Heat of Transfer Between Heavy and Normal Water for Some Inorganic Acid Salts

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Heats of dilution of several inorganic acid salts were measured in normal and heavy water. From the resulting data, heats of transfer for the salts passing between the isotopic solvents were calculated. The heats of transfer indicate that all the salts behave as structure breakers in aqueous solution and that distant hydration is responsible for the solvent structure influence exhibited by salts passing between the isotopic solvents.

In this laboratory, a continuing program is under way in which the influence of electrolytes on water structure is being investigated. As part of the investigation, heats of transfer between heavy and normal water for classes of salts are being determined. Results for the alkaline earth chlorides and the sodium salts of the C_1 to C_6 aliphatic acids have been reported (*2, 3, 5*). We report here transfer heats for the sodium salts of carbonic, nitric, sulfuric, and sulfurous acids.

The details of the experimental procedure, the calorimeter, and the thermochemical processes used to obtain the transfer values have been described (*2, 3*). The general procedure involves measuring the heat associated with the dilution of concentrated solutions of each of the salts with heavy and normal water.

Heavy water was provided by the U. S. Atomic Energy Commission, Savannah River Operations Office, Aiken, S.C. All starting salts were reagent grade. With the exception of Na_2SO_3, the salts were dried at 105° C and used without further treatment. Anhydrous sodium sulfite was used without additional drying to avoid its possible decomposition. Solutions were prepared such that the concentrations before dilution were equal in both solvents, and dilution volumes were selected such that final concentrations were also equal in both solvents.

Experimental results are presented in Table I. Initial and final concentrations are shown, along with the heats observed for each of the thermochemical processes described by Greyson and Snell (*3*). The double entries represent the results of replicate measurements for each of the processes and indicate the precision of the measurements. Accuracy is based on calibration of the calorimeter by measurement of the heat of solution of KCl in water and is estimated to be about 2%.

The transfer heats, shown in columns six and seven, represent the change in enthalpy that would be exhibited upon transfer of one mole of salt from a heavy water solution into a normal water solution at the same concentration, the volumes of both solutions being large enough so that neither suffered a concentration change. The values of the transfer heats in both the dilute and concentrated solutions can be calculated from the heats of dilution as described by Greyson and Snell (*3*).

In a recent review, Arnett and McKelvey compiled estimated values for the heat of transfer for a number of aqueous ions (*1*), based on available heat and solubility data in normal and heavy water for various electrolytes. Using the Arnett and McKelvey values for sodium, sulfate, and nitrate ions, one obtains transfer heats of −495 and −580 cal per mole in dilute solution for sodium nitrate and sulfate, respectively (no value is tabulated for carbonate or sulfite ion). The agreement between the estimates and the measured values is remarkable. The value for the dilute sodium nitrate solution, measured in this work, also compares favorably with a value (−490 cal per mole) reported (*4*) during the time this note was in review.

The dilution processes for carbonate, nitrate, and sulfate

Table I. Heats of Transfer from Heavy to Normal Water at 25° C

Salt	Initial[a] concn., aqm	Final concn., aqm	H_2O, ΔH_{dil}, cal/mole	D_2O, ΔH_{dil}, cal/mole	$H_2O \rightarrow D_2O$, ΔH_{dil}, cal/mole	$D_2O \rightarrow H_2O$, ΔH_{dil}, cal/mole	$\Delta H_{tr}(H_2O - D_2O)$, cal/mole: Concn soln	$\Delta H_{tr}(H_2O - D_2O)$, cal/mole: Dil soln
Na_2CO_3	2.500	0.0265	+2191	+2568	+2605	+2152		
			+2183	+2574	+2601	+2150	−34 ± 5	−418 ± 5
$NaNO_3$	2.500	0.0265	+927	+1088	+1417	+627		
			+934	+1099	+1417	+609	−318 ± 10	−481 ± 10
Na_2SO_4	1.250	0.0135	+1144	+1465	+1745	+886		
			+1162	+1494	+1762	+905	−266 ± 18	−591 ± 18
Na_2SO_3	1.250	0.0135	−1684	−1600	−1289	−1952	−280 ± 18	−388 ± 19
			−1694	−1563	−1291	−1964		

[a] Moles per 55.5 moles of solvent.

