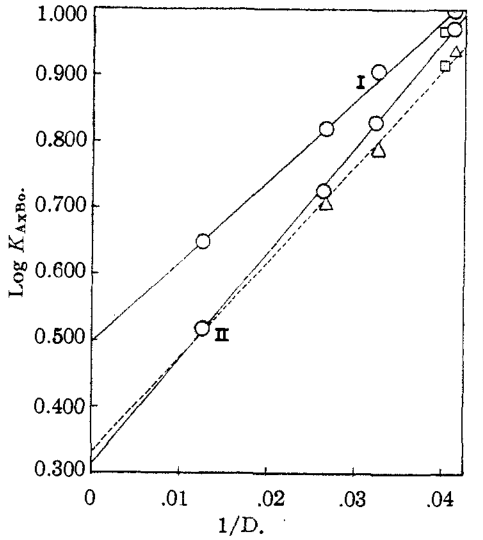


Fig. 1.—I, *p*-Cyanobenzoic acid *vs.* benzoic acid; II, *m*-cyanobenzoic acid *vs.* benzoic acid: ○, experimental values; △, calculated values; □, dioxane–water experimental values.

column of Table I. This relationship has been found to hold for the other substituted benzoic acids[5] and more recently for aliphatic acids.[6] The results for the dioxane–water mixture are also in conformity with our findings for other acids.

Table II and Fig. 1 give the corresponding results for *m*-cyanobenzoic acid.

TABLE II

RATIO OF THE DISSOCIATION CONSTANT OF *m*-CYANOBENZOIC ACID TO THAT OF BENZOIC ACID AT 25°

Solvent	Dielectric constant	$K_{A_xB_0}$ (obs.)	$K_{A_xB_0}$ (calcd. by equation 3)
Water	78.5	3.31	3.29
Ethylene glycol	37.7	5.31	5.48
Methyl alcohol	31.5	6.76	6.61
Ethyl alcohol	24.2	9.39	9.42
Dioxane–water	25	8.22	8.89

The dotted line in Fig. 2 represents the predicted value calculated on the basis of electrostatic theory.[7] The results for the pure solvents may be represented by the equation

$$\log K_{A_xB_0} = 0.314 + (16.0/D) \qquad (3)$$

for which the calculated values are given in column four of Table II. It should be noted that *p*-cyanobenzoic acid is a stronger acid than *m*-cyanobenzoic acid in all the solvents studied.

Summary

The relative acid strengths of *m*- and *p*-cyanobenzoic acids have been determined in the solvents water, ethylene glycol, methyl alcohol, ethyl alcohol and dioxane–water mixtures.

---

[5] Kilpatrick, *Chem. Rev.*, **30**, 159 (1942).

[6] Kilpatrick and Eanes, THIS JOURNAL, **64**, 2065 (1942).

[7] From the dissertation of J. N. Sarmousakis presented to the Faculty of the Graduate School of the University of Pennsylvania, December 1, 1942.

PHILADELPHIA, PA. RECEIVED DECEMBER 30, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY]

Thermal Decomposition of Hydrocarbons, Resonance Stabilization and Isomerization of Free Radicals[1]

BY ALEXANDER KOSSIAKOFF AND FRANCIS OWEN RICE

Introduction.—When a paraffin hydrocarbon such as propane is heated, the over-all decomposition, if limited to a small percentage, can be represented by the equations

$$C_3H_8 \longrightarrow H_2 + CH_2{=}CHCH_3 \qquad (1a)$$

$$C_3H_8 \longrightarrow CH_4 + CH_2{=}CH_2 \qquad (1b)$$

The actual mechanism of the decomposition has been the subject of much controversy and has been discussed in detail in a previous paper.[2] It was suggested that the most probable mechanism involves a rupture of the molecule into radicals, which initiate a series of changes resulting finally in the product molecules. A unimolecular rearrangement followed by a splitting of the molecule into the products seems unlikely on the basis of our present knowledge regarding interatomic forces.

