	.01	49	74	−.0045
.2	.04	98	146	−.0346
.3	.09	146	219	−.119
.4	.16	193	287	−.271
.5	.25	238	348	−.496
.6	.36	281	412	−.850
.8	.64	367	543	−2.03
1.0	1.00	458	700	−4.35
1.2	1.44	561	884	−8.35
1.4	1.96	675	1,095	−14.8
1.6	2.56	805	1,350	−25.3
1.8	3.24	955	1,650	−40.9
2.0	4.00	1,120	2,000	−63.4
2.5	6.25	1,610	3,040	−161
3.0	9.00	2,260	4,410	−349
3.5	12.25	3,040	5,960	−644
4.0	16.00	3,920	7,560	−1,040
4.5	20.25	4,860	9,170	−1,570
5.0	25.00	5,840	10,840	−2,250
5.5	30.25	6,860	-----------	-----------

3. THE HEAT OF SOLUTION OF HYDROGEN CHLORIDE IN WATER

The heat of solution of hydrogen chloride in water has been measured by Thomsen,[59] Berthelot and Louguinine,[60] and Wrewsky and Savaritzky.[61] The data of these investigators have been corrected to 25° C. by means of the proper values of heat capacity and are shown in Figure 7. These data are for the reaction

$$HCl \text{ (gas)} + \frac{55.508}{m} H_2O \text{ (liquid)} = HCl \cdot \frac{55.508}{m} H_2O \text{ (solution)} \quad (46)$$

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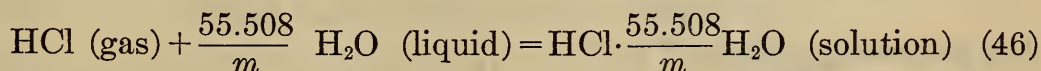
[59] Thomsen, J., Thermochemische Untersuchungen, vol. 2, Barth, Leipzig, 1886.
[60] Berthelot, M., and Louguinine, W., Ann. chim. phys., vol. 6, p. 289, 1875.
[61] See footnote 57, p. 696.

The curve shown in Figure 7 is drawn through the data of Wrewsky and Savaritzky with extrapolation to infinite dilution made with the aid of the values of $\Phi_h - \Phi_h{}^\circ$ given in Table 7.

From these data the value for the heat of solution of hydrogen chloride at infinite dilution in water at 25° C.

$$\text{HCl (gas)} = \text{HCl (aqueous, } m=0) \qquad (47)$$

is

$$\Delta H°_{298.1} = -17,880 \pm 40 \text{ g-cal.}_{15} \text{ mole}^{-1} \qquad (48)$$

4. THE HEATS OF FORMATION OF SILVER CHLORIDE AND MERCUROUS CHLORIDE

In order to utilize the data on the temperature coefficient of the emf of certain cells for obtaining the heat of formation of aqueous
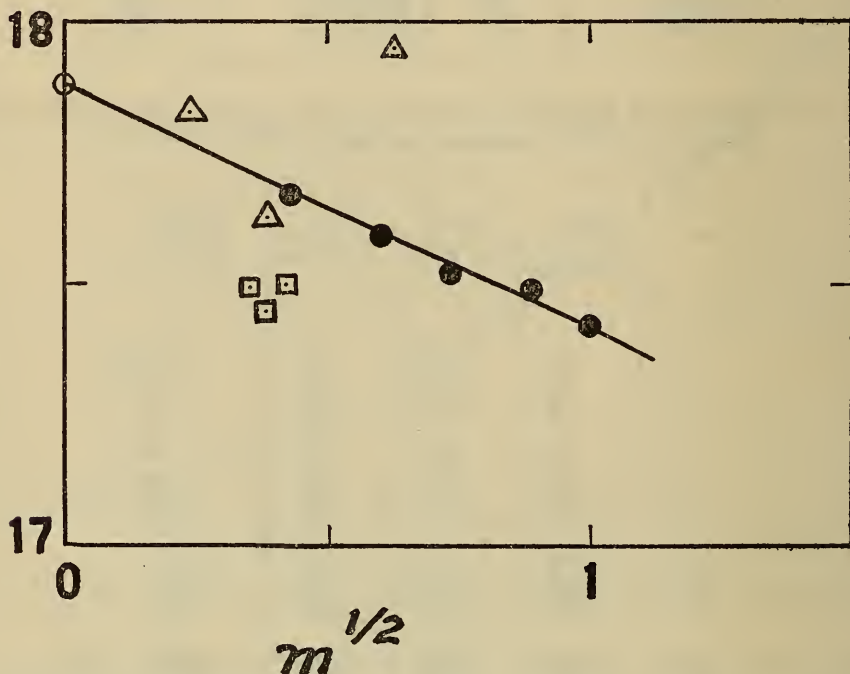
FIGURE 7.—*The heat of solution of HCl (gas) in water at 25° C.*

The scale of abscissae gives the square root of the molality.

