

$\mu_R$  = reduced viscosity  $\mu/\mu_c$   
 $\rho$  = density, g./cc.  
 $\rho_c$  = density at the critical point, g./cc.  
 $\rho_R$  = reduced density,  $\rho/\rho_c$   
 $\rho_{R_s}$  = reduced density at saturated conditions  
 $\sigma$  = collision diameter for Lennard-Jones potential, A.  
 $\chi$  = factor for probability of collisions  
 $\Omega^{2,2} * [T_{N_1\sigma_{max}}]$  = collision integral function for polar molecules

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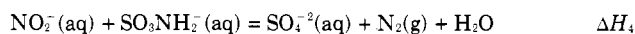
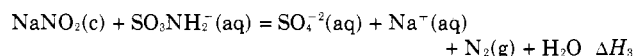
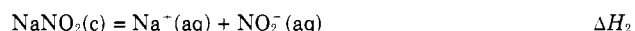
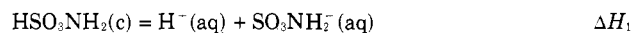
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## Thermochemistry of Sulfamic Acid and Aqueous Sulfamate Ion

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**T**HERMOCHEMICAL investigations of sulfamic acid have yielded the following heats of solution and reaction:



#### 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  $25.0^\circ \pm 0.2^\circ \text{C}$ . 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  $40^\circ \text{C}$ . 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  $\text{HNO}_2$ . We found, by collecting and measuring the evolved  $\text{N}_2$ , that the reaction

in base is  $97 \pm 4\%$  complete. This result is adequate for our needs because the heat of reaction of  $\text{NO}_2^-$  (aq) with  $\text{SO}_3\text{NH}_2^-$  (aq) is small (about 100 cal./mole).

## RESULTS

The values found for the heats of solution of  $\text{HSO}_3\text{NH}_2$ (c) and  $\text{NaNO}_2$ (c) are given in Table I. The heats of reaction of  $\text{NaNO}_2$ (c) with  $\text{SO}_3\text{NH}_2^-$ (aq) and calculated heats of reaction of  $\text{NO}_2^-$ (aq) with  $\text{SO}_3\text{NH}_2^-$ (aq), designated as  $\Delta H_4$ , 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  $\Delta H_1$  on concentration gives supporting evidence of behavior of aqueous sulfamic acid as an "almost strong" electrolyte.

The standard heat of solution of  $\text{HSO}_3\text{NH}_2$ (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  $\pm 0.05$  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 <sub>2</sub> O	$\Delta H_1$ , kcal./mole	Moles in 950 ml. NaOH	$\Delta H_2$ , 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  $\text{NaNO}_2$ (c) were determined in a slightly basic solution of sodium hydroxide. Because experimental heats of dilution of dilute aqueous  $\text{NaNO}_2$  are unknown, we assume that they are nearly the same as heats of dilution of  $\text{NaNO}_3$ (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  $\text{SO}_3\text{NH}_2^-$ (aq) with  $\text{NaNO}_2$ (c) in NaOH solution have been measured in excess  $\text{SO}_3\text{NH}_2^-$ (aq) except one in which excess  $\text{NaNO}_2$ (c) was used.

Heats of reaction of  $\text{SO}_3\text{NH}_2^-$ (aq) with  $\text{NO}_2^-$ (aq) have been calculated from  $\Delta H_2^0$  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  $\text{NO}_2^-$ ,  $\text{SO}_3\text{NH}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ , and  $\text{OH}^-$  ions, even though all solutions were dilute.

Heats of formation of  $\text{SO}_3\text{NH}_2^-$ (aq) and  $\text{HSO}_3\text{NH}_2$ (c) have been calculated to be  $-259.93$  and  $-264.47$  kcal./mole, respectively. The values of the standard heats of formation of  $\text{NO}_2^-$ (aq),  $\text{SO}_4^{2-}$ (aq), and  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ . 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  $\text{NO}_2^-$ (aq). We believe this uncertainty is about 1, or 2 kcal./mole.

Table II. Heats of Reaction of  $\text{SO}_3\text{NH}_2^-$  (aq) with  $\text{NO}_2^-$  (aq)

NaNO <sub>2</sub> (c)	Moles		Kcal./Mole	
	SO <sub>3</sub> NH <sub>2</sub> <sup>-</sup> in 950 ml. NaOH	Molarity of NaOH Sol.	$\Delta H_3$	$\Delta H_4$
0.03507	0.02565	0.0527	4.66 <sup>a</sup>	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

<sup>a</sup> This heat should be different from all others because it involves excess  $\text{NaNO}_2$ (c) rather than aqueous sulfamate ion. It was necessary to correct for  $\text{NaNO}_2$  heat of solution to obtain  $\Delta H_4$  from this value of  $\Delta H_3$  and to take number of moles or reaction based on  $\text{SO}_3\text{NH}_2^-$  rather than on  $\text{NO}_2^-$ .

Ray (5) has recently used high temperature equilibrium and heat capacity data to calculate  $-88.60 \pm 0.56$  kcal./mole for the standard heat of formation of  $\text{NaNO}_2$ (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  $\text{NO}_2^-$ (aq), as compared to the NBS (3) value of  $-25.4$  kcal./mole. Combination of this heat of formation with our  $\Delta H_4^0$  leads to  $-263.87$  kcal./mole for the standard heat of formation of  $\text{HSO}_3\text{NH}_2$ (c) and  $-259.33$  kcal./mole for that of  $\text{SO}_3\text{NH}_2^-$ (aq).

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