One of the important predictions which can be made on the basis of the radical hypothesis concerns the nature and quantities of products expected from the thermal decomposition of a saturated hydrocarbon. The chain of reactions initiated and carried by the free radicals appears to consist of at least ten to twenty cycles[3] and may be several hundred links long. For this

---

[1] Original manuscript received May 7, 1942.

[2] Rice and Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939).

[3] Frey, *Ind. Eng. Chem.*, **26**, 200 (1934).

reason the character and relative amounts of the products depend only on the chain reactions involving the attack of radicals on the hydrocarbon molecule. The first reaction of the chain is the removal of a hydrogen atom from the hydrocarbon by a radical, giving a new radical. This is followed by the decomposition of the new radical into one or more molecules and an ethyl or methyl radical or a hydrogen atom. The assumption that at low pressures and high temperatures the decomposition reaction is much faster than the bimolecular reaction with the hydrocarbon has been firmly established by the available experimental data.

For example the chain reactions for propane would be

$$R\cdot + CH_3CH_2CH_3 \longrightarrow RH + \cdot CH_2CH_2CH_3 \quad (2a)$$
$$R\cdot + CH_3CH_2CH_3 \longrightarrow RH + CH_3\underset{\cdot}{C}HCH_3 \quad (2b)$$

followed by

$$\cdot CH_2CH_2CH_3 \longrightarrow CH_2{=}CH_2 + \cdot CH_3 \quad (3a)$$
$$CH_3\underset{\cdot}{C}HCH_3 \longrightarrow CH_2{=}CHCH_3 + \cdot H \quad (3b)$$

It can be seen that reactions 2a, 3a, and the subsequent reaction of CH_3 with another molecule of C_3H_8, will lead to the products CH_4 and C_2H_4; reactions 2b and 3b will lead to H_2 and C_3H_6.

A consideration of the different kinds of radicals which can be formed by the removal of a hydrogen atom from the hydrocarbon molecule, and of their modes of decomposition, enables one to predict the products of the reaction. In order to predict the relative amounts of the products, it is necessary in addition to find a rule for calculating the relative rates of formation of the radicals, *i. e.*, the relative rates of removal of hydrogen atoms from the hydrocarbon.

In the original treatment of the problem,[4] it was assumed that the activation energy of removing a hydrogen atom depends only on whether it is primary, secondary or tertiary. The differences in activation energy were calculated from the experimental results on the decomposition of propane and isobutane. The values obtained gave a diminution of energy for removing a secondary hydrogen of 1.2 kcal. and of a tertiary of 4.0 kcal. as compared with the energy required to remove a primary hydrogen from a hydrocarbon molecule. These values were then used to predict the products of decomposition of *n*-butane, the pentanes, and the hexanes. The agreement of the calculated and observed results was excellent, showing the essential soundness of the assumption underlying the theory.

In the present paper a theoretical approach is made to the problem in an effort to account for the difference in behavior of the three types of carbon-hydrogen bonds. The result predicts that the activation energy for removing a hydrogen atom decreases approximately linearly with the number of carbon atoms attached to the parent carbon. The treatment is presented in section (2) of the paper.

When a radical may decompose in two different ways, it has been customary to assume equal probabilities for the two processes. The theoretical treatment, however, predicts that the rates will, in general, be quite different, and provides a means of estimating this difference. This problem is discussed in section (3).

If a hydrogen atom is removed from the end of a long hydrocarbon molecule, say of six or more carbon atoms, the possibility of isomerization of the resulting radical arises. This problem and its bearing on the decomposition of *n*-hexane and higher hydrocarbons are discussed in section (4) of the paper.

The last section is devoted to the prediction of the products of decomposition of the hexanes, heptanes and octanes.