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are endothermic, and that for the sulfite is exothermic. Despite the variation from endothermicity to exothermicity for the dilution processes, all the heats are exothermic for the transfer from heavy into normal water. This is interpreted as an indication that the salts all possess a structure-breaking influence (*3*). The heat of transfer decreases in absolute value with increased solution concentration, providing further confirmation of the hypothesis suggested previously (*5*), that distant hydration is responsible for the solvent structure influence exhibited by salts passing between the isotopic solvents.

LITERATURE CITED

(1) Arnett, E. M., McKelvey, D. R., "Solute-Solvent Interactions," J. F. Coetzee, C. D. Ritchie, Ed., p 371, Marcel Dekker, New York, 1969.

(2) Greyson, J., Snell, H., *J. Phys. Chem.*, **73**, 3208 (1969).

(3) Greyson, J., Snell, H., *ibid.*, p 4423.

(4) Krishnan, C. V., Friedman, H. L., *ibid.*, **74**, 2356 (1970).

(5) Snell, H., Greyson, J., *ibid.*, **74**, 2148 (1970).

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Solubility of Lithium Carbonate at Elevated Temperatures

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The aqueous solubility of lithium carbonate (Li_2CO_3) has been measured between 100° and 300° C. Platinum-lined nickel tubing ¼ in. in diameter was weld-sealed at the ends, thus enclosing about 1 ml liquid plus excess salt. This was equilibrated at temperature, and the supernatant liquid was isolated from the excess salt by pinching the tube at the middle. When the tube was cool, the upper part was separated, and its contents were analyzed. The data correlated well with literature values. All available data were combined and an equation was generated for calculating solubility at temperatures between 0° and 300° C.

There is a probability that lithium hydroxide (LiOH) will be used as an additive in steam generators. When this substitution is made for the presently used sodium hydroxide (NaOH), it will be necessary to discontinue the concurrent addition of phosphate for precipitation of the hard water contaminants, calcium and magnesium. Whereas these phosphates settle as a mobile mud that is easily blown out, lithium phosphate (Li_3PO_4) deposits as a hard, adherent, insoluble layer on heat exchange surfaces to cause overheating and rapid deterioration in an operating boiler. A substitute additive presently considered for use with LiOH is a chelating agent such as ethylenediaminetetraacetic acid (EDTA) which would assume the tetralithium salt form at boiler alkalinity levels (pH 10–11), and would be expected to chelate calcium and magnesium ions to prevent their deposition.

There is one negative factor in this use of EDTA; a slow thermal decomposition occurs at boiler temperature (*ca.* 300° C) which could generate carbon dioxide (CO_2). Since this would react with LiOH to form the slightly soluble lithium carbonate (Li_2CO_3), it is important to know the carbonate solubility up to 300° C.

A search of the literature revealed a number of measurements over the period from 1856 to 1961 (*1-4, 6, 7, 9, 10*), most of which were at atmospheric pressure and at temperatures up to 100° C. Elenevskaya and Ravich (*3*), however, made determinations almost to the critical point of water. Since their method involved filtration and a possible thermal disturbance by water vaporization while the sample was being withdrawn, it was decided to redetermine values up to 300° C.

EXPERIMENTAL

Lithium carbonate solubility determinations at several temperatures between 100° and 302° C were made by placing an excess of solid Li_2CO_3 in a 1-ml, water-filled container formed from a 9-cm length of quarter-inch platinum-lined nickel tubing. This tubing had been deformed into an oval-shaped cross section with an area slightly less than one-half the original to allow for liquid expansion. Air space above the sample was kept to a minimum by freezing the liquid and arc welding the pinched tube end. The tube was clamped upright at or near its lengthwise center in an isothermal zone of a furnace by a screw-operated pinching device, and the furnace heat cycle was started. For temperature readings, two calibrated Pt-Pt + 10% Rh thermocouples were used; one was firmly taped to the upper end of the sample tube, and the other near the pinch zone. The outputs were read with a precision potentiometer with an overall accuracy of ±0.5° C. The isothermicity of the tube was ±0.4° C.

After a tube had equilibrated for from 30–115 hr in the furnace, the pinching device was screwed tightly shut so as to squeeze the sides of the tube together and isolate, at temperature, the supernatant liquid in the upper half from the excess undissolved solids in the bottom. The furnace was then allowed to cool, the tube removed, and the upper and lower sections were separated with a pinch-off tool. The upper portion was then weighed, opened, and its contents were rinsed into a flask for titration. The empty tube was dried and tared.

The amount of carbonate dissolved was obtained by titration of the sample with 0.1*N* hydrochloric acid (HCl) using a 1-ml semimicro buret. Use of a double–end point technique

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