The scale of ordinates gives the heat of the reaction $\text{HCl}_{(gas)} + \frac{55.508}{m} \text{H}_2\text{O}_{(liquid)} = \text{HCl} \cdot \frac{55.508}{m} \text{H}_2\text{O}_{(solution)}$ at 25° C., in kg-cal.₁₅ per mole of HCl.

The points designate the experimental values (corrected to 25° C.) of the following investigators: ●, Wrewsky and Savaritzky; △, Berthelot and Longuinine; and □, Thomsen. The point marked ○, at $m^{1/2} = 0$, gives the value for infinite dilution.

hydrogen chloride, it is necessary to have accurate values for the heats of formation of silver chloride and mercurous chloride. Fortunately, data are available for calculating these values with considerable accuracy.

For the reaction

$$\text{Ag (solid)} + 1/2 \text{ Cl}_2 \text{ (gas)} = \text{AgCl (solid)} \qquad (49)$$
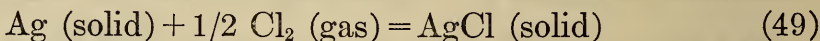
the free energy change [62] is

$$\Delta F°_{298.1} = -26,211 \pm 9 \text{ g-cal.}_{15} \text{ mole}^{-1} \qquad (50)$$

The entropy change for reaction (49) can be calculated from two independent sources: (1) From values of the entropies of silver,

[62] See p. 692. The difference in free energy between crystalline and chemically precipitated silver chloride was found by Randall and Young (see footnote 7, p. 680) to be zero within the limits of uncertainty.

chlorine, and silver chloride; and (2) from a knowledge of the temperature coefficient of the emf of the cell in which reaction (49) occurs. New data on the heat capacity of silver and silver chloride down to low temperatures have been obtained recently. From such measurements, Eucken, Clusius, and Woitinek [63] obtained for silver, $S°_{298.1} = 10.16$; Giauque and Meads [64] reported a preliminary value for silver, $S°_{298.1} = 10.01$; and Eastman and Milner [65] gave for crystalline silver chloride $S°_{298.1} = 22.97 \pm 0.08$. The entropy of silver will be taken as 10.09 ± 0.07. Combining these data with those of Giauque and Overstreet [66] on chlorine one finds for reaction (49)

$$\Delta S°_{298.1} = -13.77 \pm 0.12 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{51}$$

For the temperature coefficient of the emf of the cell in which reaction (49), with chemically precipitated silver chloride, occurs, Gerke [67] found for 25° C., the value

$$\frac{dE}{dT} = -0.000595 \pm 0.000006 \text{ international volt ° C.}^{-1}$$

Correcting the chlorine to unit fugacity, one obtains for reaction (49)

$$\Delta S°_{298.1} = -13.69 \pm 0.14 \text{ g-cal.}_{15} \text{ mole}^{-1} \text{ ° C.}^{-1} \tag{52}$$

The average of (51) and (52) gives for reaction (49)

$$\Delta S°_{298.1} = -13.73 \pm 0.12 \text{ g-cal.}_{15} \text{ mole}^{-1} \text{ ° C.}^{-1} \tag{53}$$

By means of equations (2), (50), and (53) one finds for reaction (49)

$$\Delta H°_{298.1} = -30,304 \pm 40 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{54}$$

Within the limits of uncertainty this value is apparently that for either crystalline or chemically precipitated silver chloride.

For calculating the heat of formation of mercurous chloride, a slightly different procedure is necessary because an accurate value for the entropy of mercurous chloride is not available.

For the cell in which the reaction was

$$\text{Ag (solid)} + \text{HgCl (solid)} = \text{AgCl (solid)} + \text{Hg (liquid)} \tag{55}$$

Gerke [68] found, at 25° C., with chemically precipitated salts

$$\frac{dE}{dT} = 0.000338 \pm 0.000002 \text{ international volt ° C.}^{-1} \tag{56}$$

and

$$E°_{298.1} = 0.0455 \text{ international volt} \tag{57}$$

This latter value is well substantiated [69] by measurements of other investigators, and the uncertainty can be taken as ± 0.0003 volts.

