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.

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[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

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[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).

removed from solution the largest species with a reversal, as yet unexplained, between Na^+ and Li^+.

In the present work the principal purpose was to study, in a preliminary way, the use of base-exchange materials of high capacity in rare earth separations and to arrive at working hypotheses with regard to the mechanism of base-exchange as it concerns the ions of these elements.

Qualitative Behavior of Zeolites

The fact that ions of many types, including those of the rare earths, were removed from solution by "zeolites" was proved by causing dilute solutions to flow through short towers of various base-exchange materials in the form of the acid or of the sodium salt; the filtrates (effluents) were then tested for the ions concerned by the addition of the appropriate reagents. In all cases the total amount of ion in the original solution was less than that required to reach the capacity of the exchange-material. No particular effort was made to allow the optimum contact time and this may in part explain the fact that, in certain cases, complete removal of the ions was not obtained.

Such preliminary experiments indicated that the siliceous exchange-material Crystallite #20, a synthetic type,[11] readily and completely removed Mg^{+2}, Y^{+3} and mixed yttrium-group ions from dilute solutions of the nitrates, La^{+3} ion was similarly removed by Eimer and Amend "Permutit, acc. to Prof. Otto Folin" and Ag^+ and Cu^{+2} ions by the zeolite Decalso.[12] On the other hand, solutions of the ions Fe^{+3} or Th^{+4} in contact with the treated-natural zeolite Super Zeo Dur[12] gave evidence of partial hydrolysis and precipitation and these ions were only partially removed from the solution; similar behavior was obtained with a solution of ZrO^{+2} using Hizeco[13] and with a solution of UO_2^{+2} using Super Verdite[11]—each of these exchange-materials being of the treated-natural type; a neutral nitrate solution of Sc^{+3} behaved in the same way with Crystallite #20. The ions Th^{+4}, Fe^{+3} and Mn^{++} were completely removed from solution by the carbonaceous exchange-material Zeo Karb[12] when the operations were conducted on the H^+-cycle; however, this same medium removed practically no Sn^{+2} from a solution of stannous chloride in excess hydrochloric acid.

In the cases of those ions which hydrolyze readily at slightly higher *p*H values, interferences of this side reaction are to be expected since the *p*H often increases when a neutral solution passes through siliceous zeolite materials. This difficulty may be obviated, as the experiments indicate, by the use of exchange-materials operating on the hydrogen cycle. In the case of the $SnCl_4^=$ solution the rather large hydrogen ion concentration which was present without doubt offered competition for the small concentration of Sn^{+2}, since the former is, itself, a regenerant for this exchange-material. For this reason removal of the metallic ion from the solution may have been prevented.

Separations of the Rare Earths

In the preceding the behavior of certain zeolitic materials toward rare earth solutions was briefly described. In these the ratio by weight of exchange-medium to removable ions was such that the latter were *completely* removed since they possessed, apparently, the necessary physical and chemical characteristics for entry into the "zeolite lattice" and since they were present to an extent less than the capacity of the exchange-material. In the following are to be described the results obtained when the exchange-material was in all cases "overloaded," that is, subjected to contact with a greater amount of exchangeable ions of mixed type than could be accommodated by the weight of exchange-material used.

Single-stage Fractionation

Ce-group Material.—From a rare earth fractional crystallization series there was taken a fraction composed mainly of La and Nd with small amounts of Pr and Sm. The rare earths were precipitated as oxalate and the average atomic weight determined to be 141.7 (±0.9) by an oxalate to permanganate, oxalate to oxide procedure.[14] The oxalate was ignited to oxide, the latter dissolved in nitric acid, the solution evaporated just to dryness and the residue taken up in distilled water. Portions of this solution, containing rare earths to the extent of approximately five times the capacity of the exchange-material, were poured fifteen times through similar weights of natural (Super Zeo Dur, Grachohy,[15] Super Verdite, Hizeco), synthetic (Crystallite #20) and carbonaceous (Zeo Karb) exchange-materials. The average atomic weights of the rare earths in the filtrates were determined and compared with those obtained from the regenerates. Insignificant differences in the atomic weights were interpreted to mean that little separation had occurred in these cases.

Y-Group Material.—1. A 12-gram sample of light brown mixed yttrium group oxides of unknown source was dissolved in nitric acid, the solution evaporated just to dryness and the residue taken up in one liter of distilled water. The solution was poured six times through a 50-g. sample of Crystallite #20 contained in a 12-in. length of 16-mm. diameter Pyrex tubing. The zeolite was regenerated with concentrated sodium chloride

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(11) The International Filter Co., Chicago, Ill.