Rates of Removal of Hydrogen Atoms by Radicals—Resonance in Radicals.—The difference in behavior of primary, secondary and tertiary hydrogens has long been known to chemists, the evidence indicating that primary hydrogens are held the most tightly, tertiary the least. Smith and Taylor[5] obtained values for the rates of reaction of radicals with ethane, neopentane, butane and isobutane. Their conclusions substantiated this hypothesis. It is the purpose of this paper to present a theoretical picture of this behavior in order to provide a better understanding of the phenomenon. The assumption is made that the differences in the rates of removal of hydrogens are due substantially to one effect, and that this effect involves a certain type of resonance in the radicals formed in the reaction. It will be seen that this assumption leads to results which are in excellent agreement with experiment.

In considering the properties of hydrocarbon free radicals, Wheland[6] has pointed out that the unfilled orbital on the trivalent carbon atom can

---

[4] Rice, THIS JOURNAL, 55, 3035 (1933).

[5] J. O. Smith, Jr., and H. S. Taylor, *J. Chem. Phys.*, 7, 390 (1939).

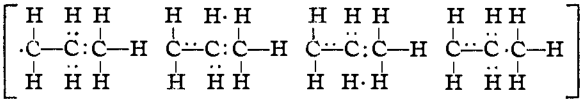
[6] Wheland, *ibid.*, 2, 477 (1934).

conjugate with bonding electrons on adjacent carbon atoms. The effect is similar in nature to that obtained in olefinic free radicals in which an unfilled orbital β to the double bond conjugates with an electron pair in the double bond, giving two resonating structures which stabilize the radical by[7] perhaps 15 kcal.

The stabilization to be expected in the case of paraffin free radicals is much smaller than this value, due to the fact that the conjugating electrons are more tightly held. As Wheland[6] has pointed out, however, the magnitude of the effect is probably sufficient to account for the difference in behavior between primary, secondary and tertiary radicals.

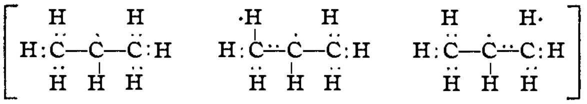
The effect may be illustrated by considering *n*-propyl and *s*-propyl radicals:

n-propyl radical



I IIa IIb IIc

s-propyl radical



I II (3 structures) II′ (3 structures)

The difference in energy between structures I and II is in the neigborhood of 50 kcal. This figure can be estimated roughly by considering the energy required to break a C–H or C–C single bond and to complete a C–C double bond, using bond energies.[8] The computation of the resonance energy due to contribution of the conjugated structures has not been attempted because of the complications and uncertainties attending such calculations. A reasonable estimate of the resonance energy of an *n*-propyl radical would be about 5 kcal.

While the values of the resonance energy for the different radicals are not available, it can be seen that a secondary radical possesses twice as many conjugated structures as a primary, and consequently about twice the resonance energy. Similarly, a tertiary radical should be stabilized by three times as much resonance energy as a primary.

In considering the relative rates of removal of primary, secondary and tertiary hydrogens we are dealing not with the energies of the resulting radicals, but with the energies of the transition states in these reactions. In the transition state the hydrogen atom is moved approximately half way from the parent molecule to a radical which is reacting with it. Even in this case conjugation will occur, although not to the fullest extent. The stabilization of the transition states will be only a fraction of that of the radicals. It will still be true, however, that the stabilization of a secondary radical will be about twice as great as that of a primary, and that of a tertiary about three times as great. As a matter of fact, the type of resonance which we have been considering in radicals exists in hydrocarbon molecules, although to a much smaller degree, and has been given the name "hyperconjugation" by Mulliken.[9]

If we let ΔE be the difference in activation energy for removing a primary and secondary hydrogen, and $2\Delta E$ be the difference between a primary and tertiary hydrogen, the value of ΔE which gives best agreement with experiment turns out to be 2.0 kcal. This value is in substantial agreement with the experimental results of Smith and Taylor. They give for the activation energies of removing a primary, secondary and tertiary hydrogen, 8.3, 5.5 and 4.2, respectively. At 600°, the relative rates of removal of hydrogen atoms would stand in the ratios 1:3.2:10.3 instead of 1:2:10 as was assumed in the original calculation. The new values give considerably better agreement with experiment,[10] as is shown in Fig. 1.

