Thermodynamics of Transfer of HCl from Water to Aqueous Alcohols at 25° C

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Calorimetric enthalpies of transfer of hydrochloric acid at ca. 0.002*m* from pure water to aqueous 2-propanol, 1-propanol, and propylene glycol were determined at 25° C. The enthalpies together with those previously studied in the methanol and ethanol systems were combined with free energies obtained from electromotive force measurements to yield $T\,\overline{\Delta S}_2$, where $\overline{\Delta S}_2$ is the entropy of transfer. The effect of the alcohol on aqueous solution structure is discussed briefly by examining the variation of the isentropic composition of transfer with alkyl chain length.

Addition of small quantities of nonelectrolytes such as low-molecular-weight alcohols to pure water frequently leads to profound changes in solvent properties (*4*). Thermodynamic studies of electrolyte transfer from pure water to a series of water–alcohol mixed solvents provide data which contribute to a better understanding of such important systems. Robinson and Stokes (*6*) have tabulated electromotive force values for cells of the type $H_2/HCl/AgCl/Ag$ from which equimolal free energies of transfer $\overline{\Delta F}_2$ in kcal/mol may be calculated for the process HCl (in H_2O) = HCl (in ms):

$$\overline{\Delta F}_2 = 23.06\,(E^0_{\mathrm{w}} - E^0_{\mathrm{ms}}) \qquad (1)$$

where E^0_{w} and E^0_{ms} are the standard cell potentials on the molal scale in the water and in the mixed solvent, respectively. Electromotive force results summarized by Bates (*1*) for aqueous methanol and ethanol are in good agreement with those reported by Robinson and Stokes. It may be noted that equimolal $\overline{\Delta F}_2$ have been reported to increase linearly, or nearly so, with X_3, the nonelectrolyte mole fraction, for such diverse systems as HCl in water–acetic acid (*9*), HCl in water–ethylene glycol (*10*), and NaCl in water–urea (*8*) over wide mixed solvent composition ranges.

There have been few calorimetric studies of enthalpies of transfer $\overline{\Delta H}_2$ of electrolytes to aqueous alcohols. These include $\overline{\Delta H}_2$ of HCl to methanol and ethanol by Hepler and his co-workers (*2*), HCl (*10*), and $HClO_4$ (*11*) to ethylene glycol in this laboratory. All curves of $\overline{\Delta H}_2$ vs. X_3 over the mixed solvent range from $X_3 = 0$ to 1 are sigmoidal,

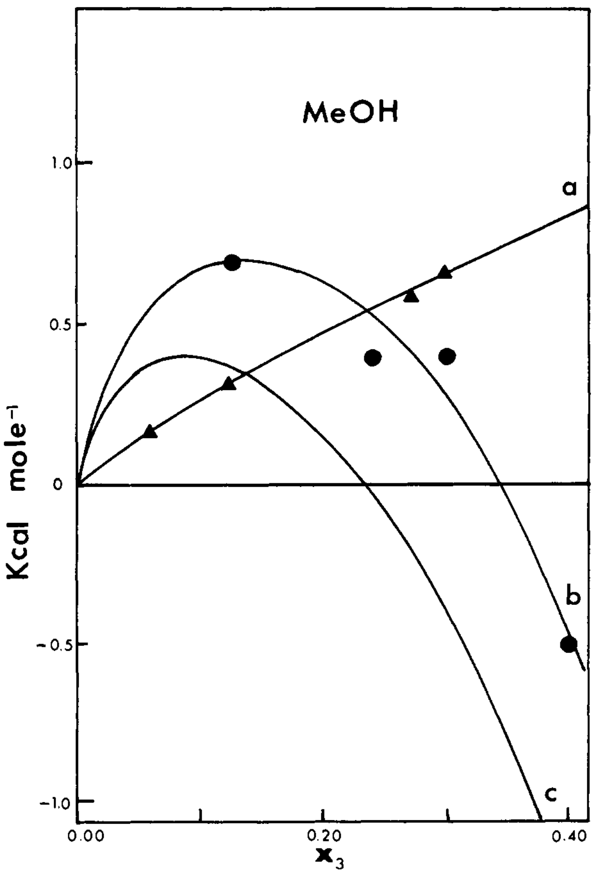

Figure 1. (*a*) $\overline{\Delta F}_2$, (*b*) $\overline{\Delta H}_2$, and (*c*) $T\overline{\Delta S}_2$ for methanol

