COMMUNICATIONS TO THE EDITOR

FRACTIONAL PARTITION OF THE RARE EARTHS

Sir:

The usual tedious methods of rare earth separation depend upon steps for which the enrichment factor is often fairly large, but in which advantage is taken of the enrichment only once or twice a day, as in fractional crystallization. Processes which may be operated continuously, therefore, offer much more hope for satisfactory solution of the rare earth separation problem, even though the enrichment factor in any one step may not be as great as in fractional crystallization.

A possibility which suggests itself is fractional partition of rare earths between two immiscible solvents. Suggestions in this connection have been made by Fischer, Dietz and Jübermann, [*Naturwissenschaften*, **25**, 348 (1937)].

We have investigated the possibility of finding suitable compounds and solvents for this process. The chloride, iodide, nitrate, thiocyanate, glycolate, lactate, citrate, and acetylacetonate of neodymium were prepared and shaken with a wide variety of hydrocarbons, ethers, alcohols, ketones, and esters. The nitrate is soluble in acetone; and a mixture of acetone, diethyl ether and water gives two layers, but the densities of the two layers are so nearly the same that they separate very slowly. The acetylacetonate is soluble in benzene and in a variety of other organic solvents, but in the authors' experience it is scarcely stable enough to permit its use in a counter-current solvent extraction column.

The thiocyanate of neodymium was found to be very soluble in *n*-butyl alcohol. Although this solvent is appreciably soluble in water, it appeared to offer the best hope of success.

A mixture of lanthanum and neodymium oxides containing 38.1% La_2O_3 was prepared and converted to the thiocyanate by treating the dissolved sulfates with barium thiocyanate and centrifuging off the precipitated barium sulfate. (Professor L. F. Audrieth, of the University of Illinois, has since pointed out to the authors that fusion of the oxide with ammonium thiocyanate is a much easier method of preparing rare earth thiocyanates.) Lanthanum and neodymium were chosen because of their availability and because their magnetic susceptibilities are sufficiently different as to permit accurate analyses to be made.

An aqueous solution of the mixed thiocyanates was thoroughly shaken in a separatory funnel with an equal volume of *n*-butyl alcohol. The separate layers were then withdrawn, the rare earth content was converted to the oxides and analyzed. The water layer contained 38.7% of lanthanum, the alcohol layer 37.4%, the initial concentration being 38.1%. The ratio of neodymium to lanthanum in the alcohol layer to that in the aqueous layer is 1.06.

It is to be anticipated that neodymium would concentrate in the alcohol layer because of its slightly diminished ionic radius over that of lanthanum.

Although the enrichment factor is quite small and will doubtless be considerably smaller between rare earths such as neodymium and praseodymium, yet the process lends itself to continuous operation and may lead to comparatively rapid separation of these elements. Development of suitable counter-current extraction apparatus is being undertaken.

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RECEIVED JUNE 9, 1941

THE STRUCTURE OF ALICYCLIC COMPOUNDS

Sir:

We have compared the entropies of cyclopentane obtained from thermal data determined in this Laboratory down to 11.1°K., with those obtained from molecular and spectroscopic data based on three ring models, a planar model (D_{5h}), a non-planar model with one atom out of the plane (C_s), and a non-planar model with two atoms out of the plane (C_2). The first of these has a symmetry number of $\sigma = 10$, the second of $\sigma = 1$, and the third of $\sigma = 2$. The results for the ideal gas at 230, 260, 323.2°K. and 1 atmosphere are given in Table I.

The spectrum used was chosen on the basis of the discussion of Reitz [*Z. physik. Chem.*. **B33,**

TABLE I

THE ENTROPY OF CYCLOPENTANE IN THE IDEAL GAS STATE

	Cal./deg./mole		
	230°K.	260°K.	323.2°K.
Calorimetric	65.26 ± 0.15	67.50 ± 0.15	71.2 ± 0.5
Translational + Rotational ($\sigma = 10$)	57.18	58.15	59.85
Vibrational	3.90	4.89	7.69
Total, D_{5h} ($\sigma = 10$)	61.08	63.04	67.54
Total, C_2 ($\sigma = 2$)	64.27	66.23	70.73
Total, C_s ($\sigma = 1$)	65.65	67.61	72.11
Total vibrational with γ_1 changed to 56 and γ_2 to 88	8.08	9.13	12.05
Total, D_{5h} ($\sigma = 10$) $\gamma_1 = 56$, $\gamma_2 = 88$ cm.$^{-1}$	65.26	67.28	71.90