It may be of interest to mention a very simple empirical rule which was found to give good results in calculating the relative rates of the chain reactions. It was assumed that the rate of removing a hydrogen is proportional to the number of C–H bonds formed by carbon atoms adjacent to the point of attack. Thus there are two C–H bonds α to the primary hydrogen in propane and six C–H bonds α to the secondary hydrogen. This gives us the relative rates of removal of 1:3, instead of 1:3.2 as in the previous calculation. The success of this simple scheme suggests that C–H bonds conjugate with the free orbital in radicals to a greater extent than do C–C bonds. However, the experimental data are not sufficiently accurate to provide an adequate check of this possibility.

---

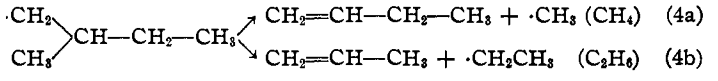
(7) C. A. Coulson, *Proc. Roy. Soc.* (London), **164**, 383 (1938); F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938).

(8) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y. 1939.

(9) R. S. Mulliken and C. A. Rieke, THIS JOURNAL, **63**, 1770 (1941).

(10) Compare with Figs. 1 and 2, *ibid.*, **55**, 3035 (1933).

Decomposition of Radicals.—Many of the radicals formed in the decomposition of pentane and higher paraffins can decompose by two possible mechanisms. For example, the isopentyl radical can break up in two ways



$$\cdot CH_2(CH_3)CH—CH_2—CH_3 \begin{cases} \rightarrow CH_2{=}CH—CH_2—CH_3 + \cdot CH_3\ (CH_4) & (4a) \\ \rightarrow CH_2{=}CH—CH_3 + \cdot CH_2CH_3\ (C_2H_6) & (4b) \end{cases}$$

We can estimate the relative rates of reactions 4a and 4b from a consideration of the energies of the radicals formed in the two processes. The ethyl radical formed in 4b possesses resonance energy, while the methyl radical does not. It is reasonable to assume that the stabilization of the transition states in these reactions would be about the same as that in reactions involving the removal of a hydrogen atom from R_3C-H by a radical. This would give a difference in activation energy of 2 kcal., making 4b three times as fast as 4a at 600°. Actually, no 1-butene was reported in the products. In the decomposition of the 3-hexyl radical the calculated ratio is again 3, while the observed ratio is 2. In general, this calculation always predicts which of two reactions will predominate, but fails to give the ratio very accurately.

It has been assumed that at low pressures radicals larger than ethyl decompose faster than they react with hydrocarbon molecules. Actually, even ethyl radicals probably decompose to an appreciable extent. From a consideration of the graphs, it will be noted that an improvement would result if the calculated values of ethane were reduced by about 20% and those for ethylene and hydrogen increased by a corresponding amount. *s*-Propyl radicals, which must also lose a hydrogen atom in order to decompose, would react still more slowly with the hydrocarbon, due to their greater stabilization. For these radicals the decomposition reaction is much faster, and only small amounts of propane are formed.

Decomposition of Long-Chain Hydrocarbons.—The chain decomposition of *n*-hexane proceeds through the formation of three radicals which decompose according to the reactions

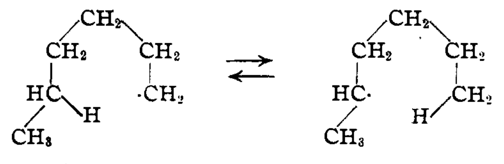
$$CH_3CH_2CH_2CH_2CH_2CH_2\cdot \longrightarrow 2C_2H_4 + C_2H_5\ (C_2H_6) \quad (5a)$$

$$CH_3CH_2CH_2CH_2\dot{C}HCH_3 \longrightarrow C_3H_6 + C_2H_4 + CH_3\ (CH_4) \quad (5b)$$

$$CH_3CH_2CH_2\dot{C}HCH_2CH_3 \begin{cases} \rightarrow C_4H_8 + C_2H_5\ (C_2H_6) & (5c) \\ \rightarrow C_5H_{10} + CH_3\ (CH_4) & (5d) \end{cases}$$

