Procedure.—All absorption spectra were measured by means of a Beckman model DU spectrophotometer and 1-cm. silica cells at 26 ± 1°. In the determination of the ionization constants the spectra of buffered solutions were measured in "50%" aqueous ethanol (100 ml. of the solution contained 50 ml. of water; remainder of the solution consisted of 95% ethanol). The concentration of all compounds was 5×10^{-5} *M*. The ionization constants were calculated[7] by the equation $pK_a = pH_m + \log (E_B - E_m/E_m - E_{BH^+})$ where E_B, E_{BH^+} are the optical densities of base and salt and E_m is the optical density of a mixture of base and salt at an intermediate pH_m fairly close to the value of the pK_a of the compound.

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The Preparation of S-Succinyl Coenzyme A[1]

BY ERIC J. SIMON[2] AND DAVID SHEMIN

RECEIVED FEBRUARY 27, 1953

We have previously concluded that a succinyl derivative is a precursor of protoporphyrin.[3] This succinyl intermediate may be identical with S-succinylcoenzyme A. We have found that this compound is readily formed by succinylating coenzyme A with succinic anhydride, as shown by the disappearance of the sulfhydryl group (nitroprusside reaction),[4] the formation of a hydroxamic acid,[5] and an increased light absorption of 232 mμ.[6] When the product is warmed for a few minutes on a steam-bath, the sulfhydryl group reappears, the reaction with hydroxylamine no longer occurs and there is a decreased light absorption at 232 mμ. Also, this synthetic preparation behaved as succinyl-coenzyme A in enzymatic systems.[7]

Thirty-five mg. of a coenzyme A preparation (Pabst) was dissolved in 30 ml. of ice cold water. To this solution 3 mg. of succinic anhydride was added, followed by sodium bicarbonate until the *p*H was 7–7.5. The mixture was kept in an ice-bath and shaken frequently. The reaction appeared to be completed within 30 minutes at which time over 90% of the sulfhydryl groups had disappeared. At 0° the succinyl coenzyme A is stable at *p*H 7–7.5 for several hours, at room temperature it is half hydrolyzed in about 1–2 hours, as measured by the nitroprusside and hydroxamic acid methods. However, at *p*H 1, at room temperature, the succinyl coenzyme is much more stable than at neutrality. The hydroxamic acid test was carried out on the formed succinyl coenzyme A after the complete hydrolysis of any unreacted succinic anhydride.

Succinyl coenzyme A has previously been enzymatically prepared from α-ketoglutarate.[8,9] Acetic anhydride has been used for the synthesis of acetyl-coenzyme A.[10] This anhydride method may be applicable for the preparation of other acyl coenzyme A derivatives.

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[2] Aided by a fellowship from the National Foundation of Infantile Paralysis. Present address: Payne Whitney Clinic, Cornell Medical College, New York, N. Y.

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(7) We are indebted to S. Kaufman, C. Gilvarg, M. J. Coon and J. R. Stern for these enzymatic experiments.

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On Some Partial Molal Volumes of Gases in Solution[1]

BY RICHARD H. SCHUMM AND OLIVER L. I. BROWN[2]

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This note reports measurements of the partial molal volumes of carbon tetrafluoride and methane in some non-polar solvents at 27.0°.

Carbon tetrafluoride, obtained from the Minnesota Mining and Manufacturing Company, was led through a Dry Ice trap. Methane, Research Grade from the Phillips Petroleum Company, had been analyzed by mass spectrometer as 99.7% pure. Benzene was obtained thiophene-free or was freed of thiophene by washing with sulfuric acid, sodium carbonate and water, and dried over calcium chloride. Reagent grade (A.C.S.) carbon tetrachloride was used without further purification. *n*-Hexane, *n*-heptane and "isooctane" (2,2,4-trimethylpentane) from the Phillips Petroleum Company were all of 99 mole per cent. purity.

