# Heat of Solution of Hydrogen Chloride

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**The heat of solution of HCl in $H_2O$ at 25° has been measured. Corrected to the ideal gas state and infinite dilution, the result is $-17.88 \pm 0.014$ kcal. mole$^{-1}$.**

A RECENT COMMENT (*10*) that some disagreement exists between calorimetric and electrochemical determinations of the standard heat of formation of aqueous HCl has led us to redetermine the heat of solution of hydrogen chloride in an effort to improve the data leading to the thermochemically very important heat of formation of chloride ion.

## EXPERIMENTAL

Hydrogen chloride was prepared by reaction of NaCl with $H_2SO_4$ and purified by passage over finely divided uranium prepared by decomposition of $UH_3$(*7*). Analysis of the melting curve (*2*) indicated $2 \times 10^{-4}$ mole fraction impurity. The samples were sealed in bulbs similar to those used for diborane (*3*) and weighed to 0.1 mg. After the runs, the solution and washings were titrated potentiometrically with NaOH standardized against National Bureau of Standards potassium acid phthalate; results ranged from 99.86 to 99.91% of theoretical. The weighing is considered more reliable.

Gold ID calorimeter (*3*) was used; 375 ml. of distilled water and 1 ml. of 0.1$N$ HCl were added to the bomb (except for the last run, where 325 ml. was used) and deaerated by a stirring and pumping program known to remove >99% of dissolved air and <1% of the solution. A thermistor bridge was used for temperature measurements. After each run the calorimeter was twice calibrated electrically over the same temperature interval as that of the reaction. All runs were initiated at 25.00 ± 0.02° C.

## RESULTS AND DISCUSSIONS

Results are given in Table I. The heat-evolved values are those observed; for the calculation of $\Delta H$ there is added to these a correction of 0.0120 $V$ cal., where $V$ is the bulb volume in ml., to account for the endothermic evaporation of water into the broken bulb, 0.0134 $V$ cal., and the exothermic $PV$ compressional work, 0.0014 $V$ cal. The heat of breakage of similar bulbs has been found to be negligible (*3*); the much larger vaporization and compression heats for ammonia at 25° have been measured and found to agree with calculation (*4*).

Table I. Heat of Solution of HCl

| HCl., Mg. | Bulb Vol, Ml. | Heat Evolved, Cal. | $\Delta H°$, Kcal. Mole$^{-1}$ |
|---|---|---|---|
| 245.8 | 58.3 | 115.10 | 17.865 |
| 234.7 | 56.4 | 110.00 | 17.882 |
| 316.7 | 75.7 | 148.42 | 17.889 |
| 284.3 | 65.4 | 133.40 | 17.903 |
| 303.1 | 72.4 | 142.10 | 17.899 |

The observed heats of reaction at constant volume are converted to constant pressure by subtraction of $RT$ and are corrected to the ideal gas state for HCl: from the Berthelot equation with critical constants from the International Critical Tables (*6*), $(\partial H/\partial P)_T$ is calculated to be $-11.3$ cal. mole$^{-1}$ atm.$^{-1}$; the total correction is then $-0.032$ kcal. mole$^{-1}$ for the sample pressures in these runs (2.8 to 2.9 atm.).

The values of $\Delta H°$ are calculated at infinite dilution, using the heat of dilution data (*9*), which is essentially the same as that of Harned and Oven (*5*) and allowing for the effect of the HCl initially in solution. Effects due to change of volume and vapor pressure of the solution and to HCl remaining in the gas phase are negligible. The average of $\Delta H°$ is $-17.888 \pm 0.014$ (uncertainty interval is twice the standard deviation of the mean).

The NBS tables (*9*) give $-17.960$ for this process. Bichowsky and Rossini (*1*) and Rossini (*8*) review the earlier work and prefer the value of Wrewskii and Savaritzkii (*11*), $-17.88 \pm .04$. However, application of the NBS dilution data (*9*) to the measurements of Wrewskii and Savarizkii gives about $-17.84$.

## LITERATURE CITED

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