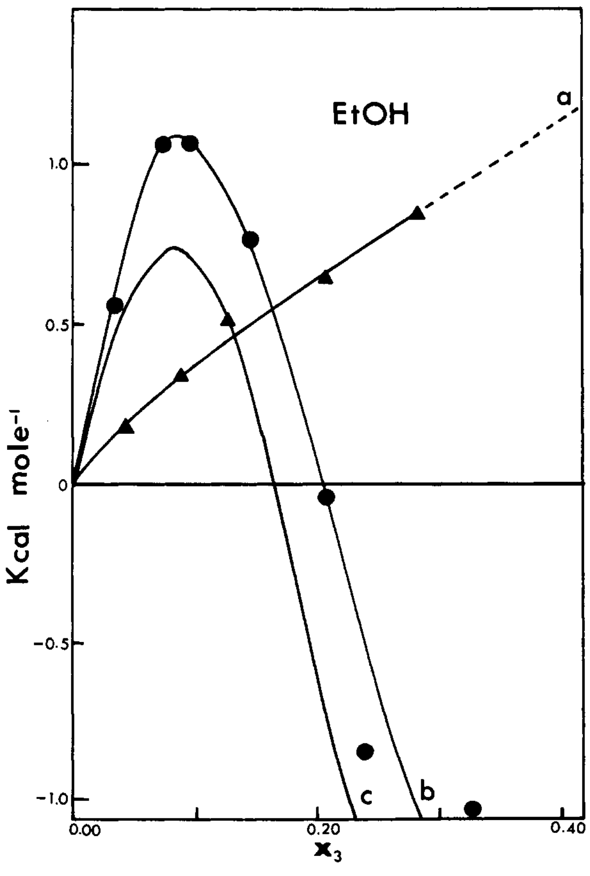

Figure 2. (*a*) $\overline{\Delta F}_2$, (*b*) $\overline{\Delta H}_2$, and (*c*) $T\overline{\Delta S}_2$ for ethanol

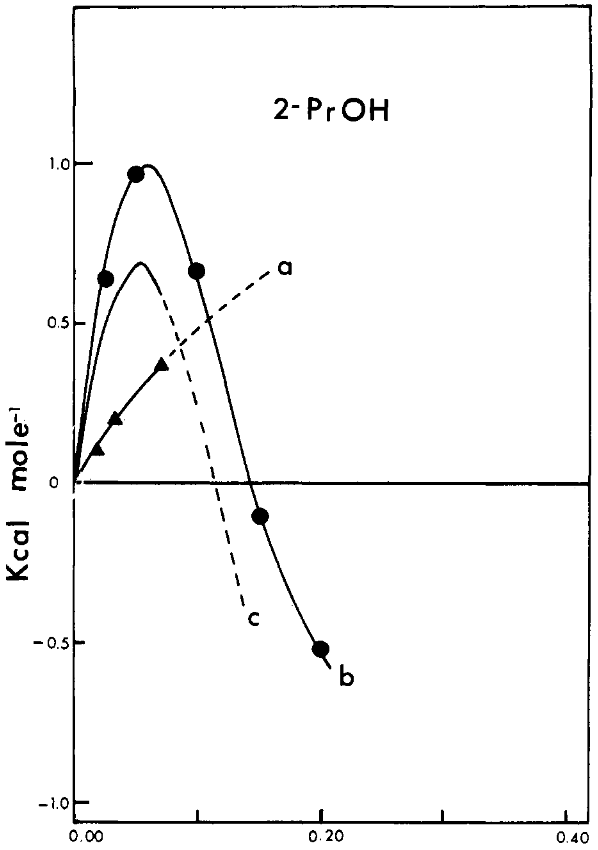

Figure 3. (a) $\overline{\Delta F_2}$, (b) $\overline{\Delta H_2}$, and (c) $T\overline{\Delta S_2}$ for 2-propanol

