istence of a species with a strongly basic site such as $RH^+CO_2^-$ seems unlikely where the solvent is of sufficiently high acidity to cause appreciable protonation of the carboxylic acid itself.[18] We therefore conclude that, while the mechanism for decarboxylation of azulenecarboxylic acid proceeds only *via* the ampholyte $RH^+CO_2^-$ and evidence suggests that this type of species is frequently involved for other systems, it is questionable whether it is an essential intermediate for all aromatic decarboxylations.

# Thermal Diffusion in Nuclear Reactor Fuels

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**Abstract:** Experiments of Beisswenger, Bober, and Schumacher on the thermal diffusion of mixtures of $CeO_2$–$UO_2$ and $PuO_2$–$UO_2$ are discussed in the light of the authors' kinetic model of thermal diffusion. The heats of transfer $Q^+$ are derived from these experiments: for $CeO_2$–$UO_2$ at 2050°K, $Q^+ = 25$ kcal/mol; for $PuO{-}_2UO_2$ at 2673°K, $Q^+ = 58$ kcal/mol. In both cases the result of the kinetic model that the heat of transfer should be lower than the heat of activation for the rate-determining step is confirmed. A few remarks on future work are added.

Recently Beisswenger, Bober, and Schumacher obtained first results from a systematic experimental study of thermal diffusion in mixtures of $CeO_2$–$UO_2$ and $PuO_2$–$UO_2$.[1] One reason their data are of special interest is that they were able for the first time to reach a common interpretation of their own and other experimental work and to draw important conclusions of a general nature concerning the segregation of uranium and plutonium mixtures in oxide fuel of nuclear reactors. I would like to make a few remarks concerning the interpretation of these results, and I am very happy to contribute thereby to this memorial issue to Peter Debye. It was in Debye's laboratory about 30 years ago that we did our first experimental and theoretical work on thermal diffusion in condensed phases, work that gained much by the interest and stimulating advice of Debye.[2] The present work of Beisswenger, *et al.*, is directly linked with these studies. At that early date no one was able to foresee that today in nuclear reactors, inside mixed oxide fuel pins, temperature gradients of hitherto unknown size appear that could make segregation of uranium and plutonium by thermal diffusion a primary technical and safety problem.

If segregation in a temperature gradient reaches equilibrium, the molar fractions $\lambda$ and $1 - \lambda$ of the two components are connected with the Soret constant

$$S = \frac{1}{\lambda(1 - \lambda)}\frac{d\lambda}{dT} \tag{1}$$

In this case diffusion and thermal diffusion are in equilibrium

$$-D \text{ grad } \lambda - D'\lambda(1 - \lambda) \text{ grad } T = 0 \tag{2}$$

with $D$ = diffusion constant and $D'$ = thermal diffusion constant. One gets

$$S = -D'/D \tag{3}$$

It is well known from the work of Eastman and Wagner[3] that the heat of transfer $Q^+$ that characterizes the equilibrium is connected with $S$ by

$$S = Q^+/RT^2 \tag{4}$$

In our above-mentioned earlier work, a kinetic interpretation of eq 4 has been developed for the case that the diffusion process involves activated steps of migration or of exchange of places in which case the temperature dependence of the diffusion constant is as follows

$$D = D_0 \exp(-q/RT) \tag{5}$$

where $D_0$ does not depend strongly on temperature and $q$ = energy of activation.

From the kinetic interpretation it follows that in general $q$ consists of different parts that refer to different positions of the migration step; namely, $q_H$ = energy necessary at the primary position of the migrating particle; $q_R$ = energy necessary to open the lattice to let the migrating particle pass, $q_L$ = energy necessary to open a hole at the new position. From this kinetic model a relation between $Q^+$ and the difference $q_H - q_L$ follows.

$$Q^+ = q_H - q_L \tag{6}$$

More generally we expect a relation of the type

$$Q^+ \leq q \tag{7}$$

In case there is not just one atom migrating through a lattice, but the elementary step consists of the exchange of places of particles, the model has to be adapted correspondingly, but the conclusions that yield eq 6 and 7 are in principle the same. With respect to

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[1] (a) A. A. Bauer, H. Beisswenger, *et al.*, Argonne Conference on Safety, Fuels and Core Design of Fast Reactors, Oct 1965, ANL-7120, Argonne National Laboratory, Argonne, Ill., p 400; (b) H. Beisswenger, M. Bober, and G. Schumacher, *J. Nucl. Mater.*, **21**, 38 (1967); (c) H. Beisswenger, M. Bober, and G. Schumacher, Proceedings of the IAEA Symposium on Plutonium as a Reactor Fuel, Vienna, 1967, p 273.

