Thermochemistry of Potassium Peroxydisulfate and of Peroxydisulfate Aqueous Ion

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THERMOCHEMICAL DATA tabulated in (*2*) for $K_2S_2O_8(c)$ and $S_2O_8^{-2}(aq)$ are based upon old experiments (1892) of uncertain reliability. The authors have therefore measured the heat of solution and the solubility of $K_2S_2O_8(c)$ and used these data with other recently obtained data that they considered reliable for thermochemical calculations.

EXPERIMENTAL

The solution calorimeter used in this investigation has been described in detail (*6, 7*). The calorimetric apparatus consists of a Dewar vessel in a metal can submerged in a water bath. Temperatures are followed with a Maier transposed bridge with thermistors in the temperature-sensing arms. The calorimeter vessel contains an electric heater for calibration. Each run was made with 950 ml. of distilled water in the Dewar. All calorimetric measurements were carried out at 25.0° ± 0.2° C.

$K_2S_2O_8$ (Baker and Adamson, reagent grade) was purified by recrystallizing it three times from distilled water. Solutions of potassium peroxydisulfate were never heated above 60° C. during the recrystallization process. The crystalline $K_2S_2O_8$ so obtained was dried in a vacuum desiccator for 30 days.

The solubility of $K_2S_2O_8(c)$ in water was determined by a gravimetric method, which also yielded the density of the saturated solution. Aliquots were taken with a calibrated pipet from saturated solutions maintained at constant temperature. The aliquot solutions were weighed, treated with excess $BaCl_2$, and boiled to precipitate $BaSO_4$ which was collected and weighed.

RESULTS

Results of present determinations of the heat of solution of $K_2S_2O_8(c)$ in water are given in Table I. The calorimetric reaction is

$$K_2S_2O_8(c) = 2K^+(aq) + S_2O_8^{-2}(aq) \cdot \Delta H_1 \qquad (1)$$

Heats of dilution have been estimated with the aid of data (*2*) for $K_2SO_4(aq)$ and combined with values for ΔH_1 (Table I) to obtain $\Delta H_1^0 = 16.14 \pm 0.12$ kcal. per mole where ± 0.12 is our estimate of the total uncertainty. The data in (*2*) for $K_2S_2O_8$ lead to $\Delta H_1^0 = 15.0$ kcal. per mole.

Table I. Heats of Solution of $K_2S_2O_8(c)$

Grams $K_2S_2O_8$/950 Ml. H_2O	ΔH_1, Kcal./Mole
1.0233	16.24
1.2756	16.36
1.5077	16.26
2.0311	16.28
2.4921	16.28

Table II. Solubility of $K_2S_2O_8(c)$ in Water

° C. (±0.05°)	Molality, Satd. Soln. (±0.001)	Density, Satd. Soln.
20.00	0.165	1.0264
25.00	0.2213	1.0327
30.00	0.2658	1.0402

Results of our solubility and density experiments are given in Table II.

Seidell (*4*) gives data from which molarities of saturated solutions may be calculated that are in good agreement with molarities calculated from the authors data.

THERMOCHEMICAL CALCULATIONS

Our heat of solution ΔH_1^0 is used with the standard heat of formation of $K^+(aq)$ (*2*) and the standard heat of formation of $K_2S_2O_8(c)$ recently determined by Stull (*5*). The heat of formation of $K_2S_2O_8(c)$ found by Stull is −456.78 ± 0.50 kcal. per mole and is to be preferred to the older value (*2*). We calculated −320.56 kcal. per mole for the standard enthalpy of formation of $S_2O_8^{-2}(aq)$.

The standard free energy of solution of $K_2S_2O_8(c)$ is calculated from $\Delta F_1^0 = -RT \ln 4m^3\gamma_\pm^3$ where m represents the molality of saturated solution and $\gamma_\pm$ represents the mean activity coefficient of $K_2S_2O_8$ in saturated solution. The authors estimated $\gamma_\pm = 0.35$ at 25° C. from the known activity coefficient of $K_2SO_4(aq)$ at the same molality as the saturated $K_2S_2O_8$ solution (*3*). The authors obtained $\Delta F_1^0 = +3.73 \pm 0.24$ kcal. per mole at 298.15° K., where the ± 0.24 includes uncertainty derived from the estimated activity coefficient.