In the earlier calculations it had been assumed that radicals larger than ethyl decompose before they can attack another molecule of the hydrocarbon. However, when the radical in question has a long carbon skeleton, it is quite possible for it to coil around and react with itself to produce an isomer. Thus, the 1-hexyl radical can isomerize into a 2-hexyl radical.

The activation energy for such a reaction is certainly much smaller than that for the decomposition and as a consequence, an equilibrium between the two radicals is probably established. The isomerization of a 1-hexyl to a 3-hexyl radical, however, is less likely for geometrical reasons, so that the rate of isomerization of the 1 to the 3 isomer is probably insufficient to maintain equilibrium. Similar arguments are advanced by Benson and Kistiakowsky[11] to account



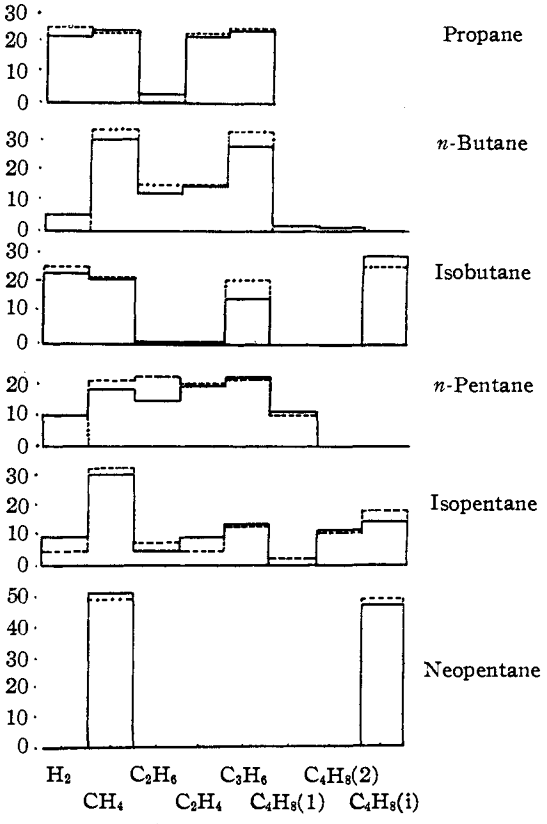


Fig. 1.—Thermal decomposition of hydrocarbons: full curve, experimental; dotted curve, calculated.

---

[11] S. W. Benson and G. B. Kistiakowsky, THIS JOURNAL **64**, 80 (1942).

for the products of the photochemical decomposition of cyclic ketones.

In order to calculate the relative over-all rates of reactions 5a and 5b, it is necessary to estimate the equilibrium constant of reaction 6. Lacking data on the resonance energies of the radicals, we may assume that about half of this energy is developed in the transition complex. This gives $2\Delta E$ or 4 kcal. for the difference in energy of a primary and secondary radical, resulting in a Boltzmann factor of 10 at 600°. The statistical factor is 4/6, since the primary radical can be formed by removing any one of six hydrogens, while the secondary can be formed in four ways. The equilibrium constant is 10 × 4/6 or 7. Fortunately, the results are not very sensitive to the value of the constant in most cases. The rates of decomposition of the two radicals should be nearly the same. The extra stability of the secondary radical is almost entirely preserved, the methyl group conjugating with the double bond in propylene nearly to the same extent as it does with the free orbital in the radical.