[2] P. Debye, *Ann. Physik*, **36**, 284 (1939); H. Korching and K. Wirtz, *Naturwiss.*, 27, 110 (1939); K. Wirtz, *Physik. Z.*, **44**, 221 (1943); *Z. Physik*, **124**, 482 (1948).

[3] E. D. Eastman, *J. Am. Chem. Soc.*, **48**, 1482 (1926); **50**, 283, 292 (1938); C. Wagner, *Ann. Physik*, **3**, 629 (1929); **6**, 370 (1930).

more recent discussions in the literature,[4] it may be pointed out that this model and especially the relation 6 and 7 can only hold in cases where the model is applicable. There may exist entirely different elementary causes for the origin of a heat of transfer. The model holds only if the elementary step of diffusion is an activated one and the main part of the energy transfer is linked with the activated step.

From the work of Beisswenger, *et al.*, we can derive for the thermal diffusion of cerium oxide in uranium oxide and of plutonium oxide in uranium oxide the quantities shown in Table I. Instead of $D'$, Beisswenger uses a factor $\alpha$ that is related to $D'$ by

$$\alpha/T = D'/D \qquad (8)$$

For both values of $Q^+$, relation 7 is fulfilled.

**Table I.** Thermal Diffusion Data for Stoichiometric Mixtures of $(Ce_{0.13}U_{0.87})O_2$ and of $(Pu_{0.15}U_{0.85})O_2$

| | $T$, °K | $D$, cm²/sec | $\alpha$ | $q$, kcal/mol | $Q^+$, kcal/mol |
|---|---|---|---|---|---|
| Ce | 2050 | $5.4 \times 10^{-8}$ | 6 | 110 | 25 |
| Pu | 2673 | $3.4 \times 10^{-10}$ | 11 | 100 | 58 |

Because we do not know details about the elementary step of migration of cerium oxide and plutonium oxide in uranium oxide, we shall not try to speculate about the individual parts $q_H$ and $q_L$ of the activation energy $q$. The values of $q$ and $Q^+$ are far too uncertain anyway and may show a strong dependence on temperature. But these very preliminary results show in what direction any future work should go. Beisswenger, *et al.*, were able not only to give an interpretation of their own work with the help of their values of $\alpha$, $q$, and $D$ but also to describe the results of Zebroski, *et al.*[5] This demonstrates the great value of deriving from experimental results the basic physical properties such as activation energy, heat of transfer, diffusion constant, etc. In the technical literature dealing with segregation problems in reactor fuels this relation to basic physical properties is sometimes omitted. Cerium migration may be characteristic of the migration of cerium and other fission products in nuclear fuel, the plutonium migration of the enrichment of plutonium at the hottest part of the fuel element. We need more data about $D$, $q$, $\alpha$, and $Q^+$ at different temperatures in the case of cerium as well as of plutonium. It is not unlikely that $Q^+$ will show a marked dependence on temperature. In the case of plutonium, the fairly high value of $Q^+$ at such a high temperature has to be confirmed. It indicates that strong segregation will take place if the temperature is high enough to cause the diffusion process to become effective. This apparently is the case above 2300°. We believe that the history of the coprecipitated mixture of $PuO_2$–$UO_2$ will not influence strongly the behavior at high temperatures because of the annealing process that takes place at this temperature. There is little doubt that in the special case of high-temperature, gas-cooled reactors using mixed oxide fuels this effect might be of the foremost importance. At the moment it is very difficult to reach temperatures above 2400° in an out-of-pile experiment. Therefore, a temperature dependence of the effect mainly of $Q^+$ should be detectable more easily in the case of cerium oxide. These experiments are going on at Karlsruhe. In the case of plutonium, one could first think about experiments inside a reactor. This would have the advantage that radiation effects are included in the results, but so far it seems that for moderately high burn-ups, in-pile and out-of-pile results are not too different because the in-pile results of Zebroski, *et al.*, and the out-of-pile results of Beisswenger, *et al.*, apparently yield the same value of $\alpha$. If this important conclusion turns out to be correct, it would be much more advisable to perform out-of-pile experiments also with Pu, because they can be evaluated more easily and more reliably. The reason for the similar behavior inside an irradiation field and outside may be again that at high temperatures any effect of the radiation will be annealed very fast. Presently at Karlsruhe we are trying to increase the temperature in the out-of-pile Pu experiment to about 2600°

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(4) For a review and more literature, see A. B. Lidiard, Proceedings of the IAEA Symposium on Thermodynamics of Nuclear Materials, Vienna, 1966, Vol. II, p 3.

(5) P. E. Novak, T. A. Lauritzen, J. H. Prostig, J. H. Davies, and E. L. Zebroski, ref 1c, p 392.