Use of ΔF_1^0 and ΔH_1^0 in the relation $\Delta F^0 = \Delta H^0 - T\Delta S^0$ permits calculation of ΔS_1^0, which is found to be 41.6 cal. per degree mole. This entropy of solution is used with the standard partial molal entropy of $K^+(aq)$ (*2*) and the Third Law entropy of $K_2S_2O_8(c)$ as determined by Stull (*5*) (66.90 ± 0.10 cal. per degree mole) in calculating that the standard partial molal entropy of $S_2O_8^{-2}(aq)$ is 59.5 cal. per degree mole.

From data given above and in (*2*) we calculated the standard free energies of formation of $K_2S_2O_8(c)$ and $S_2O_8^{-2}(aq)$ to be −404.68 and −266.01 kcal. per mole, respectively. We also calculated $E^0 = -1.92$ volts for

$$2SO_4^{-2}(aq) = S_2O_8^{-2}(aq) + 2e^- \qquad E^0 = -1.92 \text{ volts}$$

DISCUSSION

The standard partial molal entropy of $S_2O_8^{-2}(aq)$ reported here, 59.5 cal. per degree mole, is very close to that reported earlier for $Cr_2O_7^{-2}(aq)$, 57.2 cal. per degree mole (*1*).

If it is assumed that the principal contribution to these entropies comes from solute-solvent interaction this is what we should expect for two ions such as $S_2O_8^{-2}(aq)$ and $Cr_2O_7^{-2}(aq)$ which have the same net charge and roughly the

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same charge distribution. We can therefore estimate that the entropy of $S_2O_7^{-2}$(aq) is about 58 cal. per degree mole.

Entropies of $Cr_2O_7^{-2}$(aq) and $S_2O_8^{-2}$(aq) are considerably greater than entropies of the more compact species SO_4^{-2}(aq) and CrO_4^{-2}(aq), which are more effective in orienting solvent dipoles because of their more concentrated charges.

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An Experimental Determination of the Thermal Conductivity of Several Greases

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MOST OF THE previous research efforts devoted to the determination of the properties and characteristics of greases have been concerned with lubricity, stability, and other properties directly connected with the use of greases as lubricants. Some work involved the microstructure of greases—the manner in which soap fibers are intermingled with oil. Vold (7) has examined the properties of soap itself, particularly thermal properties, such as thermal transitions (5).

An examination of the literature showed, however, that few results have been reported for thermal conductivity of greases. The purpose of this work was to measure the thermal conductivity of greases made from several different oils and soaps or solids as a function of temperature and soap content, and to relate the thermal conductivity of the grease to the thermal conductivities of the pure constituents.

EXPERIMENTAL APPARATUS AND PROCEDURE

Description of Apparatus. The apparatus was a guarded, steady-state, concentric cylinder cell with an annular space to contain the test sample. The cell included a central cylindrical bar broken lengthwise into three independent heater sections: a middle heater, and two guard heaters, one on either side of the middle heater. Each guard heater was separated from the middle heater by a Teflon (DuPont trademark) plug. The dimensions of the cell are shown in Figure 1.

This central bar was surrounded by an aluminum tube 11.26 inches long and 1.6500 inches in I.D. × 1.868 inches in O.D. leaving an annular space of 1.4975 inches in diameter and 1.650 inches in diameter for the sample. The outer aluminum tube and the central bar were concentrically aligned by means of Teflon spacers located at each end of the cell.

The middle heater and the two guard heaters were each constructed by tightly winding a glass-insulated, 24-gage constant wire into a spiral groove on the outside of a

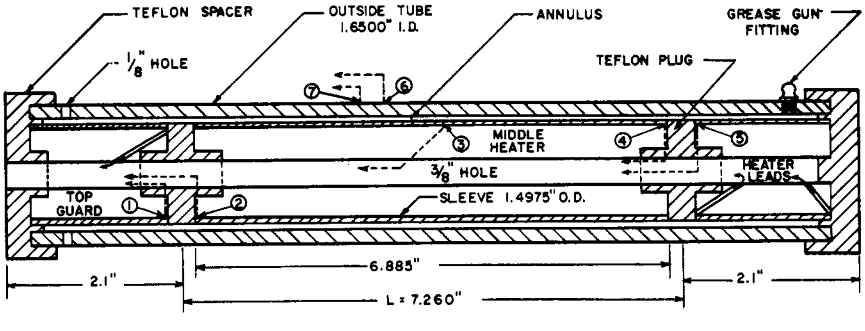

Figure 1. Drawing of conductivity cell

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