The apparatus and procedure were essentially the same as those of Horiuti[3] and of Gjaldbaek and Hildebrand.[4] The volume of the bulb was approximately 150 cc. The capillary stems had a capacity of about 8.5 cu. mm. per cm. Two dilatometers were used during each run; gas was dissolved in one and the other was used as a blank to correct for small temperature variations in the bath. Compression of the solution by the increased head of mercury in the capillaries was avoided by pulling a sufficient vacuum in one capillary to return the mercury in the other capillary to its original height.

To check the procedure against that of Horiuti and of Gjalbaek and Hildebrand the partial molal volume of methane in benzene was determined at 25.0°. Values of 53.51 and 51.22 cc. per mole were found, which agree well with Horiuti's value of 52.0 and Gjaldbaek and Hildebrand's value of 52.5 cc. per mole. The results of the measurements are summarized in Table I. It will be noted that the value determined for methane in *n*-hexane at 27° differs considerably from the value of 60.0 cc. per mole at 25° found by Gjaldbaek and Hildebrand and that it does not vary in the direction to be expected from the two-degree temperature difference. Horiuti found that the partial molal volume of methane in carbon tetrachloride increased 6.8% in going from 0 to 25°.

As shown by Gjaldbaek and Hildebrand, the partial molal volumes of methane, ethane and nitrogen decrease consistently with increasing solubility parameter of the solvent except for solutions in carbon disulfide. This exception they attribute to the effect of differences in the size and shape of the component molecules. However, if the data for these gases, as given here and in

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[1] This note is based on the Master's Thesis of R. H. Schumm, 1952.

[2] Department of Chemistry, Connecticut College, New London, Conn.

(3) J. Horiuti, *Sci. Papers, Inst. Phys. Chem. Res., Tokyo*, **17**, 125 (1931).

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TABLE I

PARTIAL MOLAL VOLUMES OF GASES

Gas	Solvent	Temp., °C.	Gas absorbed vol., Mmole	Cu. mm.	$\bar{v}_2$	Mean $\bar{v}_2$
CH_4	*n*-Hexane	27.0	0.6679	38.28	57.32	
			.5639	31.78	56.35	56.83
CH_4	*n*-Heptane	27.0	.9498	52.82	55.61	
			.9032	49.67	54.99	55.43
			.7582	42.22	55.69	
CH_4	Isoöctane	27.0	.9149	52.83	57.74	
			.8844	48.86	55.25	
			.9829	55.79	56.75	56.60
			.8062	45.69	56.67	
CF_4	Benzene	26.8	.3822	31.72	82.98	
			.3868	32.37	83.70	83.24
CF_4	CCl_4	26.9	.5453	43.44	79.65	
				46.85	79.78	79.72
CF_4	*n*-Heptane	27.0	.5436	47.25	86.92	
			.4983	42.82	85.93	86.43
CF_4	Isoöctane	27.0	.5738	48.94	85.30	
			.5726	48.93	85.44	85.37

Table II of their paper, are plotted against the solubility parameters of the solvents, it will be seen that the data are fairly well fitted by curves of parabolic shapes with minima at a solubility parameter of about 9. The data given in this paper for carbon tetrafluoride exhibit no regular variation, possibly because of the small range of solubility parameters investigated.

It is reasonable to expect a minimum in the partial molal volume of a gas. The partial molal volume of a solute increases with the change of volume on mixing, which is given by[5]

$$\Delta V^{M} = \beta_0 \Delta E_{V}^{M}$$

where β_0 is the compressibility of the isolated components and ΔE_V^M is the change of internal energy on mixing at constant volume. ΔE_V^M is directly related to the absolute difference in solubility parameters of the components[5]

$$\Delta E^{M} = (N_1V_1 + N_2V_2)(\delta_1 - \delta_2)^2\phi_1\phi_2$$

where N denotes the number of moles of a component, and ϕ its volume fraction. It follows, therefore, that the partial molal volume should exhibit a parabolic dependence on the solvent solubility parameter and show a minimum where the solubility parameters of the components are equal. The minimum for nitrogen, on the basis of three points,[4] seems to occur at a solvent solubility parameter of about 9, whereas Gjaldbaek and Hildebrand,[6] on the basis of solubility data, assign a solubility parameter of 5.2 to nitrogen gas at 25°.

