however, to consider these as rather high values of Γ for a compound having such a high water capacity as MEHSO does, suggesting that some homologs might show better combinations of salt rejection and water capacity.

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NOMENCLATURE

a_1 = activity coefficient of water (mole fraction scale, reference state pure water)
A = anion of quaternary ammonium salt
$D(s)$ = distribution coefficients $[s]_{org}/[s]_{aq}$ of the substance s
m_s = moles of the substance s per kilogram of water
Q^+ = quaternary ammonium cation
X_1 = mole fraction of water
$\gamma_\pm$ = mean activity coefficient of an inorganic salt (molality scale, reference state infinite dilution
Γ = activity coefficient ratio $\gamma_\pm^*/\gamma_\pm$
$*$ = refers to components in the organic-rich phase

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Heat of Formation of Sulfamic Acid

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The reaction of sulfamic acid with sodium nitrite has been investigated in both acidic and alkaline solutions. The reaction to yield nitrogen proceeds to a negligible extent in alkaline solution but is quantitative in acidic solution. Calorimetric measurements with acid solutions lead to values of ΔH_f° = −164.0₂ and −163.8₅ kcal. per mole for crystalline sulfamic acid.

MEASUREMENTS of the heat of reaction of sulfamic acid with sodium nitrite in alkaline solution have been reported (*6*), and the heat of formation has been calculated from the observed ΔH. Chernick (*1*) had previously measured the heat of reaction of sulfamic acid with sodium nitrite in acidic solution, but his results and derived heat of formation of sulfamic acid have not been published. Because there is a large discrepancy between the results of these earlier workers, new investigations of the reaction chemistry and thermochemistry of sulfamic acid have been carried out and form the basis for this report.

Experiments in both of the authors' laboratories confirm that the reaction between sulfamic acid and sodium nitrite does not proceed satisfactorily in the alkaline solutions used by Wu and Hepler (*6*) but does proceed quantitatively in various acidic solutions.

Chernick's measurements (*1*) in Manchester (0.1*N* sulfuric acid as solvent) led to ΔH = −95.8 kcal. per mole for the reaction that could be represented by

$$H_2NSO_3H(soln) + NaNO_2(c) = NaHSO_4(soln) + N_2(g) + H_2O(liq)$$

Preliminary measurements in Pittsburgh with conditions nearly the same as those used by Chernick led to ΔH = −95.3 kcal. per mole for this reaction. The reaction proceeds equally readily in pure water as solvent, and the subsequent measurements reported here were made using purely aqueous sulfamic acid solutions.

EXPERIMENTAL

For the work done at the University of Manchester, B.D.H. microanalytical standard reagent sulfamic acid was used without further treatment. Sodium nitrite was B.D.H. AnalaR quality, and was recrystallized, dried, and stored in a desiccator prior to use. Volumetric analysis of the sample against permanganate indicated purity >99.9%. The reaction calorimeter, of the constant temperature environment type, has been described previously (*2*). The calorimeter was charged with a dilute solution of sulfamic acid (1081 grams of water and 6 mmoles of sulfamic acid), and the glass ampoule contained 3 mmoles of crystalline sodium nitrite. All heat measurements (*1*) are referred to 25° C.

For the work done at Carnegie-Mellon University, the sulfamic acid and the sodium nitrite were both Fisher Certified reagents and were purified as previously described (*6*). The calorimeter used for these measurements was patterned after one previously described (*3*). The calorimeter consisted of a Dewar vessel suspended in a brass can that was submerged in a water bath maintained at constant temperature. Temperatures were determined with a nickel resistance thermometer connected to a Leeds and Northrup Mueller G-2 Bridge and a Beckman Model 14 Breaker Amplifier. The resistance thermometer and manganin calibration heater were both contained in a glass spiral filled with mineral oil. For each measurement, a sample of crystalline sodium nitrite was introduced to a solution containing a two to fivefold excess of sulfamic acid. All measurements are referred to 25° C.

The calorimetric reaction investigated in Manchester can be represented precisely by the equation:

$$NaNO_2(c) + 2(NH_2SO_3H \cdot 10000\ H_2O) = N_2(g) + NaHSO_4 \cdot NH_2SO_3H \cdot 20001\ H_2O \qquad (1)$$

Results of five measurements lead to ΔH_1 = −96.94 kcal. per mole (average deviation from mean ±0.09). The mean

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value from four measurements in Pittsburgh (slightly different concentrations) is $\Delta H_1 = -97.11$ (± 0.13) kcal. per mole.

