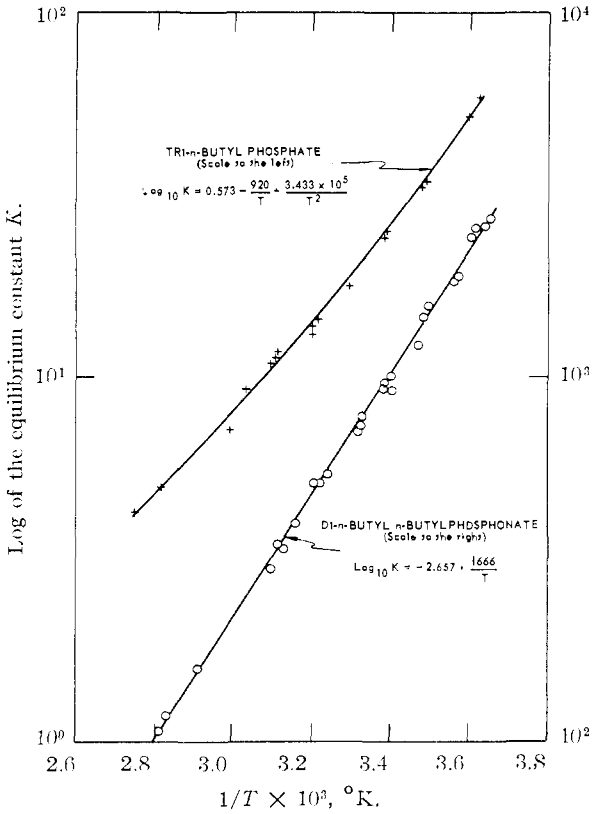

Fig. 2.—Extraction of $UO_2(NO_3)_2$ by tri-*n*-butyl phosphate and by di-*n*-butyl *n*-butylphosphonate.

ether is a very poor solvent for uranyl nitrate as compared to the alkyl ethers. Gordy and Stanford[6] give spectroscopic evidence that benzylamine forms abnormally strong hydrogen bonds with methyl alcohol, but weak bonds are formed by benzyl esters and benzaldehyde with methyl alcohol. It is tempting to conclude that for some reason the benzyl radical has the expected effect when nitrogen is the electron donor, but not when oxygen is the donor. Because of common elements of structure, it would not be surprising if the allyl radical followed the same trend.

On the Connection between the Extractant Strength for Uranyl Nitrate and for Nitric Acid.—Figure 1 shows that any simple connection between bonding to the uranyl ion and bonding to nitric acid is no more than a rough approximation. The rough approximation may have a certain practical usefulness, but represents only a partial fundamental connection. In this figure ΔF at 25° for the extraction of uranyl nitrate is plotted against ΔF for the extraction of nitric acid. A straight line has been drawn through the data. The size of the circles indicates the approximate standard error in the data; several of the data depart drastically from a linear relationship.

It is evident from the data in Tables I and II that a similar plot of ΔH's would fail. This is true even though a simple relation between ΔH's is more to be expected than one between ΔF's, since ΔH is directly connected with differences in bond strength and not ΔF.

Change in Heat Capacity.—For those compounds with a listed value for ΔC_p in Table I it is felt that the experimental data definitely establish that there is curvature in ΔF (or log K) as a function of $1/T$. Plots of the experimental data for TBP and DBBP are given in Fig. 2. The temperature range of the experiments with these two extractants was extended to >80° in order to obtain a better statistical situation. In other cases the least squares equations for log K were carried out as $\log K = a + b/T + c/T^2$. This was done only because a slightly better fit was obtained for purposes of interpolation. In these other cases the reality of the curvature is not sufficient to assign a value to ΔC_p. Even in the cases of definite curvature the values given for ΔC_p are only approximations.

The linearity of log K as a function of $1/T$ in the case of DBBP and the definitely established curvature in the case of TBP and trineopentyl phosphate show that at least one order-disorder reaction, more or less, is more important for the extraction reaction in one case than in the other. There is a mechanism for either absorbing or generating heat that is important in one case and not in the other.

AIKEN, SOUTH CAROLINA

(6) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARKANSAS]

The Activation Energy of the U(IV)-U(VI) Electron Exchange Reaction in the Water–Ethanol System

BY ANTONIO INDELLI AND EDWARD S. AMIS

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The rate of the exchange reaction between U(IV) and U(VI) is measured at 25, 30, 35 and 40° in mixed ethanol–water solvents of composition 30, 60, 90 and 98 volume % in ethanol. The activation energy decreases when the alcohol concentration is increased, and this corresponds to the increase in rate already observed. Light and wall effects, which could account for some orders close to zero, are ruled out by appropriate runs.