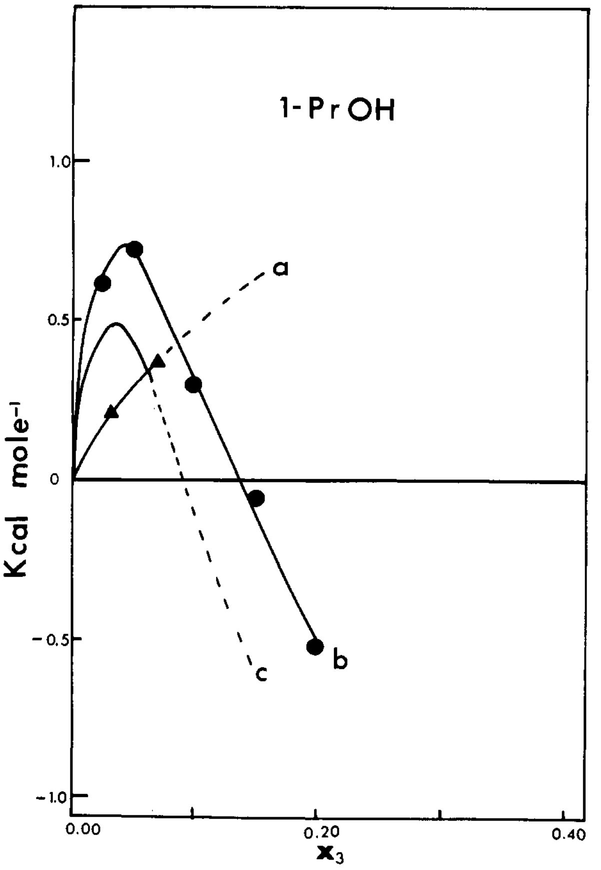

Figure 4. (a) $\overline{\Delta F_2}$, (b) $\overline{\Delta H_2}$, and (c) $T\overline{\Delta S_2}$ for 1-propanol

beginning with an endothermic peak in water-rich solutions. This contribution focuses on the water-rich region and reports the calorimetric $\overline{\Delta H_2}$ of transfer from water to 2-propanol, 1-propanol, and propylene glycol. The last was included to investigate the effect of introducing a polar hydroxide group into the nonpolar alkyl chain. Calculated or estimated graphical values of $T\overline{\Delta S_2}$ were obtained for all five alcohols including methanol and ethanol, by combination of $\overline{\Delta H_2}$ with $\overline{\Delta F_2}$. Values of $T\overline{\Delta S_2}$ are of importance since they reflect complicated solvent structure changes.

EXPERIMENTAL SECTION

Materials. The materials were from the following sources with these specifications: Hydrochloric acid, Mallinckrodt, analyzed reagent grade, assay 36–38%; 2-propanol, Mallinckrodt, analyzed reagent grade, bp range 82–83° C; 1-propanol, Mallinckrodt, analyzed reagent grade, bp range 95–98° C; propylene glycol, Matheson, Coleman, and Bell, research grade, bp range 186–187° C; water, distilled and deionized. The calorimetric HCl was prepared by dilution to 10.31*m*, determined by titration with standard NaOH. All mixed solvents were prepared by weighing immediately prior to use.

Calorimetric Measurements. The calorimeter vessel was a 660-ml Dewar flask with a polystyrene cover whose interior portion extended to a depth of 7.5 cm inside the flask. Passing through the cover were separate thermistor and heater probes, an off-center glass propeller stirrer, and a shaft for a glass rod to which an ampul with HCl was attached. Energy equivalents were displayed on a Leeds and Northrup Speedomax-G 1-mV recorder, utilizing the off-balance potential from a Wheatstone bridge amplified by a Leeds and Northrup microvolt amplifier. The bridge