(12) The Permutit Co., New York, N. Y.

(13) The Zeolite Sales Co., New York, N. Y.

(14) Based upon the method of W. Gibbs, *Am. Chem. J.*, **15**, 546-566 (1893); to be described in a forthcoming publication.

(15) The Graver Tank Co., East Chicago, Ind.

solution, the rare earths recovered from the regenerate and from the filtrate, and the average atomic weight of the rare earths in each sample determined. The results were 106.9 (±0.0) and 117.3 (±0.1), respectively. The oxide from the regenerate was very light brown in color and that from the filtrate much darker. From the colors of the oxides and the average atomic weights it was concluded that an increased concentration of Y^{+3} had been obtained in the regenerate due, apparently, to the readier removal of this ion from the solution by the zeolite.

2. Other experiments were carried out using a neutral yttrium group nitrate solution prepared from the rare earths extracted from a sample of gadolinite. The average atomic weight of the rare earths in this mixture was 111.8 (±0.1), a value in good accord with the high yttrium content of this mineral. Crystallite # 20 was again used as the exchange-medium. Five hundred ml. of the solution, containing about 125 g. of the oxide, was stirred with a 500-g. sample of the zeolite for about four hours.

During this time a small amount of light brown sludge formed in the mixture. At the conclusion of the run this was suspended in the solution by agitation and the suspension decanted from the heavier zeolite. The sludge was completely removed from the zeolite by agitating with the distilled water used for washing the latter and the sludge was then removed from the solution by filtration. Determination of the Ce in the sludge as compared with that in the original solution showed that approximately 12% of the original Ce had passed into this oxidate-hydrolyzate.

The zeolite was then regenerated with sodium chloride solution and the rare earths recovered from the regenerate and reserved. The filtrate from the sludge and the same sample of zeolite were then again stirred together for four hours as before, the filtrate separated from the zeolite, and the rare earths recovered from the zeolite by regeneration. The rare earths thus recovered were reserved. In this way there was built up, after six regenerates had been obtained, a fraction sufficiently large to start a second series which was thereafter itself carried through two fractionations.

For the purpose of estimating the composition of the various fractions, determinations of the average atomic weight were made on small samples taken at certain points during the separations and the colors of the oxides were observed. The oxides from the regenerates were increasingly lighter in color as the atomic weights decreased while the oxides from the corresponding filtrates were darker and contained heavier earths. Thus, in the first series, the medium brown oxides from the first filtrate fraction had an average atomic weight of 110.4 (±1.4) while the gradual variation from fraction to fraction was such that the reddish brown oxides from the sixth filtrate had an atomic weight of 114.9 (±0.6); from the corresponding regenerates the oxides were all light brown and the atomic weight decreased from 103.4 (±0.4) to 102.0 (±1.1). In the second series, formed by the fractionation of the combined regenerates from the first series, the first filtrate yielded light brown oxides with atomic weight 107.1 (±0.4) while the first and second regenerates yielded pale brownish-white oxides with the atomic weights 95.0 (±0.1) and 96.2 (±0.1), respectively.

The preceding data may be interpreted if several facts are recalled. The ionic radii of the rare earths decrease[16] from La^{+3} (1.22 Å.) to Lu^{+3} (0.99 Å.) with the associated Y^{+3} having a radius (1.06 Å.) intermediate between Dy^{+3} (1.07 Å.) and Ho^{+3} (1.05 Å.). The atomic weights, on the other hand, increase from 138.92 for La to 174.99 for Lu but Y is much lighter, 88.92. Furthermore, with regard to the color of oxide mixtures, the higher oxide of Pr is black and, while this element is of low abundance, the content of its oxide largely determines the color of cerium-group mixtures. In the case of yttrium group oxide mixtures the color is similarly determined by the content of the very rare Tb, the higher oxide of which is very dark, and by the content of the principal diluent, the white oxide of the relatively very abundant Y.

From the data obtained it is concluded, then, that yttrium, and possibly even the rare earths with atomic weight greater and (crystal) ionic radii less than that of Y^{+3}, was particularly concentrated in the later *regenerates* of the second series while the elements heavier than yttrium, and of larger radii, were progressively concentrated in the later *filtrates* of the first series.

