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ANNUAL PROGRESS REPORT
FOR PERIOD ENDING MAY 31, 1971

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REACTOR CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT

For Period Ending May 31, 1971

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PART I. MOLTEN SALT CHEMISTRY

FLUORIDE SYSTEMS

RELATIONSHIP BETWEEN SONIC VELOCITY AND ENTROPY IN MOLTEN SALTS

Stanley Cantor

Sonic velocity in molten salts can be estimated from absolute entropy by means of an equation developed from the Debye theory of specific heats. The equation is:

$$C = \frac{k}{h} \left(\frac{4\pi V}{3Nn}\right)^{1/3} T \exp\left(\frac{4}{3} - \frac{S}{3nR}\right)$$

where C is the sonic velocity, V is the molar volume, n is the number of atoms in the chemical formula of the compound (e.g., n = 2 for NaCl), T is the absolute temperature, S is the molar entropy, and R is the gas constant (expressed in the same units as S); k, h, and N are Boltzmann's, Planck's, and Avogadro's constants.

When tested on 29 molten halide compounds for which the required data (i.e., C, V, and S) are available, the equation reliably predicts the sonic velocity and its (negative) temperature dependence; discrepancy between predicted and experimental sonic velocities seldom exceeds 20%. When applied to molten alumina, the equation predicts the magnitude of the sonic velocity but does not yield the correct temperature dependence.

More complex molten salts, such as nitrates and sulfates, require that the molar entropy be modified if satisfactory agreement between predicted and experimental values is to be obtained. If the total molar entropy is diminished by subtraction of the contributions from interatomic vibrations and free rotation of the polyatomic ion, the equation yields predictions in excellent agreement with experiment for these molten salts. This agreement suggests that "gas-like" degrees of freedom present in the liquid have very little effect on sonic velocities in molten salts containing polyatomic anion species.

MOLAR VOLUMES IN NEW METHODS FOR ESTIMATING ENTROPIES OF INORGANIC COMPOUNDS

Stanley Cantor

For binary, crystalline diamagnetic compounds, the standard entropy at 298.15°K can be reliably predicted by a newly developed equation:

$$S^{o}_{298} = A + 1.5\ nR\ \ln MV^{2/3} \qquad (1)$$

where A is a correlation constant dependent on the formal ionic charge of the ions in the compound, n is the number of atoms in the chemical formula, R is the gas constant, M is formula weight in grams, and V is molar volume (from x-ray cell parameters). To apply eq. (1) in predicting the entropy of a particular class of binary compounds (e.g., the alkali halides), it is necessary to obtain of A from a calorimetrically determined entropy for one compound of that class. For example, if we derive A solely from the experimental value of S^{o}_{298} for crystalline KCl the calculated entropy for 15 other alkali halides differs from the experimental entropy by at most 1.2 cal/(mole-degr).

This new method for estimating entropy of crystalline inorganic compounds explicitly uses the molar volume in addition to the molar mass. The most widely used estimational methods[1,2] rely almost completely on molar masses. The form of the mass and volume ($MV^{2/3}$) used in eq. (1) is suggested by dimensional arguments based on the Debye theory of specific heats.

Equation (1), slightly modified, also holds for binary compounds in the molten state:

$$S^{o}_{T}(liq) = A_T + 1.5\ nR\ \ln\ (M\ V_T^{\ 2/3}) \qquad (2)$$

where V_T and A_T are, respectively, molar volume and the correlation constant at absolute temperature T. For molten salt compounds with polyatomic anions (e.g., fluoroborates, carbonates, sulfates) two easily calculated entropy terms involving anionic free rotation and intra-ionic vibration, when added to the right-hand terms of eq. (2), yield an entropy in good agreement with experimental values.

[1] W. M. Latimer, J. Am. Chem. Soc. 73, 1480 (1951).

[2]K. S. Pitzer and Leo Brewer in "Thermodynamics" by Lewis and Randall, 2nd Edition, McGraw-Hill, New York (1961) p. 517.