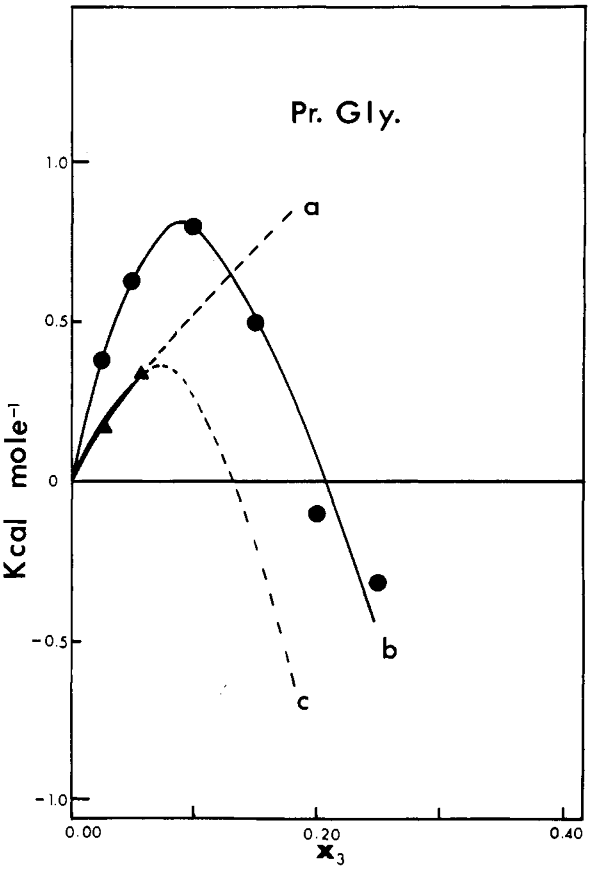

Figure 5. (a) $\overline{\Delta F_2}$, (b) $\overline{\Delta H_2}$, and (c) $T\overline{\Delta S_2}$ for propylene glycol

Table I. Enthalpies of Dilution of HCl

System	X_3	h_2	mm_2	mm_1	h'	mm'	9 ΔH_2	$\overline{\Delta H}_2$[a]
Pure water	0.00	−2.194	0.8539				−2.625	
		−2.419	0.9393				−2.575	
		−2.302	0.8869				−2.596	
		−2.384	0.9527				−2.502	
							$\Delta H^0_{2\,\mathrm{mean}}$ = −2.57 ± 0.03	
2-Propanol	0.025	−1.943	0.9640	5.190		[b]	−1.929	
		−1.831	0.9340	5.029			−1.874	
		−1.899	0.9145	4.924			−1.990	
							$\Delta H_{2\,\mathrm{mean}}$ = −1.93 ± 0.03	0.64 ± 0.04[c]
	0.05	−1.785	0.9258	4.985	−0.3057	6.128	−1.668	
		−1.740	0.9385	5.053	−0.2760	6.405	−1.596	
		−1.670	0.9437	5.081	−0.2988	6.250	−1.511	
		−1.732	0.9243	4.977	−0.3140	6.317	−1.615	
							$\Delta H_{2\,\mathrm{mean}}$ = −1.60 ± 0.03	0.97 ± 0.04
	0.10	−2.840	0.9872	5.315	−0.9757	6.300	−2.010	
		−2.559	0.9370	5.045	−1.099	6.333	−1.865	
		−2.678	0.9872	5.315	−0.9377	6.100	−1.856	
							$\Delta H_{2\,\mathrm{mean}}$ = −1.91 ± 0.05	0.66 ± 0.06
	0.15	−3.390	0.9475	5.102	−1.140	6.100	−2.609	
		−3.213	0.9213	4.960	−1.215	6.344	−2.518	
		−3.395	0.9475	5.102	−1.337	6.122	−2.614	
							$\Delta H_{2\,\mathrm{mean}}$ = −2.58 ± 0.03	−0.01 ± 0.04
	0.20	−3.908	0.9452	5.090	−1.276	6.328	−3.026	
		−3.897	0.9355	5.037	−1.303	6.222	−3.056	
		−4.039	0.9445	5.086	−1.255	5.972	−3.167	
							$\Delta H_{2\,\mathrm{mean}}$ = −3.09 ± 0.04	−0.51 ± 0.05
1-Propanol	0.025	−2.030	0.9288	5.001		[b]	−2.013	
		−1.988	0.9288	5.001			−1.968	
		−1.825	0.8898	4.791			−1.879	
							$\Delta H_{2\,\mathrm{mean}}$ = −1.95 ± 0.04	0.62 ± 0.05
	0.05	−2.256	1.007	5.420	−0.4208	5.817	−1.902	
		−1.782	0.9160	4.932	−0.3581	5.673	−1.606	
		−1.983	0.8404	4.525	−0.3380	6.144	−2.021	
							$\Delta H_{2\,\mathrm{mean}}$ = −1.8 ± 0.1	0.7 ± 0.1
	0.10	−3.017	1.035	5.574			−2.317	
		−2.657	0.9789	5.271			−2.117	
					−0.6915	5.934		
		−2.855	0.9108	4.904			−2.536	
		−2.637	0.9669	5.207	−0.6592	6.211	−2.129	
							$\Delta H_{2\,\mathrm{mean}}$ = −2.27 ± 0.09	0.30 ± 0.09
	0.15	−3.239	0.9774	5.263	−0.6669	5.279	−2.652	
		−3.122	0.9565	5.150	−0.7538	6.267	−2.602	
		−2.904	0.8898	4.791	−0.7862	6.461	−2.601	
							$\Delta H_{2\,\mathrm{mean}}$ = −2.62 ± 0.02	−0.05 ± 0.04
	0.20	−3.405	0.9475	5.102	−1.360	5.872	−2.786	
		−3.628	0.9804	5.279	−0.8795	6.228	−2.893	
		−3.329	0.9235	4.973	−0.5779	6.405	−2.797	
							$\Delta H_{2\,\mathrm{mean}}$ = −2.82 ± 0.03	−0.25 ± 0.05
Propylene glycol	0.025	−2.070	0.9460	5.094	−0.0674	6.211	−2.188	
		−2.088	0.9580	5.158			−2.179	
		−2.079	0.9452	5.090			−2.199	
							$\Delta H_{2\,\mathrm{mean}}$ = −2.19 ± 0.01	0.38 ± 0.04
	0.05	−2.053	0.8921	4.803	−0.2893	6.283	−2.188	
		−1.864	0.9475	5.102	−0.1345	6.233	−1.784	
		−2.030	0.9640	5.190	−0.2238	6.267	−1.923	
							$\Delta H_{2\,\mathrm{mean}}$ = −1.94 ± 0.09	0.63 ± 0.09
	0.10	−1.949	0.8980	4.836	−0.5866	6.133	−1.702	
		−2.429	0.9497	5.114	−0.5394	6.261	−2.089	
		−1.929	0.9467	5.098	−0.5138	6.117	−1.569	
		−2.174	0.9812	5.283	−0.5153	6.267	−1.747	
							$\Delta H_{2\,\mathrm{mean}}$ = −1.8 ± 0.1	0.8 ± 0.1
	0.15	−2.745	0.9685	5.215	−0.9182	6.350	−2.021	
		−2.711	0.9130	4.916	−0.9577	6.372	−2.156	
		−2.458	0.8936	4.811	−0.9492	6.000	−1.937	
							$\Delta H_{2\,\mathrm{mean}}$ = −2.04 ± 0.06	0.53 ± 0.07