Multiple-stage Fractionation

The preceding experiments indicated that a zeolite expresses a preference for certain rare earth ions when a solution containing an assort-

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(16) V. M. Goldschmidt, "Kristallchemie," Handworterbuch der Naturwissenschaften, 2nd ed., G. Fischer, Jena, 1934.

ment of these is subjected to its action provided that the content of the solution exceeds the capacity of the exchange-material. However, the extent of the individual separations plainly showed the necessity of multiple-stage rather than single-stage operations if reasonable efficiency was to be obtained and minimum labor expended.

A 50-ft. column of 10-mm. Pyrex glass was therefore set up and filled with Crystallite # 20 which had been regenerated with sodium chloride solution and thoroughly washed with distilled water. At the top of the column about 500 ml. of the rare earth solution, of the same composition and concentration as used in the preceding experiment, was added to a reservoir and was permitted to drip slowly into the zeolite column. The effluent at the base was tested continuously for rare earths. Approximately 250 ml. of filtrate was collected before the presence of rare earths was detected; at this point the addition of solution at the top was discontinued and fractions of 8-ml. volume were taken from the base while the column was allowed to drain.

The rare earths were recovered from the individual filtrate fractions by precipitating the oxalates and igniting them to oxides. Fractions 1–14 each contained only a few tenths of a gram of oxide which was insufficient for convenient study of the absorption spectra or for the determination of the atomic weight. From the oxides of the remaining fractions, however, solutions were prepared to contain 1 g. of the oxide as nitrate in 10 ml. of 1 *N* nitric acid. The absorption spectra of constant thicknesses of these solutions were examined by the use of a hand spectroscope and were compared with the absorption spectra of standard solutions. The results of these analyses are shown in Table IA. Furthermore, the arc spectra of most of the fractions were photographed, mainly in the region λ 3900–4900 Å., using the Baird Associates grating spectrograph.

After the column had drained, the zeolite was washed with 250 ml. of water, the first and last 50-ml. portions being collected separately; both of these showed faintly the strongest Nd band in the absorption spectrum. From these extreme portions of washings the rare earths were recovered as oxalates and ignited to oxides; the latter were light brown in color. The average atomic weights were 109.2 (±0.1) and 108.0 (±0.4), respectively.

Following this partial washing, the zeolite was regenerated with 10% sodium chloride solution which was held in a container at the top and allowed to drain slowly through the column. The first portion of the solution issuing from the column contained small amounts of rare earth ions; there was approximately 50 ml. of this. The next portion contained no rare earth ions and very little chloride; there was approximately 200 ml. of this solution. The third portion contained rare earths and sodium chloride. Fractions of this last solution, each of 8-ml. volume, were taken off continuously during the regeneration and until only very small amounts of rare earths were being displaced. The composition of these small fractions was studied, as the filtrate fractions had been before, by absorption and arc spectra, color of the oxide and average atomic weight. The results are shown in Table IB.

The evidence from the intensities of the lines in the arc spectra is conclusive upon at least one point, namely, that La, Nd, and Sm are strongly concentrated in the filtrate fractions while the abundant Y, accompanied by Er and Yb, is strongly concentrated in the regenerate fractions. With respect to the way in which these elements are concentrated among the various individual fractions of the filtrate and regenerate portions, the arc spectra give little evidence, but the absorption spectra, the colors of the oxides and the atomic weight determinations permit somewhat more definite conclusions.

In the filtrate fractions La is the first to appear at the base of the column; this is followed by Nd

TABLE I

FRACTIONATION OF AN YTTRIUM GROUP MIXTURE BY MULTIPLE-STAGE OPERATIONS

Orig. av. at. wt. 111.8 (±0.1)

Fraction No.	Absorption	Color of oxide, At. wt.
	A. Filtrate Fractions	
1–3	...	Very light brown
4–10	...	Light brown
11–14	...	Medium brown
15	Nd weak	Medium brown
16	Nd weak	Medium brown
17	Nd medium, Pr?, Sm faint	Red brown
18	Nd medium, Pr?, Sm faint	Red brown, 127.6 (±0.1)
	B. Regenerate Fractions	
1	Nd medium, Pr?, Sm weak	Medium brown
2	Nd medium, Pr?, Sm weak	Medium brown, 105.9 (±0.0)
3	Nd medium	Medium brown
4–5	Nd weak	Light brown
6	Nd faint	Light brown
7	Nd faint	Very light brown, 106.2 (±0.4)
8–9	None	Very light brown
10	None	Very light brown, 104.1 (±0.1)
11–17	None	Yellowish white, 93.8 (±0.3)

and apparently by Sm. In the regenerate fractions the first to appear at the base of the column is Nd (accompanied by the small amount of La which is still present) and apparently followed by Sm, Y, Er and Yb in that order.