HIGH-TEMPERATURE PHASE EQUILIBRIA IN LITHIUM-, SODIUM- AND THORIUM-FLUORIDE MIXTURES

R. E. Thoma

The need to understand equilibrium crystallization behavior in the system $LiF-NaF-ThF_4$, to assist in estimation of the consequences of intermixing MSBR fuel and the sodium fluoroborate coolant, prompted a renewed investigation of liquid-solid phase behavior in this very complex system. Crystallization behavior critical to such understanding remained unresolved until crystal structure studies by Brunton and Sears[1] established that the stoichiometric ratio of alkali metal/thorium prevailing in one of the crystallizing solids was 7/6. More recently, we have shown from correlations of the optical properties and x-ray diffraction data, that the primary phase field of a hexagonal phase inferred initially to be that of a ternary compound, $2LiF \cdot NaF \cdot 2ThF_4$,[2] and later from structure studies as that of the compound $7(Li,Na)F \cdot 6ThF_4$,[1] is actually that of an extensive solid solution with a formal host structure, $7NaF \cdot 6ThF_4$, space group, P3c1 (not isomorphous with the large group of rhombohedral crystal phases of this composition). From equilibrium data it was deduced that Li^+ may substitute for Na^+, i.e., to the composition, $LiF-NaF-ThF_4$ (35.9-17.9-46.2 mole %). Experimentally determined lie-lines involving this solid solution were used to construct phase diagrams of isothermal sections and a polythermal projection of the liquidus surface. Fourteen invariant and singular points occur in the system, with temperatures at these points lying in the range 505 to 825°C.

[1]G. D. Brunton and D. R. Sears, Acta Cryst., B25, 2519, 1969.

[2]R. E. Thoma *et al.*, Reactor Chemistry Division Annual Progr. Rept. for Period Ending January 31, 1965, ORNL-3789, p. 23.

DIFFERENTIAL THERMAL ANALYSIS APPARATUS FOR USE WITH SEALED SPECIMENS TO 1500°C

L. O. Gilpatrick

A differential thermal analysis (DTA) unit capable of reaching 1500°C with controlled heating and cooling rates from 1 to 25°C per minute has been designed and constructed. This device, which treats hermetically sealed and outgassed samples in inert containers, has greatly simplified study of phase behavior in systems which have components (such as CeF_3 or ThF_4) melting well above 1000°C.

The heating unit consists of a vertically mounted tube furnace (8 in. in length by 0.75 in. diameter) wound with Pt-10% Rh resistance wire. Temperatures were monitored and controlled by an alumina insulated thermocouple of Pt, Pt-10% Rh in the center of the furnace. Two additional identical thermocouples served as the specimen supports and as the monitors of the differential temperatures. To one of these couples was spot-welded a sealed capsule of platinum containing αAl_2O_3. The other thermocouple carried a similar platinum cell containing the (75 mg) sample under investigation. Temperature measurement and control was provided by a commercial DTA unit previously described.[1]

The specimen containers were prepared from 0.125-in. diameter platinum tubing. After sealing the bottom (by inert gas welding) and loading of the specimen, the capsule was evacuated during heating to 450°C before flattening of the top and sealing. Several cells could be prepared sequentially from a single 6-in. tube by this procedure.

Performance of the system with many compositions in the CeF_3-ThF_4 system has been quite satisfactory. Liquidus, solidus, and subsolidus reactions have been easily and reproducibly measured in the temperature range 800° to 1500°C.

[1] Thermal Analysis, Vol. 1, ed. by R. F. Schwenker, Jr. and Paul D. Sarn, p. 85, Academis Press, N. Y. and London, 1969.

PHASE RELATIONS IN THE SYSTEM CeF_3-ThF_4

L. O. Gilpatrick, C. J. Barton, and H. Insley

Plutonium-trifluoride is of potential use as the initial fuel material for Molten Salt Breeder Reactors, and its phase behavior in MSBR melts is of obvious interest. The radioactivity and the toxicity of this material, however, make careful glove box techniques essential to its study and greatly complicate exploratory researches with this compound. Fortunately, cerium-fluoride is, insofar as phase behavior is concerned, an excellent "stand-in" for PuF_3. We have, accordingly, used this innocuous material for studies of the subsystems necessary to definition of the phase behavior of LiF-BeF_2-ThF_4-PuF_3 quaternary. Examination of the CeF_3-ThF_4 binary, for which a tentative diagram has previously been reported,[1] is continuing as a part of this study.

Minor modifications in furnace design and substitution of Rodar (an alloy of Fe, Ni, Co, and Mo. 51-29-17-3 atom %) for Ni have minimized the failure rate of the quench tubes used in this study, but further improvements in this quenching technique for temperatures above 1000° are still needed.

