TABLE I

PARTIAL MOLAL VOLUMES OF GASES

Gas	Solvent	Temp., °C.	Gas absorbed vol., Mmole	Gas absorbed vol., 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]

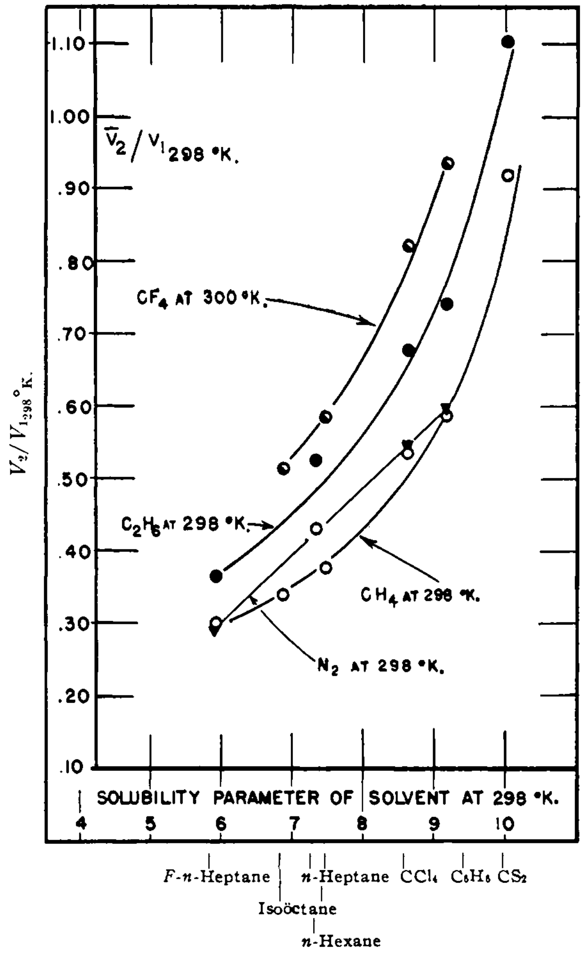

Fig. 1.

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

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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

RECEIVED JANUARY 24, 1953

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).

ther HCl was evolved, was found to contain somewhat above 12% Cl.

Reyerson and Bemmels[2] show that the adsorption of hydrogen chloride on silica gel is normal in magnitude, reversible and decreases with elevation of temperature. It follows that Rao and Rao are in error in considering the Cl retained after CCl_4 treatment to be present as HCl. Rather, the product must be regarded as of the nature of an oxychloride of silicon with chlorine chemically bound to silicon, since HCl as such would not remain in the gel under the conditions of the preparation.

(2) L. H. Reyerson and C. Bemmels, *J. Phys. Chem.*, **46**, 35 (1942).

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Reversible Bleaching of Chlorophyll by Metallic Salts

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The interaction of chlorophyll with metallic salts possessing oxidizing and reducing properties is of importance in considering the participation of chlorophyll in oxidation–reduction systems. Addition of an oxidizing salt to an alcoholic or acetone solution of chlorophyll a or b causes bleaching to a straw yellow color within one or two seconds. Immediate subsequent addition of a reducing salt causes a reversion to green. The reversible reaction

$$\text{Chlorophyll} \underset{\text{reducing salt}}{\overset{\text{oxidizing salt}}{\rightleftarrows}} \text{"oxychlorophyll"} \qquad (1)$$

has been proposed, where "oxychlorophyll" is merely the designation of the unstable bleached form of chlorophyll.[1] The reversibility of (1) has not received complete credence among biochemists as the absorption spectra of the regenerated green solutions were significantly different from the initial spectra in some cases where regeneration of chlorophyll was claimed.

