Heat of Solution of Potassium Carbonate

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IN TESTING the use and accuracy of a vacuum-flask calorimeter, the solution of anhydrous potassium carbonate in water was investigated. Values found for the heat of solution differ sufficiently from those reported in the literature to be worth recording.

A recent compilation of thermodynamic properties (*7*) lists enthalpies of formation at 25° C. for crystalline potassium carbonate and its aqueous solution. For the variation of enthalpy of formation, ΔH_f° (aq.), with concentration of the solution, reference is made to the work of Berthelot (*2*) and Muller (*6*). Bichowsky and Rossini (*3*) have also compiled thermochemical data for this system at 18° C., basing their values on the results of a number of workers (*7*). Values of ΔH_f° (aq.) at concentrations less than 0.139*M* have been estimated by these authors.

EXPERIMENTAL

Measurements were made in a stirred vacuum-flask calorimeter having a heat capacity near 200 cal. deg.$^{-1}$ In each run this value was found by electrical calibration following solution of the salt and was reproducible to 0.4%. The temperature of the calorimeter was determined by measuring the resistance of a thermistor using a Wheatstone bridge, the off-balance d.c. potential of which was amplified and recorded on a Speedomax recorder. The operation was thus semiautomatic and when using maximum sensitivity a full-scale deflection of the recorder corresponded to about 10^{-2} deg. when 1.5 volts was applied to the bridge. A standard thermometer was used to calibrate the thermistor. The method of evaluating temperature changes from temperature-time records has been described (*8*).

Granular potassium carbonate (Baker analyzed reagent of 100.0% assay) was dried at 110° C. before use, and the water used was free from carbon dioxide and inorganic ions.

Heats changes during solution runs varied from 5 to 200 cal. and the internal consistency of the results was found to be ±0.4% over this range. Values for the heat of solution of sodium chloride agreed with those found by Benson and Benson (*1*) within this experimental error. In all cases solution was effected at 25° C. No correction was made to the experimental heat change other than allowing for the heat of opening the empty sample cell, found in separate experiments to be 0.04 cal. (cooling).

RESULTS

Figure 1 and Table I show the results found. Corresponding values (*3, 7*) are given in the figure for comparison.

Solution occurs less exothermically at very low concentrations, a fact not indicated by previous work. This variation is no doubt a result of the reaction

$$CO_3^{-2} + H_2O \rightleftarrows HCO_3^- + OH^-$$

which occurs to an increasing extent in dilute solutions with an enthalpy change of 9.7 kcal. per mole [calculated from ΔH_f° data at infinite dilution (*7*) for the species involved in the reaction]. Using a value of 5.6×10^{-11} for K_2, the second dissociation constant of carbonic acid, the above reaction is found to occur to the extent of 3.4% at 0.15*M* and 17.4% at 0.005*M*. The corresponding changes in ΔH_s due to this reaction are shown in Figure 1 where the calculated curve has been fitted to the experimental results at 0.15*M*. Considering the neglect of ionic interaction effects in using K_2 and ΔH_f° values, the experimental points are seen to agree well with the calculated curve.

Table I. Heat of Solution of Potassium Carbonate in Water at 25° C.

Molality	ΔH_s, Cal./Mole	Molality	ΔH_s, Cal./Mole
0.0042	-5200	0.0598	-6978
0.0099	-6028	0.0952	-6985
0.0171	-6446	0.1014	-7074
0.0312	-6615	0.1398	-7080
0.0480	-6952	0.1630	-7067
0.0518	-6872	0.0507[a]	-7983 initial -9170 final

[a] CO_2 present.

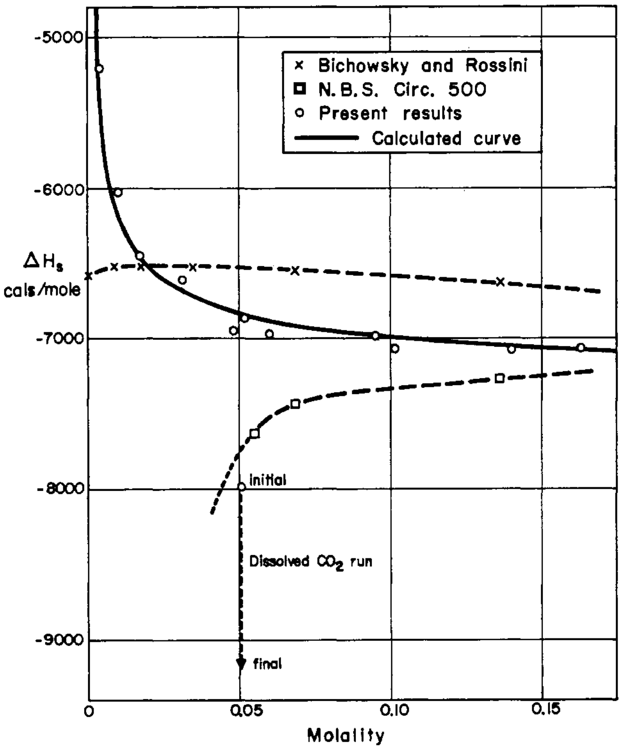

Figure 1. Heat of solution of potassium carbonate in water at 25° C.