179 (1936)] applied to his data and those of Kohlrausch and Seka [*Ber.*, **69,** 729 (1936)], namely

Ring: $\omega_1 = 886$; $\omega_2 = 1050$; $\omega_3 = 1050$; $\omega_4 = 1216$; $\omega_5 = 1216$; $\omega_6 = 967$; $\omega_7 = 967$; $\gamma_1 = 165$; $\gamma_2 = 285$; CH$_2$ internal: $^{10}\nu = 2900$; $^{5}\delta = 1446$; CH$_2$ waving: $^{5}\delta_1 = 772$; $^{5}\delta_2 = 1028$; $^{5}\delta_3 = 1283$

As can be seen, the experimental data fit best the value of $\sigma = 1$, corresponding to the C_s configuration. In order to get an idea of what revision in the frequency assignment would be necessary to get agreement for $\sigma = 10$, in the last two lines of Table I we have compared the experimental values with those calculated using the above frequency assignment except with $\gamma_1 = 56$ cm.$^{-1}$ and $\gamma_2 = 88$ cm.$^{-1}$ and taking $\sigma = 10$. These frequencies were chosen to give agreement at the lowest temperature. Inasmuch as the lowest of the frequencies in benzene is 406 cm.$^{-1}$, these values of γ are quite unlikely. Further, they give a poor fit with the calorimetric data at the higher temperatures. At present the indication is that the cyclopentane ring has the non-planar configuration C_s.

Inasmuch as strong hydrogen repulsions have been indicated in other compounds [Aston and Kennedy, THIS JOURNAL, **62,** 2567 (1940)], it is suggested that it is this repulsive action on the carbon tetrahedra that pushes one (or two) atoms out of the plane. We have also made similar comparisons on methylcyclopentane based on data of Huffman, Parks and Barmore [*ibid.*, **53,** 3876 (1931)] down to 90°K., which lead to the same conclusion. With cyclohexane, by the same method and taking $\gamma_1 = 377$, $\gamma_2 = \gamma_3 = 250$, we have found a configuration with $\sigma = 6$ as is to be expected. [It should be noted that Langseth and Bak, *J. Chem. Phys.*, **8,** 403 (1940), consider that the spectroscopic evidence points to a planar configuration ($\sigma = 12$), with little justification, however.]

Our results are in agreement with those of Beach from the electron diffraction by tetrahydrofuran which lead also to the adoption of a non-planar configuration [Beach, private discussions and *J. Chem. Phys.*, **9,** 54 (1941)].

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RECEIVED MAY 23, 1941

ON THE LUMINESCENT OXIDATION OF LUCIFERIN

Sir:

Bioluminescence, the result of the oxidation of luciferin by luciferase and oxygen, has been the subject of numerous studies from this Laboratory.[1] The following observations are reported since they throw some light on the nature of the luminescent reaction and the structure of the luciferin molecule. Application of ultramicro analysis[2] to the highly purified extracts of *Cypridina* luciferin[3] shows that carbon, hydrogen and oxygen are the only constituents (tests for nitrogen, sulfur, halogen and ash were all negative). Deduction from available evidence (conditions of benzoylation[3]; irreversible inhibition by cyanide[4]; irreversible step in the luminescent oxidation[5]) lead us to the conclusion that luciferin contains a keto-hydroxy side chain which is oxidatively degraded in the luminescent reaction. Evidence for a keto group was derived from the fact that the addition of hydroxylamine acetate gave a microcrystalline precipitate which is inactive toward luciferase, but on acid hydrolysis gave light with the enzyme. If our deduction as to the nature of the side chain and its role in the luminescent reaction is correct, the irreversible step[5] in the luminescent reaction may be formulated as

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(1) E. N. Harvey, "Living Light, Princeton, 1940."

(2) D. G. Foulke and F. Schneider, *Ind. Eng. Cnem., Anal. Ed.*, **10,** 104 (1938).

(3) R. S. Anderson, *J. Gen. Physiol.*, **19,** 301 (1935).

(4) A. C. Giese and A. M. Chase, *J. Cellular Comp. Physiol.*, **16,** 237 (1940).

(5) R. S. Anderson, *ibid.*, **8,** 26 (1936).