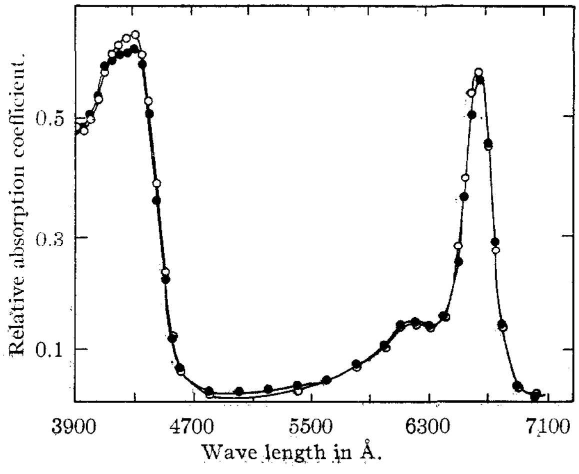

Fig. 1.—Regeneration of the spectrum of non-allomerized chlorophyll a: —●—, 5 × 10^{-6} m. chlorophyll a in methanol; —○—, after bleaching with ferric chloride and regeneration by cuprous chloride.

The data now presented confirm that chlorophyll undergoes a reversible reaction of type (1) within the accuracy of modern spectrophotometric methods, after allowance for a small amount of allomerized chlorophyll also produced. The reversion to green on addition of sodium chloride or standing exposed to air is not regeneration of chlorophyll but formation of allomerized chlorophyll. The reversion of color by hydroquinone is by production of yet another green compound.

Experimental Methods and Materials.—Chlorophylls a and b were prepared by a modification of Zscheile and Comar's method.[2] Purified chlorophyll was kept in ether at −10° in the dark till required, and then transferred to methanol by evaporating and condensing on a vacuum apparatus with avoidance of complete drying-off of solvent. Spectral measurements were made using conventional 1-cm. cells in a Beckman spectrophotometer. Methanolic solutions of salts were added directly to chlorophyll solutions in the Beckman holder from syringes.

Experimental Results and Discussion.—The spectrum after bleaching by ferric chloride and regeneration by cuprous chloride is illustrated in Fig. 1. Apart from the small increase in the main violet maximum and reduction in the minor violet maximum, typical of allomerization,[3] the chlorophyll was almost quantitatively regenerated. A chlorophyll solution left at room temperature till partially allomerized also underwent regeneration of spectrum except for slight further allomerization. The sensitivity of the bleached compound to traces of water was confirmed[1]; water of hydration of 10^{-5} mole/l. ferric chloride caused a marked loss of chlorophyll a on regeneration.

The bleached solution returned to green on standing. However, the spectrum was characteristic of allomerized chlorophyll.[3] (Figure 5 of the original paper[1] shows that the spectra of allomerized chlorophyll was also observed, though its spectrum at that time had not been independently characterized.) This removes the main, and recognized,[1] anomaly of reversion on standing.

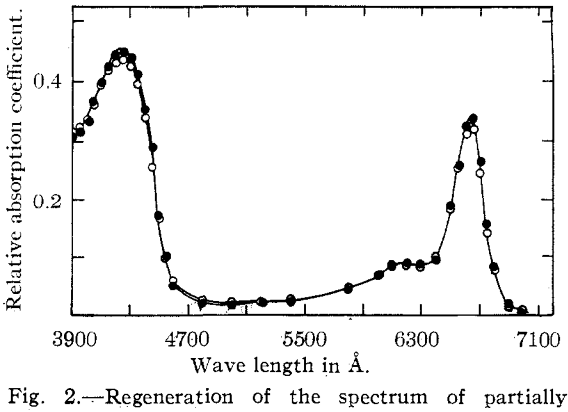

Fig. 2.—Regeneration of the spectrum of partially-allomerized chlorophyll a: —○—, partially-allomerized chlorophyll a in methanol; —●—, after bleaching with ferric chloride and regeneration by cuprous chloride.

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(1) E. Rabinowitch and J. Weiss, *Proc. Roy. Soc. (London)*, **A162**, 2511 (1937).

(2) R. Livingston, D. Sickel and A. Uchiyama, *J. Phys. Colloid Chem.*, **51**, 777 (1947).

(3) E. I. Rabinowitch, "Photosynthesis," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 613.