In a previous paper[1] Mathews, Hefley and Amis have reported that the U(IV)–U(VI) exchange reaction has orders which vary with the solvent composition in the water–ethanol system. It is obviously impossible to compare rigorously the rate constants in different media, as a consequence of

(1) D. M. Mathews, J. D. Hefley and E. S. Amis, *J. Phys. Chem.*, **63**, 236 (1959).

TABLE I

RATES OF THE REACTION U(IV) $\rightleftarrows$ U(VI) AS A FUNCTION OF THE ALCOHOL CONCENTRATION AND THE TEMPERATURE

Alcohol concn.	30%		60%		90%		98%	
T, °C.	$10^5 R$	$10^5 R_{\text{int}}$	$10^5 R$	$10^5 R_{\text{int}}$	$10^5 R$	$10^5 R_{\text{int}}$	$10^5 R$	$10^5 R_{\text{int}}$
25	9.4	9.5	11.3	11.5	1.37	1.40	7.94	7.56
30	20.8	20.6	25.0	24.0	2.70	2.64	10.8	11.3
35	45.4	43.3	47.4	48.6	4.75	4.91	16.3	16.6
40	85.8	88.9	96.5	96.4	9.13	8.97	23.8	24.2
45	..	..	..	..	..	..	36.8	34.8

the change of dimensions due to the changes in order. Nevertheless, it appears that in the concentration range prevailing in the quoted experiments (U(IV), 0.006–0.02; U(VI), 0.005–0.03; HCl, 0.05–0.3 moles/l.) the reaction rate increases when increasing the amount of ethanol, at least up to 90 volume %. It seemed therefore useful to measure the reaction rate at different temperatures, to ascertain whether this increase in the reaction rate is accompanied by a decrease in the activation energy. Moreover, since at high alcohol concentrations orders close to zero were found with respect to U(VI),[1] it seemed useful to check for eventual wall or light effects.

Experimental

Solid UCl_4 and $UO_2Cl_2 \cdot H_2O$ were prepared as described elsewhere.[2] For the runs at 30 and 60% alcohol, weighed amounts of UCl_4 were dissolved in oxygen-free dilute HCl, of known concentration. The total U concentration of the resulting solutions was checked by evaporating an aliquot to dryness with an infrared lamp, adding some dilute nitric acid, evaporating again and finally igniting and weighing as U_3O_8. Values slightly larger (less than 0.5%) than those calculated from the weight of UCl_4 usually were found. The U(IV) concentration was measured adding an aliquot of the solution to a known excess of $KBrO_3$, mixed with a great excess of KBr. The mixture was left overnight in a well stoppered flask (ground glass stopper with silicone lubricant). Then an excess of KI was added, and the liberated iodine was back titrated with standard $Na_2S_2O_3$. Duplicate titrations showed good agreement (within 0.5%) and indicated that about 98% of the total uranium was in U(IV) form. These solutions of UCl_4 were used as rapidly as possible and always were kept under nitrogen. Repetition of the $KBrO_3$ titration after 8 days showed that they undergo negligible oxidation. The ratio between the concentrations of U(IV) and U(VI) was in agreement with the ratio of the radioactivities of the two separate fractions, after the equilibrium was established in the kinetic runs. For the runs at 90 and 98% alcohol, weighed amounts of UCl_4 were dissolved in oxygen free alcoholic solutions of HCl. Only the total uranium content of these solutions was determined, and the relative amounts of U(IV) and U(VI) were estimated by the ratio of the radioactivites in the kinetic runs. In this case too about 98% of the total uranium was found to be in U(IV) form. For the runs at 30, 60 and 90% alcohol, solutions of $UO_2Cl_2 \cdot H_2O$ in water were prepared and analysed by evaporation and ignition to U_3O_8. For the runs at 98% alcohol, a weighed amount of $UO_2Cl_2 \cdot H_2O$ was dissolved in the same alcoholic solution of HCl used for UCl_4. No appreciable decomposition was observed after 20 days. Apparently the hydrochloric acid had a stabilizing effect on these solutions.[2]