Use of this modified quenching technique and application of the high temperature DTA apparatus (previous section, this report) have shown some inaccuracies in the tentative diagram previously reported.[1] The compound CeF_3-$2ThF_4$ exists but its lower temperature stability limit appears to be 885°C rather than the 860°C value listed earlier. The peritectic at 1155°C now appears doubtful and the primary phase field of the CeF_3 rich solid solution appears to extend from the liquidus to about 975°C. The extent of this CeF_3 phase field is still incompletely defined; there are indications that the available CeF_3 contains an impurity sufficient to obscure this region. Additional data with a better preparation of CeF_3 should soon permit a complete definition of the phase diagram for this system.

[1] L. O. Gilpatrick, H. Insley, C. J. Barton, MSR Program Semiann. Progr. Rept. Aug. 31, 1970, ORNL-4622, p. 89.

PHASE EQUILIBRIUM IN THE SYSTEM $LiF-BeF_2-CeF_3$

L. O. Gilpatrick, C. J. Barton, and H. Insley

Continuing study[1] of this system by both DTA and quenching techniques has progressed to permit preparation of a tentative phase diagram[2] which is now being finally detailed and refined.

The $LiF-CeF_3$ binary system shows no intermediate compounds; the eutectic is at 755°C and contains 20 mole % of CeF_3. The binary system BeF_2-CeF_3 also shows no intermediate compounds. The very high viscosity of BeF makes attainment of equilibrium very difficult near the binary eutectic; equilibration times of more than three weeks have been used before quenching in this region of the system. The single eutectic now appears to be at 6 $\pm$ 1 mole % of CeF_3 and at 540 $\pm$ 5°C.

The four primary phase fields (CeF_3, LiF, BeF_2, and $2LiF \cdot BeF_2$) in the ternary system have been identified and largely defined. As expected from its very high melting point (1459°C), the field of CeF_3 is by far the largest of the four. The lowest melting compositions in the system adjoin the small phase field of $2LiF \cdot BeF_2$. The lowest melting ternary eutectic has a liquidus at 358°C and consists of 47.5 mole % LiF, 52 mole % BeF_2, and 0.5 mole % CeF_3. Addition of CeF_3 to this melt causes a very sharp rise in the liquidus; at 3 mole % CeF_3 the liquidus has climbed to 640°C.

The modified quenching techniques and the DTA apparatus described in previous sections of this report would permit detailed examination of the entire composition range for this system. We intend, however, to restrict our attention only to the regions of direct interest as low melting reactor fuels (when PuF_3 is substituted for CeF_3).

[1] L. O. Gilpatrick *et al.*, Reactor Chem. Div. Ann. Progr. Rept. May 31, 1970, ORNL-4586, p. 6.

[2] L. O. Gilpatrick *et al.*, MSR Program Semiann. Progr. Rept. Aug. 31, 1970, ORNL-4622, p. 89.

DISPROPORTIONATION OF UF_3 SOLUTIONS IN GRAPHITE CONTAINERS

L. M. Toth

A careful examination by absorption spectroscopy has been used to define the disproportionation equilibria for dilute solutions of UF_3 in $LiF-BeF_2$ mixtures contained in graphite and to demonstrate the magnitude of solvent effects by molten fluoride systems of practical interest to molten salt reactor technology on this equilibrium. In these studies the previously described[1] spectrophotometric cell of graphite with diamond windows served as the container; observation of intensity of the UF_3 and UF_4 spectra served to determine the equilibrium as functions of solvent used and temperature employed.

The equilibrium reaction appears to be

$$4UF_3 + 2C_{(graphite)} \rightleftarrows 3UF_4 + UC_2$$

from measurements of the stoichiometry of the soluble species; the equilibria have been shown to be reproducible when approached from either the forward or reverse direction.

These studies show that in the $LiF-BeF_2$ (66-34 mole %) solvent the UF_3 is always less than 10% of the total dissolved uranium; the ratio of U^{3+} to total uranium is markedly affected by solvent composition and by temperature. For example, in solutions where the total uranium is 0.07 mole % the experimentally determined ratio of UF_3 to total uranium is shown in the table below.