(Continued on next page)

Table I. (*Continued*)

Propylene glycol	0.20	−3.281	0.9123	4.912	−1.236	6.261	−2.552	
		−3.744	0.9497	5.114	−1.265	6.450	−2.897	
		−3.431	0.9714	5.231	−1.120	5.939	−2.487	
						$\Delta H_{2\text{ mean}}$ =	−2.6 ± 0.1	−0.1 ± 0.1
	0.25	−3.963	0.9932	5.348	−1.423	6.244	−2.762	
		−3.813	0.9430	5.077	−1.350	6.072	−2.816	
		−3.687	0.8576	4.618	−1.410	6.033	−3.071	
						$\Delta H_{2\text{ mean}}$ =	−2.88 ± 0.09	−0.31 ± 0.09

[a] Values at $m_2 = 0$ assumed approximately equal to $\overline{\Delta H}_2$ (5, 7). [b] Very low and almost negligible values of h'/mm' at $X_3 = 0.025$ obtained by graphical interpolation between $X_3 = 0$ and $X_3 = 0.05$. [c] Uncertainty intervals for ΔH_2^0 and ΔH_2 (e_0 and e, respectively) are standard deviations of the means, and those for $\overline{\Delta H}_2$ equal $[(e_0)^2 + (e)^2]^{1/2}$.

consisted of two decade resistances, a linear potentiometer and a Fenwal thermistor with a resistance of 2000 Ω at 25° C, and was powered by a 1.35-V mercury battery. The 95.51-Ω Karma wire calibration heater coil was wound on a Teflon core immersed in Octoil and contained in a thin glass tube.

