

that the substance surpasses phthiocol by far in vitamin K activity. The observation that the pure oxide [Fieser, Campbell, Fry and Gates, *THIS JOURNAL*, **61**, 3216 (1939)] is fully effective in the chick assay at a dosage of 5 γ prompted the investigation of other oxides of 2-alkyl and 2,3-dialkyl 1,4-naphthoquinones, and it was found that the hydrogen peroxide procedure [Fieser, *et al.*, *loc. cit.*] provides a convenient route to a number of substances of both types. Farnesyl-naphthoquinone oxide [found: C, 78.88; H, 8.16] and phytyl-naphthoquinone oxide [found: C, 79.91; H, 9.76] were obtained as nearly colorless oils showing, respectively, very weak and weak (500 γ) antihemorrhagic activity. These substances are cleaved by alkali to a mixture of 2-hydroxy-1,4-naphthoquinone and its 3-alkyl derivative. Crystalline oxides were obtained from 2,3-dimethyl-1,4-naphthoquinone [m. p. 104–104.5°, found: C, 71.26; H, 5.09; active at 25 γ] and 2-methyl-3-cinnamyl-1,4-naphthoquinone [m. p. 85–86°, found: C, 78.94; H, 5.47].

Vitamin K₁ was converted in nearly quantitative yield into the 2,3-oxide, which was obtained as an almost colorless oil [found: C, 79.85; H, 9.69]. Any uncertainty as to the structure is eliminated by the observation that the absorption spectrum corresponds closely with that of 2,3-dimethyl-1,4-naphthoquinone oxide. The K₁ oxide shows antihemorrhagic activity of about the same order as the vitamin (1.5 γ) and gives no purple-blue color with alcoholic alkali. The properties of the oxide are of interest in connection with the reports of Fernholz, Ansbacher and co-workers [*THIS JOURNAL*, **61**, 1613 (1939); *Proc. Soc. Exptl. Biol. Med.*, **42**, 655 (1939)] stating that they have isolated from alfalfa concentrates a nearly colorless substance of high potency which does not give the Dam-Karrer color test characteristic of vitamins K₁ and K₂. However, in our hands, there is no great difference in the ratio of the effective dose of the oxide and of vitamin K₁ when assayed by the six and eighteen hour method.

We have found that the oxides of vitamin K₁ and of methyl-naphthoquinone can be reduced smoothly to vitamin K₁ hydroquinone and methyl-naphthohydroquinone with sodium hydrosulfite in aqueous alcohol, even at room temperature. This lends plausibility to the hypothesis that the high potency of the oxides is due to a reduction in the organism to the corresponding quinones or hydroquinones; possibly the 2-methyl oxide is

converted in part into the comparatively inactive phthiocol.

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RECEIVED APRIL 20, 1940

MISCIBILITY OF CARBON DIOXIDE AND WATER UNDER HIGH PRESSURE

Sir:

Wiebe and Gaddy [*THIS JOURNAL*, **62**, 815 (1940)] report the solubility of carbon dioxide in water and make the following statement: "The compositions of the gas and liquid phases at 12° and 600 atm. were identical." My understanding of the behavior of carbon dioxide-water systems is that compression at 12° to about 47.7 atm. will change the phases from a gas (predominantly carbon dioxide) and liquid (mostly water) to a gas (mostly carbon dioxide), a liquid (mostly carbon dioxide), and a liquid (mostly water). Further attempts to compress the system will cause the gas phase to change to a liquid (mostly carbon dioxide) phase and leave at its disappearance two liquids, one predominantly water and the other predominantly carbon dioxide.

Their data show that compression of the two phases increases the carbon dioxide content of the water phase only from 0.03 mole fraction to less than 0.04 mole fraction. Lowry and Erickson [*ibid.*, **49**, 2729 (1927)] indicated that the water concentration in the liquid carbon dioxide was much lower than the above concentration of carbon dioxide in the water phase. Wiebe and Gaddy [*ibid.*, **61**, 315 (1939)] state the mutual solubility of water and carbon dioxide as liquid-liquid system is affected by pressure to only a slight extent.