It is evident that two fractional separations are obtainable by the action of a zeolite upon a rare earth solution. These separations occur, in the first place, upon the original contact of the solution with the zeolitic material and, secondly, upon the regeneration of the material by the action of concentrated sodium chloride solution.

The Mechanism of Zeolite Action

When the rare earth solution is run through the zeolite column, the ions for which the lattice has most affinity are most strongly held toward the top of the column. The others are forced to pass farther down before they, in turn, are admitted to the lattice in exchange for Na^+ ions. When fresh material is again added at the top, the ions most loosely held are driven still farther down the column. In this way, if the capacity of the zeolite is reached (by forcing into contact with it more ions than it can hold) and if the conditions for equilibrium are approached, then the first ions to be ejected from the base of the column are those for which the affinity of the base-exchange medium is least. Under the conditions of the experiments here reported the ion with least tendency to be held in the lattice is La^{+3}.

Upon regeneration of the zeolite even the most strongly-held ions are removed by the action of the high concentration of Na^+ ion; they pass down the column ahead of the most concentrated layer of regenerating solution but force ahead of them, in the same way, the ions which are even more readily removed. The latter, then, are the first to come from the column and the others follow in the order of increasing affinity for the lattice with Y^{+3}, and probably the ions Ho^{+3} to Lu^{+3}, issuing last.

The Concentration Effects

From the equilibrium principle it seems reasonable to expect that an ion with somewhat lesser affinity for the lattice would be held in the zeolite even more strongly than an ion with normally greater affinity for the lattice if the former were much more abundant in the solution. The existence of such an effect has been indicated by Bray[7] and has been suggested also by some work of the present writers in which solutions of Fe^{+3} and Th^{+4}, with various ratios of the concentrations of the two cations, have been run through short columns of the base-exchange resin Amberlite IR 1.[17] The effect of varying proportions of the individual rare earths in the original mixture, therefore, is as yet unknown but it is felt that it may be considerable, great enough possibly even to reverse the order of preference, especially in the case of neighboring elements of closely the same size.

S. W. Melsted and R. H. Bray have indicated the existence of a further concentration effect in base-exchange reactions. They have stated[18] "that both the total concentration of the solution and the nature of the base-exchange material may be so modified as to either increase or decrease the relative accumulation of a given ion on the exchange material and that if the valence of one of the ions could be changed it would change its relative accumulation." Ivanov and Gapon, on the other hand, have concluded[19] that dilution of the solution does not affect to a different extent mixed ions of the same valence.

A further examination of the importance of such concentration effects as well as more quantitative studies of other aspects of the zeolite–rare earth ion equilibria will be undertaken in this Laboratory.

Acknowledgment.—Thanks must be expressed to The International Filter Company, The Permutit Company, The Graver Tank Company, The Zeolite Sales Company and The Resinous Products and Chemical Company, all of which generously made available samples of their various base-exchange materials.

Summary and Conclusions

The phenomenon of base-exchange is more general than has often been supposed. In this preliminary study no cation was encountered the valence or the size of which was so large that it was unable to enter into base-exchange reactions.

Fractional separations within the rare earth group are obtainable by means of zeolite action when concentrated solutions, containing sufficient ions to exceed the capacity of the exchange-material, are used. The rare earth ions of decreasing (crystal) ionic radius are held more firmly in the zeolite lattice while the larger ions

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[17] The Resinous Products and Chemical Co., Philadelphia, Pa.

[18] Personal communication.

[19] A. N. Ivanov and E. N. Gapon, *C. A.*, **36**, 4005 (1942).

are held less firmly. The removal of rare earth ions by regeneration of the base-exchange material may also be carried out in a fractional manner with the largest, most loosely-held ions being removed first.