A smooth curve was drawn through the experimental points. Values of the heat of solution of potassium carbonate in water at 25° C. at rounded molality values were:

Molality	ΔH_s, Cal./Mole	Molality	ΔH_s, Cal./Mole
0.005	-5450	0.05	-6900
0.01	-6020	0.10	-7050
0.025	-6560	0.18	-7050

In seeking a possible explanation for the differences between these and earlier results, the heat of solution was found in one instance using water nearly saturated with carbon dioxide. A rapid heat change occurred as in the other runs, and this was followed by a slow evolution of heat, about 30 minutes being required for its completion. The initial and final values thus found for the heat of solution in this run are also shown in Figure 1. Removal of dissolved carbon dioxide from water is known to occur endothermically (*3, 7*). The exothermic effects observed in this case might be connected with displacement of the equilibria present in aqueous carbon dioxide on solution of potassium carbonate. It is known (*4, 5*), for instance, that the reaction

$$CO_2\,(aq.) + OH^- \rightarrow HCO_3^-$$

proceeds at a rate comparable to the slow thermal effect described above.

Small amounts of dissolved carbon dioxide in the water used for solution could therefore explain the lower values of ΔH_s compiled from earlier data (*7*), and this was the reason suggested by Muller (*6*) for the difference between his results and those of Berthelot (*2*) in aqueous potassium carbonate.

LITERATURE CITED

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Partition Function Ratios and Equilibrium Constants for Oxygen-18 Exchange Reactions

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KNOWLEDGE of partition functions can be applied in predicting suitable exchange reactions for the enrichment of isotopes. Our present discussion is confined only to the two stable isotopes of oxygen—viz., 16 and 18. The procedure of calculating the equilibrium constants from the spectroscopic data was first given by Urey and Rittenberg (*19*) and later applied to a number of systems by Urey (*18*). Bigeleisen and Mayer (*5*) have further simplified this procedure, and in our calculations we have used their final expression

$$\ln \frac{Q}{Q'} = \sum_i \left(\frac{1}{2} + \frac{1}{e^{u_i} - 1} - \frac{1}{u_i} \right) \Delta u_i \quad \ldots \qquad (1)$$

where

Q = partition function for isotopic molecule
Q' = partition function for normal molecule
u_i = $h\nu_i/kT$
ν_i = vibrational frequency
h = Planck's constant
k = Boltzmann's constant
T = temperature
u_i' = $u_i + \Delta u_i$

In this article Δu_i is $\ll u_i$ for all the systems considered. In deriving Equation 1, anharmonicity is also neglected. Thus, in calculating the partition function ratio, we require the vibrational frequencies of the normal molecule and the frequency shifts. If all this information is experimentally available, extremely reliable values of the equilibrium constants can be determined, as recently shown by Begun and Fletcher (*4*) for isotopic nitrogen exchange. For almost all the molecules in which we are interested, no such experimental data are available. We have, therefore, calculated the vibrational frequencies of the isotopic molecules from known frequencies of normal molecules in conjunction with theoretical formulas for the valence force model (*10*). This particular model is chosen in view of its success for polyatomic molecules, and it has reproduced the measured frequency shifts (*4*) precisely, when proper choice of the force constants is made.

Table I. Vibrational Frequency of Normal and Isotopic Molecules[a]

Molecule	ν_1, Cm.$^{-1}$	ν_2, Cm.$^{-1}$	ν_3, Cm.$^{-1}$	ν_4, Cm.$^{-1}$
$N^{14}O^{16}$	1904.03			
$N^{14}O^{18}$	1854.02			
$N_2^{14}O^{16}$	1300.3	596.5(2)	2276.9	
$N_2^{14}O^{18}$	1257.7	591.8(2)	2269.2(2)	
$N^{14}O_2^{16}$	1357.8	756.8	1665.5	
$N^{14}O_2^{18}$	1309.0	727.5	1633.7	
$C^{12}O_2^{16}$	1351.2	672.2(2)	2396.4	
$C^{12}O_2^{18}$	1273.9	661.9(2)	2359.8	
$N^{14}O^{16}Cl^{35}$	1800.0	604.7	332.4	
$N^{14}O^{18}Cl^{35}$	1754.7	602.6	322.0	
$N^{14}O_3^{16}$-	1049.2	830.9	1375.6(2)	716.8(2)
$N^{14}O_3^{18}$-	989.2	820.4	1361.2(2)	674.3(2)
$N^{14}O_2^{16}$-	1326.0	808.0	1232.0	
$N^{14}O_2^{18}$-	1296.2	766.0	1208.2	
$S^{32}O_2^{16}$	1151.4	517.8	1360.5	
$S^{32}O_2^{18}$	1102.4	495.5	1361.1	
$H_2^1O^{16}$	3825.3	1653.9	3935.6	
$H_2^1O^{18}$	3815.5	1647.8	3919.4	

[a] Number in parentheses indicates multiplicity of degenerate frequency.

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