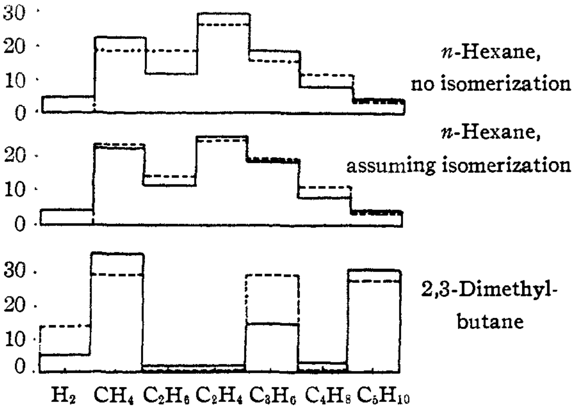


Fig. 2.—Thermal decomposition of hexanes: full curve, experimental; dotted curve, calculated.

The composition of the products calculated assuming an equilibrium between 1- and 2-hexyl radicals agrees with experiment considerably better than does the original calculation. The results are shown in Fig. 2. In the case of still higher hydrocarbons, such as n-octane, all the radicals can exist in equilibrium with each other and the improvement becomes more marked. The results for n-octane are also shown in Fig. 3.

The possibility that radicals having only five carbon atoms can isomerize to an appreciable extent should not be ignored. The results for n-pentane and iso-pentane would be slightly improved by the inclusion of such a process.

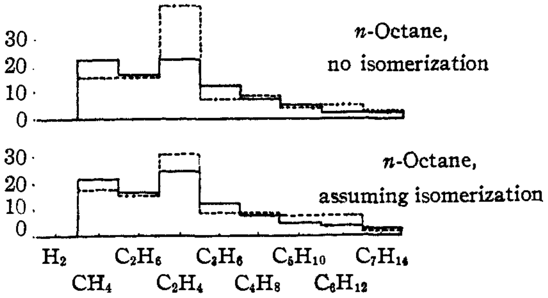


Fig. 3.—Thermal decomposition of n-octane: full curve, experimental; dotted curve, calculated.

Prediction of the Products of Decomposition of the Hexanes, Heptanes and Octanes.—It was thought desirable to apply the considerations discussed in the previous sections to the prediction of the decomposition products of the hexanes, the heptanes, and several of the more important octanes. The results of the calculations were summarized in figures similar to those published in this paper and have been reproduced in photoprints 6 × 8 inches by the American Documentation Institute.[12] The authors will be glad to supply copies of these or the detailed results to anyone interested.

The results apply only to decompositions occurring at low pressures and short contact times. Steric effects have not been taken into account, and may possibly complicate the picture in the case of highly branched compounds. The expected errors are of the order of 5%, as judged from the available data.

An investigation of the products of decomposition of 2,2-dimethylbutane offers a possibility of determining whether or not C–C bonds conjugate with the free orbital in radicals as well as C–H bonds. If they do not, the amounts of C_2H_6 and of 2-methylbutene-1 should be smaller than those given in the figure. An investigation of the products of decomposition of 2-methylhexane would be of particular interest in connection with isomerization of radicals. If isomerization does not occur, the amount of isobutene obtained should be about 10% instead of 18% as predicted.

Acknowledgment.—The authors wish to thank Dr. A. L. Sklar of this University for valuable suggestions and criticism.

Summary

1. Hydrocarbon free radicals, which are formed in the chain decomposition of paraffin

---

(12) American Documentation Institute Document No. 1658, 2101 Constitution Ave., N.W., Washington, D. C.; 25¢ for microfilm and 70¢ for photocopies.

hydrocarbons, have been shown to be stabilized by resonance. This stabilization is least in primary radicals, greatest in tertiary radicals and is very probably responsible for the observed difference in rates of removal of primary, secondary and tertiary hydrogen atoms.

2. This approach gives a method for predicting the relative rates of decomposition of radicals, as well as their relative rates of formation.

3. Long chain radicals have the ability to isomerize unimolecularly. This factor has been taken into account in calculating the products of decomposition of hexanes, heptanes and octanes.