Using the Gibbs-Helmholtz relation

$$\Delta H = NF\left(T\frac{dE}{dT} - E\right) \tag{58}$$

one finds for reaction (55)

$$\Delta H°_{298.1} = 1276 \pm 16 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{59}$$

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[63] Eucken, A., Clusius, K., and Woitinek, H., Z. anorg. Chem., vol. 203, p. 39, 1931.
[64] Giauque, W. F., and Meads, P. F., see footnote 6, p. 680.
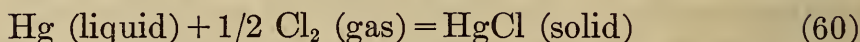[65] Eastman, E. D., and Milner, R. T., personal communication.
[66] See footnote 6, p. 680.
[67] See footnote 36, p. 692.
[68] See footnote 36, p. 692.
[69] See footnote 7, p. 680.

Combination of reactions (49) and (55) gives

$$\text{Hg (liquid)} + 1/2 \text{ Cl}_2 \text{ (gas)} = \text{HgCl (solid)} \tag{60}$$

for which

$$\Delta H^\circ_{298.1} = -31{,}580 \pm 45 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{61}$$

5. THE HEAT OF FORMATION OF AQUEOUS HYDROGEN CHLORIDE

It is possible to obtain a fairly accurate value for the heat of formation of hydrogen chloride in aqueous solution from data on the temperature coefficient of certain cells and the heats of formation of silver chloride and mercurous chloride.

Lewis and Randall,[70] Ellis,[71] and Harned and Brumbaugh [72] measured at a series of temperatures the emf of cells in which the reaction was

$$1/2 \text{ H}_2 \text{ (gas)} + \text{HgCl (solid)} = \text{Hg (liquid)} + \text{HCl (aqueous, } m) \tag{62}$$
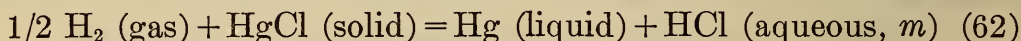
and from these data calculated, by the Gibbs-Helmholtz relation, ΔH for reaction (62). By adding to (62) the reaction for the formation of mercurous chloride (solid) one obtains

$$1/2 \text{ H}_2 \text{ (gas)} + 1/2 \text{ Cl}_2 \text{ (gas)} = \text{HCl (aqueous, } m) \tag{63}$$
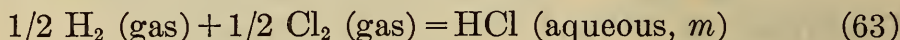
In an analogous manner one can combine the data of Noyes and Ellis,[73] Harned and Brumbaugh,[74] and Butler and Robertson [75] on cells in which the reaction was

$$1/2 \text{ H}_2 \text{ (gas)} + \text{AgCl (solid)} = \text{Ag (solid)} + \text{HCl (aqueous, } m) \tag{64}$$
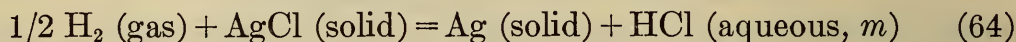
with the heat of formation of silver chloride to obtain the heat of formation of aqueous hydrogen chloride.

These data give the heat of formation of 1 mole of hydrogen chloride in an infinite amount of aqueous solution of hydrogen chloride of molality m. To the various values of ΔH for reaction (62) have been added the appropriate values of $\bar{H}_2 - \bar{H}_2^\circ$, taken from Table 7, in order to obtain the heat of the reaction

$$1/2 \text{ H}_2 \text{ (gas)} + \text{HgCl (solid)} = \text{Hg (liquid)} + \text{HCl (aqueous, } m = 0) \tag{65}$$
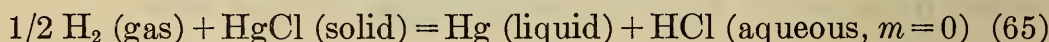
In this manner the following values for reaction (65) were obtained:

Data from—	Number of different molalities	Range of molality	$\Delta H^\circ_{298.1}$
Lewis and Randall	1	0.1	−8,429
Ellis	8	4.484−0.0333	−8,370
Harned and Brumbaugh	1	0.1	−8,400

The average of these values is −8,400, exactly the value of the latest determination, and the uncertainty can be taken as ± 30. Combination of reactions (60) and (65) gives

$$1/2 \text{ H}_2 \text{ (gas)} + 1/2 \text{ Cl}_2 \text{ (gas)} = \text{HCl (aqueous, } m = 0) \tag{66}$$

for which

$$\Delta H^\circ_{298.1} = -39{,}980 \pm 55 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{67}$$