The kinetic runs were performed as described elsewhere,[1] the only difference being that the saturator, used to adjust the water and ethanol partial pressures in the nitrogen stream, was immersed in the thermostatic bath. The volume of the mixture left in the reaction vessel after every complete run was systematically measured and compared with the initial volume minus the volume of the samples withdrawn for the analysis; the agreement was in almost every case good, confirming the balance of the vapor pressures. When some discrepancy was found, the corresponding kinetic run was discarded. HF was employed for the separation of U(IV) from U(VI).[3] Six droplets of 48% HF (amounting to about 0.075 ml.) were added from a thin polyethylene capillary to 1-ml. samples. After shaking the samples were allowed to stand for 30 minutes, after which they were centrifuged. 50 λ of the clear supernatant solution was spotted on platinum planchettes, dried, ignited and counted. The precipitate was washed with dilute HF, dissolved in a few drops of concentrated nitric acid and dried in an oven. Then 1 ml. of 6% HNO_3 was added, and 50 λ of the resulting solution was spotted on platinum planchettes, dried, ignited and counted. Usually the half-lives (measured in minutes) calculated from the counts of U(IV) and U(VI) were in good agreement (within 10%) and the average was taken. However, for the lowest concentrations in U(IV), the counts for the U(IV) fractions were sometimes rather scattered, due possibly to some oxidation of UF_4 during the washing. In those cases only the half-life calculated from the U(VI) fraction was taken in account. The platinum planchettes were cleaned by boiling in concentrated HNO_3 for some hours and afterwards leaving in concentrated HF for 0.5 hr. After this treatment, no appreciable background could be observed (less than 5 counts per minute, as compared with about 3000 counts per minute, as an average, for the spotted planchettes). The concentrations (in mole/l.) of the different reactants were

(1) at 30% alcohol, UCl_4 0.01744, UO_2Cl_2 0.01084, HCl 0.0604
(2) at 60% alcohol, UCl_4 0.01284, UO_2Cl_2 0.01074, HCl 0.1057
(3) at 90% alcohol, UCl_4 0.00422, UO_2Cl_2 0.0020, HCl 0.215
(4) at 98% alcohol, UCl_4 0.00900, UO_2Cl_2 0.00246, HCl 0.1404

The light and wall effects were tested in 98% alcohol solutions at 40 and 25°, respectively. To detect the influence of light, one run was conducted in a glass vessel covered with black wax and wrapped in aluminum foil. To detect the influence of the surface of the walls, one run was conducted in a vessel half filled with chopped glass, which had been previously boiled with HNO_3 and carefully washed with distilled water.

Results and Discussion

The results of the various kinetic runs are reported in Table I, which gives the reaction rates R, calculated by the equation[1]

$$R = \frac{ab}{a + b} \frac{0.693}{t_{1/2}}$$

The R's at different temperatures were correlated by an Arrhenius type formula

$$\log R = A - \frac{B}{T}$$

with the least squares method. The values for the rates calculated from the parameters A and B are also given in Table I as R_{int} (R interpolated). As can be seen from Table I, the reaction rates are fitted by the above equation within a standard deviation of about 3%, the maximum deviation not exceeding 5%. The real error, however, may be somewhat larger, due to the uncertainty in the concentrations, which does not influence the plot. The activation energies, as well as the parameters A and B, are reported in Table II, together with the

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(2) D. M. Mathews, J. D. Hefley and E. S. Amis, *J. Inorg. Nuclear Chem.*, in press.

(3) E. Rona, THIS JOURNAL, **72**, 4339 (1950).