4. These considerations lead to considerably improved agreement between the calculated and observed products of the decomposition of paraffin hydrocarbons.

WASHINGTON, D. C. RECEIVED DECEMBER 17, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Fractionation of the Rare Earths by Zeolite Action[1,2]

BY R. G. RUSSELL[3] AND D. W. PEARCE

The second geochemical principle of V. M. Goldschmidt[4] dealt with the fact that individual minerals are seldom "pure chemical compounds" but usually contain greater or smaller amounts of foreign elements. The explanation was made upon the size and valence relationships between the normal ion of the lattice and the foreign, replacing, ion. Thus, for example, the presence of traces of scandium in magnesium silicates crystallizing in the earlier stages of the solidification of the magma was believed due to the similarity in the ionic radii of these cations (Mg^{+2} 0.78, Sc^{+3} 0.83 Å.). The greater charge of the Sc^{+3} ion enhanced its tendency, when in the vicinity of the growing magnesium silicate lattice, to enter into the structure.[5] In much the same way the slightly smaller, rather than the slightly larger, cations seem to be preferred by the lattice when a selection must be made from a mixture containing a series of cations of the same valence and of approximately the same size.

While these observations of Goldschmidt were concerned with minerals crystallizing from the molten magma, it seemed likely to the present investigators that such replacement of one ion by another might occur in a preferential manner when materials, synthetic or natural, which were capable of ready base-exchange were put into contact with aqueous solutions containing an assortment of ions, such as those of the rare earths, of the same charge but of varying size. Indeed the work of Jenny,[6] and of Bray,[7] and of many others has dealt with such base-exchange properties of various permutits, clays and soils. Both Jenny and Bray have indicated that "valence and ion size seem to be concerned in this phenomenon."[8] However, Jenny found that the order of preference of his permutit materials for the alkali metal ions was $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ which is just the reverse of the order expected from the (crystal) ionic sizes if the assumption is made that a smaller ion of the series is preferred to a larger. He was therefore led to assume, as Wiegner had done before,[9] that the radii of the hydrated ions, the "hydrodynamic radii," were ranged in the opposite order due to the increased polarizing effect of the smaller ions upon the water molecules. The result of the latter effect, then, was assumed to be a larger water-envelope and larger over-all size for the hydrated Li^+ than for the hydrated Cs^+ ion. However, the recent work of Fajans[10] has shown that the order of apparent molar volume, at infinite dilution, of the alkali metal ions at 25° is probably $Na^+ < Li^+ < K^+ < Rb^+ < Cs^+$. If this order held during the experiment of Jenny, then the exchange-material had preferentially

---

[1] Based upon a thesis submitted by R. G. Russell to the Faculty of Purdue University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, May, 1942.

[2] Presented before the Division of Physical and Inorganic Chemistry at the 104th meeting of the American Chemical Society, Buffalo, N. Y., September, 1942.

[3] Present address, Aluminum Research Laboratories, New Kensington, Pennsylvania.

[4] V. M. Goldschmidt, *Videnskapsselskapets-Skrifter. I. Mat.-naturv. Klasse Kristiania*, 1923, No. 3; *ibid.*, 1924, No. 4.

[5] Valence compensation may be obtained, in such a case, by the more or less simultaneous entrance of another cation of similar size but of valence 1, or by the entrance into the anion of an ion M^{+1} rather than Si^{+4}, or by the formation of a defect lattice with 2 Sc^{+3} as the valence equivalent of 3 Mg^{+2}, or by combinations of such means.

[6] Hans Jenny, *J. Phys. Chem.*, **36**, 2217–2258 (1932).

[7] R. H. Bray, THIS JOURNAL, **64**, 954–963 (1942).

[8] Bray, *loc. cit.*, p. 956.

[9] G. Wiegner, *Kolloid-Z.*, **36**, 341–369 (1925).

[10] K. Fajans, THIS JOURNAL, **64**, 668–678 (1942).