WEST LAFAYETTE, INDIANA RECEIVED OCTOBER 15, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CARNEGIE INSTITUTE OF TECHNOLOGY]

Heat Capacities and Entropies of Molybdenum and Tungsten Trioxides

BY HARRY SELTZ, F. J. DUNKERLEY AND B. J. DEWITT[1]

The heat capacity measurements reported in this paper were carried out in a calorimeter described in a previous publication.[2] Several improvements have been made, however, in this apparatus. A new calorimeter can has been constructed, wound with no. 40 double silk insulated gold wire containing 0.175% of silver, and the heavy calorimeter shield was rewound with the same wire. These windings have shown consistently constant temperature-resistance readings over a period of a year. To increase the mass of the shield a heavy copper screw top was added, giving a total mass of 4890 g. The vacuum vessel for the calorimeter was rebuilt with a seal in the form of a V, which was partly filled with eutectic composition solder and into which the lid fitted loosely. The solder in this well was melted by a coil of chromel wire wound around the outside. With this type of seal no vacuum difficulties, such as were sometimes encountered with a bolted lid, appeared, and pressures between 10^{-5} and 10^{-6} mm. were readily maintained using a two-stage vapor pump backed by a Cenco Hyvac. For pumping off liquid nitrogen a second large capacity container, completely inclosing the calorimeter set-up, was made vacuum tight by a similar type of seal, and a high capacity three-stage steam ejector was employed in this pumping-off operation. Temperatures as low as 58°K. have been reached by this means.

Materials.—The molybdic oxide used in these measurements was Baker's Analyzed, containing less than 0.1% of impurities. Under the microscope it consisted of very small transparent rhombic crystals. This material was dried in an oven to constant weight and was kept in a desiccator until ready for use. The total charge in the calorimeter was 139.055 g. *in vacuo*, or 1.0316 moles.

The tungstic oxide was prepared by the method described by Schumb and Hartford.[3] A hot solution of reagent grade sodium tungstate was treated with hydrochloric acid, and the precipitated tungstic acid was washed free from chlorides. This was dissolved in hot ammonium hydroxide, and ammonium tungstate was crystallized from this solution. After three recrystallizations the hot solution of the purified tungstate was treated with nitric acid and the precipitated tungstic acid was digested on a water-bath for several hours. This material, which filtered readily, was washed, dried in an oven and finally ignited to 775° for ten hours. It was kept in a desiccator in the dark until ready for use. Under the microscope it showed very fine rhombohedral crystals. The charge of the oxide used in the heat capacity measurements was 135.446 g. *in*

TABLE I

MOLAL HEAT CAPACITIES OF MoO_3

Temp., °K.	Molal C_p	Temp., °K.	Molal C_p	Temp., °K.	Molal C_p
70.05	4.73	134.07	10.00	212.87	14.35
74.48	5.09	142.25	10.40	220.05	14.66
79.75	5.53	144.65	10.68	224.12	14.79
83.95	5.90	151.50	11.12	230.39	15.08
87.70	6.27	154.87	11.32	234.69	15.25
91.15	6.48	159.51	11.66	240.15	15.53
97.55	7.20	163.47	11.90	250.67	15.96
101.79	7.58	169.45	12.30	254.86	16.15
105.58	7.90	179.40	12.78	260.30	16.31
109.22	8.23	182.50	13.08	268.20	16.60
114.00	8.61	186.37	13.16	280.32	17.01
117.65	8.75	192.46	13.47	294.72	17.50
124.72	9.19	201.05	13.85	298.73	17.60
129.30	9.70	208.92	14.21		

TABLE II

MOLAL HEAT CAPACITIES OF WO_3

Temp., °K.	Molal C_p	Temp., °K.	Molal C_p	Temp., °K.	Molal C_p
62.90	4.21	120.52	9.58	212.20	15.75
63.37	4.34	126.86	10.18	216.13	15.99
68.98	4.87	136.30	10.90	230.95	16.70
71.55	5.21	144.96	11.43	236.40	16.90
75.25	5.44	152.88	12.06	242.85	17.25
79.68	5.94	160.16	12.68	251.79	17.50
84.20	6.26	167.68	13.15	267.50	18.19
88.90	6.68	177.86	13.75	273.68	18.46
93.80	7.18	183.46	14.09	287.03	19.10
105.22	8.30	189.08	14.40	299.20	19.55
112.44	8.73	203.95	15.26		

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(1) Abstracted, in part, from a thesis presented by B. J. DeWitt to the committee on Graduate Instruction of the Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science, June, 1941.

(2) McDonald and Seltz, THIS JOURNAL, **61**, 2405 (1939).

(3) Schumb and Hartford, *ibid.*, **56**, 2613 (1934).