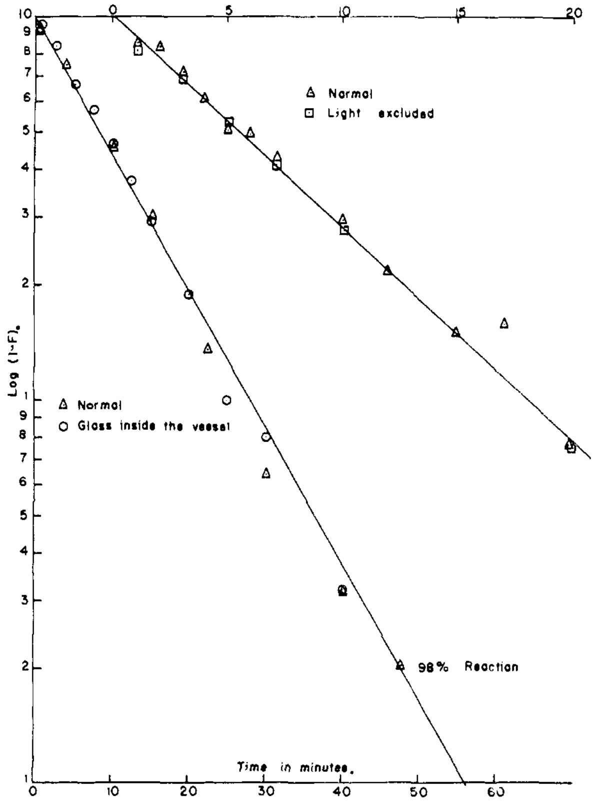

Fig. 1.—Logarithms of the fractions unexchanged *versus* time in minutes.

values for pure water, measured by Rona.[3] It is seen that the great increase in rate at the high alcohol concentrations, found previously,[1] can be correlated with the decrease in the activation energy. The shape of the curve activation energy *versus* alcohol concentration is rather similar to that found for the conductivity of UO_2Cl_2 in the water–alcohol system.[4] Figure 1 shows that under the conditions used in this investigation there are no detectable wall or light effects, so that the orders close to zero, found previously,[1] must be interpreted otherwise.

A comparison of the activation entropies for this reaction under different conditions seems impossible due to the fact that the over-all orders in water and in the various mixtures (30, 60, 90, 100% ethanol) are, respectively, 0.0, 0.3, 0.98, 1.93, 1.44.[1,3] A change in the concentration units would alter not only the absolute values of ΔS^* but also their comparative magnitude.

TABLE II

ACTIVATION ENERGY OF THE REACTION U(IV) → U(VI) AS A FUNCTION OF THE ALCOHOL CONCENTRATION

Alcohol concn., vol. %	*A*	*B*	ΔE, kcal.
0	...	..	33.4[a]
30	16.21	6032	27.6
60	15.32	5741	26.3
90	12.07	5047	23.1
98	6.41	3141	14.4

[a] From Rona, see ref. 3.

This reaction is not a simple one and hydrolysis equilibria probably are involved, as it seems proven by the influence of the hydrogen ion concentration. The measured activation energy itself is therefore not a simple quantity but could involve the energetic parameters related to the hydrolysis processes. However, the magnitude of the change is so great that it strongly suggests that non-electrostatic and specific phenomena prevail in determining the change in rate due to the change in the solvent composition. The electrostatic part of the activation energy is in fact usually of the order of 5–6 kcal.[5] The study of this reaction in other solvent systems could be therefore of a certain interest.

The authors wish to thank the Atomic Energy Commission for the financial support of this investigation.

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(4) N. Goldenberg and E. S. Amis, Presented before the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959.

(5) E. S. Amis, "Kinetics of Chemical Change in Solution," the Macmillan Co., New York, N. Y., 1949, p. 106.

[CONTRIBUTION FROM THE GENERAL ENGINEERING LABORATORY, GENERAL ELECTRIC COMPANY]

Reactions of Solid Alkaline Earth Oxides. I. BaO and SrO[1]

BY HANS J. BORCHARDT AND BARBARA A. THOMPSON

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The "solid state" reactions whereby BaO and SrO react with salts of oxyacids to yield the reciprocal pairs are re-examined. The generally held view that the reactions proceed by solid state diffusion processes is shown to be incorrect. The reactions only occur in the manner described by Hedvall[2] when impurities originating from the atmosphere (H_2O, CO_2) are present. The rate behavior can be understood readily in terms of the formation of a liquid phase.

The study of the reactions of solid alkaline earth oxides represents one of the more prominent chapters of classical solid state chemistry. The work originated with Hedvall and Heuberger[2] in 1922 and was followed by a decade of intense investigation which involved the laboratories of Tammann, Jander and other European scientists. Details on the results of these studies can be found in most modern references[3–6] on solid state chemistry. Hed-

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(1) Presented in part at the 135th National Meeting of the American Chemical Society, Boston, Massachusetts, April, 1959.

(2) J. A. Hedvall and J. Heuberger, *Z. anorg. Chem.*, **122**, 181 (1922); **128**, 1 (1923); **140**, 243 (1924).

(3) J. A. Hedvall, "Einfuhrung in die Festkorperchemie," Fr Vieweg and Sons, Braunschweig, 1952.