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.

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN D. L. KATZ

RECEIVED APRIL 18, 1940

REDISTRIBUTION REACTIONS

Sir:

Recently Calingaert and co-workers[1] 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 Redgrove[2] rule would apply, values of ΔH would 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

$$\mathrm{R_4M} + \mathrm{R'_4M} \rightleftarrows 2\mathrm{R_2R'_2M} \qquad (1)$$

$$\sigma = 12 \qquad 12 \qquad 2$$

$$\Delta S^0_\sigma = R \ln \frac{12^2}{2^2} = 7.11 \text{ units or } K = 36$$

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_σ, or randomness of distribution.

UNIVERSITY OF MISSOURI
COLUMBIA, MISSOURI ALLEN E. STEARN

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 $S^\circ_{272.66^\circ\mathrm{K.}} = 72.05 \pm 0.2$ e. u.; for *i*-butane $S^\circ_{261.44^\circ\mathrm{K.}} = 67.54 \pm 0.2$ e. u. These values, together with available heat capacity data on the gas, yield a value of $\Delta S^\circ_{298.1} = -3.7 \pm 0.3$ e. u. for the reaction

$$n\text{-butane(g)} \longrightarrow i\text{-butane(g)}$$

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(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).