The heater was energized by a Power Designs No. 4005 dc power supply. The calibrating current was determined from the potential across a standard 1-Ω resistor in series with the heater, measured by a Leeds and Northrup No. 8691 mV potentiometer. The time of heating was obtained from a msec stopclock synchronized with the heater switch. The calorimeter Dewar was immersed to the level of the cover in an enclosed water bath regulated to 0.001° C (*7*).

During a run, weighed quantities of 10.31*m* HCl were sealed into glass ampuls and crushed against the bottom of the Dewar containing 450 grams of water or mixed solvent. The final concentration, m_2, in the Dewar was ca. 0.002*m*, and all runs were made at 25° ± 0.1° C. Following a dilution run, an ampul containing a quantity of pure water approximately equal to that present in the ampul during the HCl dilution run was crushed into the mixed solvent in the Dewar. This allowed correction of dilution enthalpies for the appropriate quantity of heat evolved when water from the HCl ampul mixed with the mixed solvent in the Dewar. Enthalpies of transfer in kcal/mol were obtained from

$$\overline{\Delta H}_2 = \Delta H_2 - \Delta H_2^0 \qquad (2)$$

where ΔH_2 is the corrected enthalpy of dilution per mole of HCl in the mixed solvent for HCl (10.31*m* in H_2O) = HCl (m_2 in mixed solvent) and ΔH_2^0 is the enthalpy of dilution in pure water for HCl (10.31*m* in H_2O) = HCl (m_2 in H_2O). Values of ΔH_2 in kcal/mol were calculated from

$$\Delta H_2 = [h_2 - (h'/mm')_a mm_1]/mm_2 \qquad (3)$$

where

h_2 = observed total enthalpy (cal/run) due to dilution of mm_2 millimoles of HCl, and mixing of mm_1 millimoles of water in the ampul with mixed solvent in the Dewar

h' = observed enthalpy of mixing (cal/run) of mm' millimoles of pure water in the ampul with mixed solvent in the Dewar

$(h'/mm')_a$ = average value of all (h'/mm') terms at each mixed solvent composition

RESULTS AND DISCUSSION

Table I shows all measured enthalpy data at the experimental compositions. The mean value of ΔH_2^0 is within 2.5% of that interpolated from tabulated data in NSRDS-NBS2 (*5*). It may be noted, however, that there are no directly determined measurements of integral enthalpies of dilution of HCl in pure water from high concentrations at 25° C cited in this definitive publication for enthalpy data for 1-1 electrolytes.

Figures 1 through 5 show graphs of $\overline{\Delta F}_2$, $\overline{\Delta H}_2$, and calculated $T\overline{\Delta S}_2$ vs. X_3 for each of the five systems. The enthalpy curves and points for methanol and ethanol are based on the study of Hepler and co-workers (*2*), and the nearly linear free energies of transfer are all from standard emf data (*6*). Extrapolations of $\overline{\Delta F}_2$ and $T\overline{\Delta S}_2$ are indicated by dashed lines. In order of increasing $\overline{\Delta F}_2$ slopes, the series is MeOH, EtOH, 2-PrOH, 1-PrOH, and propylene glycol.

The positive $\overline{\Delta H}_2$ and $T\overline{\Delta S}_2$ peaks appear to be general for water-rich low-molecular-weight alcohols but not for other aqueous mixed solvents (*8, 9*). Feakins and Arnett (*3*) and Franks and Ives (*4*) have suggested that both $\overline{\Delta H}_2$ and $T\overline{\Delta S}_2$ for aqueous mixed solvents include the changes in structural environment of the transferred electrolyte, which compensate to lead to the observed and apparently much simpler net behavior of $\overline{\Delta F}_2$. The positive values of $T\overline{\Delta S}_2$ may be an indication of higher order in water-rich alcohols than in pure water; detailed arguments may be found elsewhere (*3, 4*).

At the compositions where $T\overline{\Delta S}_2$ is zero for various alcohols at maximum positive peak-width composition, the entropy of HCl and its environment is the same in water and in the mixed solvent. Up to approximately this composition, the mixed solvent may thus be more ordered than pure water. Additional quantities of alcohol beyond this point cause a shift toward net disordering relative to pure water (*10*). The isentropic compositions are shown in Table II, in order of decreasing X_3, and are taken from Figures 1 through 5. Isenthalpic compositions show a similar ranking.