These statements appear contradictory to the above quotation of identical phases. Any critical phenomena in this region would be of the liquid-liquid critical solution type and not of the type reported by Kuenen [*Commun. Phys. Lab. Univ. Leiden*, **4** (1892)] for the carbon dioxide-methyl chloride system. To become mutually soluble, it is normally expected that the two phases approach each other in composition. A consideration of the probable behavior of these two phases upon compression indicates a possible explanation of the above contradictions. At 10 to 20°,

carbon dioxide is relatively close to its critical temperature and is more compressible than water. At low pressures the predominantly water phase is the more dense but the increase of pressure to about 200 atm. and about 500 atm. at 10 and 20°, respectively, would cause the two immiscible fluids to reach the same density.

I know no reason to believe that the same density makes the two phases miscible but the formation of a relatively uniform suspension of the two phases might occur. Unless the possibility of this reversal in the positions of the two phases in the equilibrium cell were recognized, experimental results might indicate a critical state had been reached. Details of the manipulation of the equilibrium cell and quantitative results at the high pressures in the reported region of complete miscibility should show whether the proposed explanation of the unusual results is tenable.

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RECEIVED APRIL 18, 1940

REDISTRIBUTION REACTIONS

Sir:

Recently Calingaert and co-workers¹ have described a "hitherto unrecognized type of intermolecular exchange of organic radicals" which they term "redistribution reactions." These reactions are characterized by equilibrium constants which are independent of temperature through the temperature range employed, and which have values that agree with the idea of a random distribution of the exchanging radicals to within the precision of the data obtained.

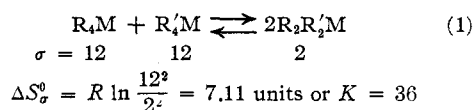
In view of the large amount of experimental work done by these authors already, it seems justifiable to point out that, while such reactions have not hitherto been recognized as a type, their existence need not surprise one; and, furthermore, given any of the reactions so far studied, the *equilibrium* results obtained could have been predicted about as closely as the experiments justify the idea of random exchange of radicals.

The significance of these reactions lies, first, in the fact that, to the precision to which a modified Redgrove² rule would apply, values of ΔH would

(1) Calingaert and Beatty, *THIS JOURNAL*, **61**, 2748 (1939); Calingaert, Beatty and Neal, *ibid.*, **61**, 2755 (1939); Calingaert and Soroos, *ibid.*, **61**, 2758 (1939); Calingaert Beatty and Hess, *ibid.*, **61**, 3300 (1939).

(2) Redgrove, *Chem. News*, **116**, 37 (1917).

be zero in all cases. Thus in every type of exchange studied certain bonds are broken and others are formed, but the latter are always identical with the former except for slight steric effects. For $\Delta H = 0$, $K = e^{\Delta S^0/R}$, and ΔS^0 for random distribution should be measured by the relative external symmetry numbers of the molecules involved in the equilibrium; *e. g.*, in the type reaction



where σ is the external symmetry number. By the nature of the reactions studied, the only remaining appreciable contributions to ΔS^0 would lie in the effect of the redistribution of mass on the translational entropies, and on the redistribution of principal moments of inertia on the possible rotational entropies. Based on six specific redistributions from systems typified by the left-hand side of equation 1, the former of the two mentioned contributions (*i. e.*, mass redistribution) averages 0.076 entropy unit (a heat effect of about 27 small calories at 350°K.); and, assuming stretched molecules and free rotation, the average of the upper limit of the second contribution to ΔS^0 mentioned above is, for the same six reactions, 0.86 entropy units (a heat effect of about 300 small calories at 350°K.).

It is therefore not surprising that the controlling factor in determining the equilibrium state for such reactions is the value of ΔS^0 , or randomness of distribution.

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RECEIVED MARCH 11, 1940

THE ISOMERIZATION EQUILIBRIUM OF *n*-BUTANE AND *i*-BUTANE AND THE THIRD LAW OF THERMODYNAMICS

Sir:

Recently complete measurements in this Laboratory of the thermal properties of the two butanes from 11°K. to their respective boiling points furnish values for the entropies of the gases at their normal boiling points. For *n*-butane $S_{272.66^\circ\text{K.}}^0 = 72.05 \pm 0.2$ e. u.; for *i*-butane $S_{261.44^\circ\text{K.}}^0 = 67.54 \pm 0.2$ e. u. These values, together with available heat capacity data on the gas, yield a value of $\Delta S_{298.1}^0 = -3.7 \pm 0.3$ e. u. for the reaction

