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

$$R_4M + R_4'M \rightleftarrows 2R_2R_2'M \qquad (1)$$

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

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

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

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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).

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 $S^0_{272.66°\text{K.}} = 72.05 \pm 0.2$ e. u.; for *i*-butane $S^0_{261.44°\text{K.}} = 67.54 \pm 0.2$ e. u. These values, together with available heat capacity data on the gas, yield a value of $\Delta S^0_{298.1} = -3.7 \pm 0.3$ e. u. for the reaction

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

The work of Moldavskii and Nizovdima[1] upon the equilibrium constant for this reaction from 70–150°, combined with the measurement of Montgomery, McAteer and Franke[2] at 27° furnishes an independent value for the entropy difference of the two isomers. Two of these equilibrium measurements, at 27° (Montgomery) and at 70° (Moldavskii) were made in the liquid phase at pressures of about 3 and 10 atmospheres, respectively. The constants were calculated to the gas phase with fugacity data for *n*-butane[3] and *i*-butane[4] reported by Sage, Webster and Lacey. The assumption that the liquid follows Raoult's law is in accord with the results of Montgomery, *et al.*[2] The other equilibrium measurements were made in the gas phase by a flow method. The heat of isomerization −2200 ± 200 cal./mole was obtained from the slope of a $\log K - \frac{1}{T}$ plot. Essentially a straight line was obtained, which indicates that over the temperature range in question ΔH is constant to within a small fraction of the experimental error in the equilibrium values. This constancy of ΔH has been confirmed by statistical mechanical calculation.

From the equilibrium data two values of ΔS°_{298} for the isomerization reaction may be obtained, one using the measured heat[5] (A), the other using the heat of isomerization from the slope of the plot (B). These two values are compared with our experimental value of ΔS°_{298} (C) in Table I.

TABLE I

$n\text{-}C_4H_{10}\ (g) = i\text{-}C_4H_{10}\ (g)$

ΔS°_{298} cal./deg./mole	Source of data
−2.1±0.6	Equilibrium measurement (Montgomery, *et al.*[2]) Heats of combustion (Rossini[5])
−3.7±0.3	Thermal data to 11 °K. *n*-butane submitted for publication in THIS JOURNAL *i*-butane, unpublished data
−4.0±0.8	Temperature coefficient of equilibrium constant. Montgomery *et al.*,[2] and Moldavskii and Nizovdima.[1]

The agreement between (B) and (C) is well within experimental error. There is thus at present no reason to doubt[6] the practical applicability of the third law of thermodynamics to these compounds.

The assistance of the Standard Oil Development Company in portions of this work is gratefully acknowledged.

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(1) Moldavskii and Nizovdima, *Compt. rend acad. sci. U. R. S. S.*, **23**, 919–20 (1939); *Chem. Abs.*, **34**, 931 (1940).

(2) Montgomery, McAteer and Franke, THIS JOURNAL, **59**, 1768 (1937).

(3) Sage, Webster and Lacey, *Ind. Eng. Chem.*, **29**, 1188 (1937).

(4) Sage and Lacey, *ibid.*, **30**, 673 (1938).

(5) Rossini, *J. Chem. Phys.*, **3**, 438 (1935).

(6) Kassel, THIS JOURNAL, **59**, 2745 (1937).

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RECEIVED MAY 6, 1940

NEW BOOKS

Die exakten Methoden der Mikromassanalyse. (The Exact Methods of Titrimetric Microanalysis.) By Dipl.-Ing. JOSEF MIKA. (Die chemische Analyse. Edited by WILHELM BÖTTGER, Hannover. XLII. Band.) Ferdinand Enke Verlag, Hasenbergsteige 3, Stuttgart W, Germany, 1939. xii + 180 pp. 19 figs. 16.5 × 25 cm. Price, RM. 18; bound, RM. 19.60.

The author limits himself to a discussion of such titrimetric methods as can be applied to samples of approximately 10 microequivalents, *i. e.*, 1 to 10 milligrams of material. As a rule it is tried to attain a relative precision of 1 part in a thousand. Methods giving a relative precision of 10 parts in a thousand are included, however, if they offer practical advantages. Hundredth normal standard solutions are suggested for the use with burets of approximately 1 ml. total capacity, which permit delivery and determination of volume with a precision o 0.001 to 0.0001 ml.

In the general part are discussed: the recognition of the end-point with the use of colorimetric, potentiometric, and conductometric methods; the concentration of the standard solutions and the determination and accuracy of their titer; burets, pipets, and aliquot partition; storing of standard solutions; containers for the titrated solutions, stands for titration; apparatus for potentiometric and conductometric titrations; and the testing for purity of the reagents and the water used as solvent. The special part comprises: neutralimetry with the use of dyestuff indicators and of potentiometric and conductometric indication of the end-point; oxidimetry, redox indicators, and electrometric indication; titrations based on the formation of precipitates or complexes with the use of colori-