Figure 1 is a plot of the ratio of the partial molal volume of the solute to the molal volume of the solvent against the solubility parameter of the solvent. All the data conform well to smooth curves. This is especially noteworthy in the case of carbon tetrafluoride inasmuch as a plot of the partial molal volume of carbon tetrafluoride against the solvent solubility parameter exhibits a very irregular variation. This plot may be useful in predicting partial molal volumes in other solvents, yielding values of $\bar{v}_2$ which can be used in correlating the solubility of these gases by the equation[6]

$$-\log x_2 = -\log a_2 + \log(\bar{v}_2/v_1) + 0.434(1 - \bar{v}_2/v_1) + \bar{v}_2(\delta_1 - \delta_2)^2/4.575T$$

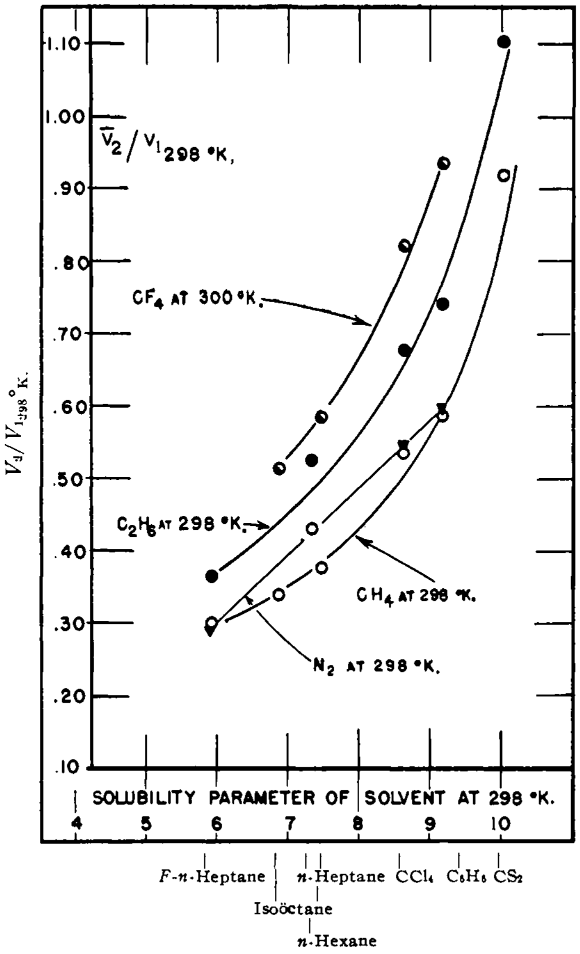

Fig. 1.

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[5] J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," third edition, Reinhold Pub. Corp., New York, N. Y., 1950, pp. 139, 129.

[6] J. Chr. Gjaldbaek and J. H. Hildebrand, THIS JOURNAL, **71**, 3147 (1949).

Action of Carbon Tetrachloride on Silica Gel

BY ROGER K. TAYLOR

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Rao and Rao[1] report that CCl_4 vapor reacts with the retained water in activated silica gel, at a rate appreciable at 110° and moderately rapid at 300°, to form $COCl_2$ and HCl. They further report that the gel firmly retains about 10% by weight of HCl.

Work in our laboratory in general confirms these observations, with the additional indication that at the higher temperatures a portion of the CCl_4 is hydrolyzed all the way to CO_2. Silica gel exposed for 24 hours at 275° to CCl_4 vapor, and then held at this temperature in a current of dry air until no fur-

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[1] J. R. A. Rao and B. S. Rao, *J. Indian Chem. Soc.*, **12**, 322 (1935).