Auxiliary data that have been combined with the above values of ΔH_1 are as follows: H_2O(liq), $\Delta H_f^\circ = -68.32$ kcal. per mole (*5*). For the heat of solution of sulfamic acid, $\Delta H = 4.54$ kcal. per mole (*6*). For $NaHSO_4$(c), $\Delta H_f^\circ =$ -269.8 kcal. per mole. This value is derived from that given by Rossini *et al.* (*4*) following recent revision (*5*) of ΔH_f° ($H_2SO_4 \cdot 200\ H_2O$). Independent measurements in Manchester lead to $\Delta H = -4.0 \pm 0.3$ kcal. per mole for the heat of solution of $NaHSO_4$(c) in a solution of $NH_2SO_3H \cdot 20000\ H_2O$. The salt dissolved slowly and more precise measurements were not possible with the calorimeter available. For $NaNO_2$(c), the authors calculate $\Delta H_f^\circ = -85.7$ kcal. per mole from its heat of solution (*6*) and ΔH_f° values (*5*) for Na^+ (aq) and NO_2^- (aq).

The measured ΔH_1 values are combined with the above auxiliary data to obtain $\Delta H_f^\circ = -164.0_2$ (Manchester) and -163.8_5 (Pittsburgh) kcal. per mole for crystalline sulfamic acid. The average $\Delta H_f^\circ = -163.9$ kcal. per mole for NH_2SO_3H(c) is, the authors believe, the best value presently available.

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Density, Surface Tension, and Viscosity of NaF–NaCl–NaI Eutectic

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Measurements of the density, surface tension, and viscosity of the 6.1 wt. % NaF–17.7 wt. % NaCl–76.2 wt. % NaI salt eutectic mixture, as a function of temperature, were undertaken in connection with the use of this salt as an electrolyte in engineering studies of lead-sodium and bismuth-sodium galvanic cells at Argonne National Laboratory. The salt mixtures used were prepared from reagent grade materials. No information on these physical properties for the NaF–NaCl–NaI eutectic mixture were noted in the literature.

THE eutectic mixture of NaF–NaCl–NaI was contained in a stainless steel crucible for making measurements of the density, surface tension, and viscosity as functions of temperature. The crucible was placed in a well of stainless steel pipe, which was attached to the bottom of a helium atmosphere glovebox; the well was heated by an electric resistance furnace. The temperature of the eutectic mixture, which melts at about 535° C., was measured by a Chromel-Alumel thermocouple.

The density measurements consisted of measuring the depth of a known weight of the salt in a crucible of calibrated cross sectional area and volume. The depth of the liquid was measured by means of a pointed stainless steel rod attached to a micrometer depth gage measuring apparatus. The rod was 1/16 inch in diameter. To make a measurement, the rod was lowered to the bottom of the crucible; after the rod had reached temperature equilibrium, the micrometer was set to zero. The rod was then raised to just above the liquid; after reaching temperature equilibrium, it was lowered until the point just touched the surface of the liquid. Contact with the melt was determined by an electrical resistance meter (ohmmeter). The micrometer was read giving the liquid salt depth. Repeated measurements were made to check the readings.

Corrections were made for the thermal expansion of the crucible, which had been calibrated at room temperature, and for the thermal expansion of the measuring rod. At the end of a series of runs, the crucible and salt were weighed to check with the weight of the salt placed in the crucible initially.

The surface tension was determined by measuring the force required to detach a calibrated surface tension ring from the surface of the molten salt. The force was measured by a balance, from which the ring was suspended. The balance, which could be raised or lowered, was located in the glovebox above the well. The surface tension ring was 3.000-cm. O.D. by 2.901-cm. I.D. The use of such a ring is described in the literature (*2, 3*).

The ring was calibrated by using it to measure the surface tensions of methanol, 2-propyl alcohol, benzene, chloroform, and water at room temperature and of sodium iodide at elevated temperature. Corrections were made for thermal

Table I. Density Measurements of 6.1 Wt. % NaF–17.7 Wt. % NaCl–76.2 Wt. % NaI Eutectic

Temperature, ° C.	Density, Grams/Cc.
541	2.56
550	2.52
551	2.57
552	2.57
554	2.57
566	2.57
575	2.50
580	2.53
599	2.51
600	2.55
601	2.49
625	2.48
631	2.47
651	2.47
674	2.45
700	2.41
751	2.38
800	2.33