μ_R = reduced viscosity μ/μ_c
ρ = density, g./cc.
ρ_c = density at the critical point, g./cc.
ρ_R = reduced density, ρ/ρ_c
ρ_{R_s} = reduced density at saturated conditions
σ = collision diameter for Lennard-Jones potential, A.
χ = factor for probability of collisions
$\Omega^{(2,2)*}[T_{N_1}\sigma_{\max}]$ = collision integral function for polar molecules

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Thermochemistry of Sulfamic Acid and Aqueous Sulfamate Ion

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THERMOCHEMICAL investigations of sulfamic acid have yielded the following heats of solution and reaction:

$$HSO_3NH_2(c) = H^+(aq) + SO_3NH_2^-(aq) \qquad \Delta H_1$$

$$NaNO_2(c) = Na^+(aq) + NO_2^-(aq) \qquad \Delta H_2$$

$$NaNO_2(c) + SO_3NH_2^-(aq) = SO_4^{-2}(aq) + Na^+(aq) + N_2(g) + H_2O \qquad \Delta H_3$$

$$NO_2^-(aq) + SO_3NH_2^-(aq) = SO_4^{-2}(aq) + N_2(g) + H_2O \qquad \Delta H_4$$

EXPERIMENTAL

The high precision solution calorimeter employed has been described in detail elsewhere (*4*). Temperature changes were followed by means of a Maier transposed bridge circuit with thermistors in two opposite arms. An electric heater made of manganin wire was used for calibration. All heats of solution and reaction were determined at 25.0° ± 0.2° C. in 950 ml. of solution.

Sulfamic acid was purified according to the method described by Sisler, Butler, and Audrieth (*1*). The crystals were dried in a vacuum desiccator, broken up with a glass rod, then dried in an oven at 40° C. for 4 hours, and again placed in a desiccator. Heats of solution of samples from several preparations were identical within the limits of our calorimetric accuracy.

Sodium nitrite was recrystallized from water and then dried in a desiccator for two months.

The extent of reaction of sulfamate ions with nitrite ions in alkaline solution has been determined by measuring in a gas buret the volume of nitrogen evolved. The reaction of sulfamic acid with nitrous acid in slightly acidic solution is known to be quantitative, but it was necessary to check the completeness of this reaction in base because the calorimetric reaction was carried out in basic solution to prevent disproportionation of HNO_2. We found, by collecting and measuring the evolved N_2, that the reaction in base is 97 ± 4% complete. This result is adequate for our needs because the heat of reaction of NO_2^-(aq) with $SO_3NH_2^-$(aq) is small (about 100 cal./mole).

RESULTS

The values found for the heats of solution of HSO_3NH_2(c) and $NaNO_2$(c) are given in Table I. The heats of reaction of $NaNO_2$(c) with $SO_3NH_2^-$(aq) and calculated heats of reaction of NO_2^-(aq) with $SO_3NH_2^-$(aq), designated as ΔH_4, are given in Table II.

The ionization constant for sulfamic acid has been reported (*2*, *6*) to be $K = 0.1$. The lack of normal dependence of ΔH_1 on concentration gives supporting evidence of behavior of aqueous sulfamic acid as an "almost strong" electrolyte.

The standard heat of solution of HSO_3NH_2(c) is taken to be $\Delta H_1^0 = 4.54 \pm 0.05$ kcal./mole from the data in Table I and estimated heats of dilution. The ± 0.05 is the estimated total uncertainty, which includes possible sample impurities, calorimetric uncertainties, and, especially, the heat of dilution estimate.

Table I. Heats of Solution

Sulfamic Acid		Sodium Nitrite	
Moles in 950 ml. H_2O	ΔH_1, kcal./mole	Moles in 950 ml. NaOH	ΔH_2, kcal./mole
0.03060	4.55	0.0415	3.26
0.02742	4.50	0.0364	3.31
0.02343	4.58	0.0294	3.38
0.02182	4.56	0.0217	3.38
0.01944	4.55	0.0201	3.25
0.01810	4.50	0.0144	3.31
0.01604	4.56	0.0114	3.28
0.01345	4.56	0.0071	3.36
0.00991	4.57		

Heats of solution of $NaNO_2$(c) were determined in a slightly basic solution of sodium hydroxide. Because experimental heats of dilution of dilute aqueous $NaNO_2$ are unknown, we assume that they are nearly the same as heats of dilution of $NaNO_3$(aq) taken from NBS Circular 500 (*3*). The standard heat of solution thus calculated is $\Delta H_2^0 = 3.32 \pm 0.06$ kcal./mole. This value is in agreement with the value calculated from NBS (*3*) heats of formation. The older data on which the NBS values are based are for relatively concentrated solutions and are considerably less precise than the value reported here.

All heats of reaction of $SO_3NH_2^-$(aq) with $NaNO_2$(c) in NaOH solution have been measured in excess $SO_3NH_2^-$(aq) except one in which excess $NaNO_2$(c) was used.

Heats of reaction of $SO_3NH_2^-$(aq) with NO_2^-(aq) have been calculated from ΔH_2^0 and data in Table II. We take $\Delta H_4^0 = 0.11 \pm 0.05$ kcal./mole. Most of the indicated uncertainty arises from the unknown heats of dilution in solutions containing NO_2^-, $SO_3NH_2^-$, SO_4^{-2}, Na^+, and OH^- ions, even though all solutions were dilute.

Heats of formation of $SO_3NH_2^-$(aq) and HSO_3NH_2(c) have been calculated to be −259.93 and −264.47 kcal./mole, respectively. The values of the standard heats of formation of NO_2^-(aq), SO_4^{-2}(aq), and H_2O at 25° C. used in these calculations are taken from NBS Circular 500 (*3*). Most uncertainties in these calculations come from the uncertainty in the heat of formation of NO_2^-(aq). We believe this uncertainty is about 1, or 2 kcal./mole.

Table II. Heats of Reaction of $SO_3NH_2^-$ (aq) with NO_2^- (aq)

Moles			Kcal./Mole	
$NaNO_2$(c)	$SO_3NH_2^-$ in 950 ml. NaOH	Molarity of NaOH Sol.	ΔH_3	ΔH_4
0.03507	0.02565	0.0527	4.66[a]	0.12
0.03098	0.03807	0.1054	3.45	0.13
0.02523	0.03335	0.0527	3.44	0.12
0.02220	0.02930	0.1054	3.45	0.13
0.02037	0.09976	0.1581	3.40	0.09

[a] This heat should be different from all others because it involves excess $NaNO_2$(c) rather than aqueous sulfamate ion. It was necessary to correct for $NaNO_2$ heat of solution to obtain ΔH_4 from this value of ΔH_3 and to take number of moles or reaction based on SO_3NH_2 rather than on NO_2^-.

Ray (*5*) has recently used high temperature equilibrium and heat capacity data to calculate −88.60 ± 0.56 kcal./mole for the standard heat of formation of $NaNO_2$(c), as compared to the NBS (*3*) value of 85.9 kcal./mole. Combination of our heat of solution with Ray's heat of formation leads to −26.00 kcal./mole for the heat of formation of NO_2^-(aq), as compared to the NBS (*3*) value of −25.4 kcal./mole. Combination of this heat of formation with our ΔH_4^0 leads to −263.87 kcal./mole for the standard heat of formation of HSO_3NH_2(c) and −259.33 kcal./mole for that of $SO_3NH_2^-$(aq).

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