The data show that this point for the straight-chain primary alcohols is a function of the length of the nonpolar alkyl group; that is, structural breakdown for the shortest methanol occurs at the highest X_3 and that for 1-propanol at the lowest mole fraction. The position of propylene glycol in Table II is an indication of the more "water-

Table II. Isentropic Compositions

Alcohol	X_3
Methanol	0.23
Ethanol	0.16
Propylene glycol	0.13
2-Propanol	0.11
1-Propanol	0.09

like" characteristics that have been attributed to polyalcohols relative to monohydric alcohols (*4*). This point is the same for HCl transfer to ethylene glycol at $X_3 \approx 0.13$ (*10*).

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Solubility of Sulfur in Liquid Sulfur Dioxide, Carbon Disulfide, and Carbon Tetrachloride

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The solubility of sulfur in liquid sulfur dioxide, carbon disulfide, and carbon tetrachloride is reported. In liquid sulfur dioxide the solubility increases with rising temperature. Between 25° and 65° C there is indication of solvent-solute interaction. At 95° C, the transition temperature between orthorhombic and monoclinic sulfur, a definite change in solubility is noted. In carbon disulfide, the solubility increases logarithmically with rising temperature. In carbon tetrachloride, the solubility also increases with rising temperature. However, between 140° and 170° C, a reaction takes place.

The solubility of sulfur in liquid gases and solvents is not well known. It is often much larger than expected. The purpose of this study was to explore the solubility of sulfur in liquid sulfur dioxide and to extend the temperature range for the sparse and old data on carbon disulfide and carbon tetrachloride.

References regarding the solubility of sulfur in liquid sulfur dioxide are all qualitative (*1, 6, 8, 11*). They suggest that there is only a slight solubility which increases with rising temperature. The solubility of sulfur in carbon disulfide, as measured by five different experimenters, has been critically summarized (*2*) for the range between −116° and +98° C. Data for the solubility of sulfur in carbon tetrachloride (*3, 5*) obtained at four temperatures indicate that the solubility changes smoothly with temperature up to 58° C with no reactions taking place. However, it is known (*10*) that above 150° C, carbon tetrachloride reacts with sulfur.

EXPERIMENTAL

Reagent grade carbon disulfide from Allied Chemical Co., and carbon tetrachloride and phosphorus pentoxide, both from J. T. Baker Chemical Co., were used. Sulfur of 99.99% purity was donated by the Freeport Sulphur Co. CP grade sulfur dioxide was drawn from Matheson Chemical Co. cylinders.

Sulfur dioxide was further purified by passing it through two columns of phosphorus pentoxide drying agent and subjecting the dried gas to two freeze-pump-thaw cycles. All other chemicals were used without further purification.

Since the solubility of sulfur in sulfur dioxide was measured up to the critical point, sealed sample tubes were necessary. Sample tubes were made from 7-mm o.d. pyrex tubing which was closed at one end and annealed. Approximately 4 in. from the sealed end, a constriction was made and the entire tube was joined to an $^{18}/_{7}$ ball joint attached to a vacuum system. The bulb served as a container for gaseous sulfur dioxide dried by passing through phosphorus pentoxide drying tubes. This procedure was similar to that reported before (*9*).

For safety reasons, sample tubes were made from medium-wall, annealed glass tubing selected from standard stock. Hot tubes were handled only with mechanical fingers to lessen the danger from explosion due to the high vapor pressures of the solvents. Protective face guards were worn, and the experiment was carried out in screen-enclosed beakers behind explosion-proof glass. However, only one or two out of a dozen sample tubes burst around the critical point of SO_2, and in most cases the failures occurred above critical conditions.

Throughout all experiments, the same basic procedure was followed to measure solubilities. We observed, within a 5° C range, when the last traces of sulfur dissolved. For this purpose, tubes were immersed in constant temperature baths and were rotated mechanically or shaken to enhance equilibration. In the cases of both liquid sulfur dioxide and carbon tetrachloride, equilibrium was approached both by raising and lowering the temperature of the bath used.

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