[70] Lewis, G. N., and Randall, M., J. Am. Chem. Soc., vol. 36, p. 1969, 1914.
[71] Ellis, J. H., J. Am. Chem. Soc., vol. 38, p. 737, 1916.
[72] Harned, H. S., and Brumbaugh, N. J., J. Am. Chem. Soc., vol. 44, p. 2729, 1922.
[73] Noyes, A. A., and Ellis, J. H., J. Am. Chem. Soc., vol. 39, p. 2532, 1917.
[74] See footnote 72, p. 700.
[75] Butler, J. A. V., and Robertson, C. M., Proc. Roy. Soc. (London), vol. 125, p. 694, 1929.

In like manner, adding the appropriate values of $\overline{H}_2 - \overline{H}_2°$ to convert the data to infinite dilution, one finds for the reaction

1/2 H_2 (gas) + AgCl (solid) = Ag (solid) + HCl (aqueous, $m = 0$)   (68)
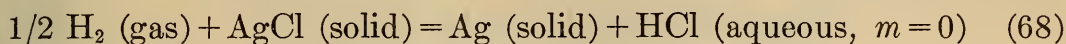
the following values:

Data from—	Number of molalities	Range of molality	$\Delta H°_{298.1}$
Noyes and Ellis	6	0. 1–0. 001	−9, 552
	1	0. 33314	−9, 643
Harned and Brumbaugh	1	0. 01	−9, 611
	1	0. 00	−9, 567
Butler and Robertson	4	0. 1–0. 01	−9, 554
	1	0. 3	−9, 638

Taking the average of these values, one finds for reaction (68)

$$\Delta H°_{298.1} = -9{,}594 \pm 50 \text{ g-cal.}_{15} \text{ mole}^{-1} \qquad (69)$$

Combination of equations (54) and (69) gives for reaction (66)

$$\Delta H°_{298.1} = -39{,}898 \pm 65 \text{ g-cal.}_{15} \text{ mole}^{-1} \qquad (70)$$

Taking the average of (67) and (70) one finds for reaction (66)

$$\Delta H°_{298.1} = -39{,}938 \pm 55 \text{ g-cal.}_{15} \text{ mole}^{-1} \qquad (71)$$

This value, fortunately, is practically identical with that obtained by combining equations (18) and (48) which give for reaction (66)

$$\Delta H°_{298.1} = -39{,}943 \pm 40 \text{ g-cal.}_{15} \text{ mole}^{-1} \qquad (72)$$

which will be taken as the best value for the heat of formation of aqueous hydrogen chloride at infinite dilution.

6. THE FREE ENERGY OF FORMATION OF GASEOUS HYDROGEN CHLORIDE

The free energy of formation of gaseous hydrogen chloride is given by equation (32) as

$$\Delta F°_{298.1} = -22{,}738 \pm 33 \text{ g-cal.}_{15} \text{ mole}^{-1} \qquad (32)$$

A value having a smaller uncertainty than the foregoing one can be calculated from equations (2), (18), and (19). This gives

$$\Delta F°_{298.1} = -22{,}775 \pm 12 \text{ g-cal.}_{15} \text{ mole}^{-1} \qquad (73)$$

7. THE ENTROPY OF AQUEOUS HYDROGEN CHLORIDE

The entropy of aqueous hydrogen chloride is the basis for the calculation of the entropies of aqueous ions according to the methods of Latimer and coworkers.[76]
For the reaction

$$1/2 H_2 \text{ (gas)} + 1/2 Cl_2 \text{ (gas)} = HCl \text{ (aqueous)} \qquad (74)$$
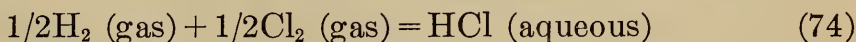
one finds by combining equations (2), (24), (27), and (72)

$$\Delta S°_{298.1} = -28.87 \pm 0.15 \text{ g-cal.}_{15} \text{ mole}^{-1} °C.^{-1} \qquad (75)$$

[76] See footnote 8, p. 681.

Then for aqueous hydrogen chloride at hypothetical 1 molal, where its heat content is the same as that at infinite dilution,

$$S^{\circ}_{298 \cdot 1} = 13.40 \pm 0.15 \text{ g-cal.}_{15} \text{ mole}^{-1} \text{ }^{\circ}\text{C.}^{-1} \qquad (76)$$

V. ACKNOWLEDGMENT

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