Solvent Composition		UF_3/Total U	
LiF	BeF_2	650°C	550°C
66	34	0.025	0.004
48	52	0.13	0.03

Such data, which provide a refinement of earlier predictions based on thermodynamic calculations,[2] can be related to previously reported[3] coordination effects for dilute U^{4+} solutions, and coordination equilibria determined from spectra of U^{4+} in other fluoride solutions can be used to estimate the stability of UF_3 in such solutions.

[1] L. M. Toth, Reactor Chem. Div. Ann. Progr. Rept. Dec. 31, 1968, ORNL-4400, p. 22.

[2] G. Long and F. F. Blankenship, "The Stability of UF . Part II. The Stability in Molten Fluoride Solution," ORNL-TM-2065, Part II, Nov. 1969.

[3] L. M. Toth, Reactor Chem. Div. Ann. Progr. Rept. May 31, 1970, ORNL-4586, p. 20.

ELECTRICAL CONDUCTANCE AND GLASS TRANSITION TEMPERATURES OF MOLTEN $NaF-BeF_2$ MIXTURES

G. D. Robbins and J. Braunstein

In the development and testing of transport theories for liquids it has been suggested that extension of measurements into the supercooled liquid region could provide useful information.[1] A hypothetical equilibrium glass transition temperature, slightly below the experimental (dynamic) glass transition temperature and related to the temperature dependence of transport processes, was proposed to represent a theoretical lower limit of the liquid state. Electrical conductance measurements in molten NaF_2-BeF_2 mixtures previously reported[2] at temperatures above the liquidus at the compositions 43, 50 and 55 mole percent BeF_2 have been extended into the supercooled liquid region, by means of an all-metal conductance cell,[3] for the glass-forming mixtures 60, 65 and 70 mole percent BeF_2. These mixtures show increasing activation energy from $\sim$13 to $\sim$17 kcal-mol^{-1} with decreasing temperatures to as low as 105°C below the liquidus.

Glass transition temperatures (T_g) have been determined by differential thermal analysis at compositions from 38 to 90 mole percent BeF_2.[4] They decrease from 129 ($\pm$ 2)°C at x_{BeF_2} = 0.38 to 117°C at x_{BeF_2} = 0.50. The region from 50 to 85 mole % BeF_2 shows little variation in T_g (117°-119°C), with the possibility of a decrease to 112-115°C at x_{BeF_2} = 0.90, the limit of detection of the thermal effect with increasing beryllium fluoride content (although pure BeF_2 also is known to form a glass). No glass transition could be observed at mole fractions below about 0.35. Investigation of the relation between the thermal glass transition temperature and the temperature dependence of activation energies is continuing.

[1]C. T. Moynihan, "Mass Transport in Fused Salts," in Ionic Interactions: Dilute Solutions to Molten Salts, ed. by S. Petrucci, Academic Press, New York, 1971; C. A. Angell and C. T. Moynihan, "Transport Processes in Low-Melting Molten Salt Systems," pp. 315-75 in Molten Salts: Characterization and Analysis, ed. by G. Mamantov, Marcel Dekker, New York, 1969.

[2]G. D. Robbins and J. Braunstein, MSR Prog. Semiann. Progr. Rept. Aug. 31, 1970, ORNL-4449, pp. 142-144.

[3]G. D. Robbins and J. Braunstein, MSR Prog. Semiann. Progr. Rept. Aug. 31, 1970, ORNL-4622, pp. 98-99.

[4]Obtained with the apparatus of L. O. Gilpatrick, whose technical advice is gratefully acknowledged; L. O. Gilpatrick, S. Cantor, and C. J. Barton, "D.T.A. Apparatus with Agitation and Sealed Specimens for Molten Salt Phase Studies," pp. 85-96 in Thermal Analysis, Vol. 1, ed. by R. F. Schwenker, Jr., and P. D. Garn, Academic Press, New York, 1969.

STRUCTURAL STUDIES

THE CRYSTAL STRUCTURE OF CsU_6F_{25}[1]

G. D. Brunton

The complex fluoride CsU_6F_{25} crystallizes with space group $P6_3/mmc$; a_o = 8.2424(4), c_o = 16.412(2) Å, Z = 2 and the calculated density = 7.0013 $g.cm^{-3}$. The U^{4+} ion is coordinated by $9F^-$ ions at distances of 2.267(8) to 2.54(6) Å and the Cs^+ ion by $12F^-$ at distances of 3.12(2) and 3.45(4) Å. The final R value is 0.0685 for 212 reflections >3σ.

[1]G. D. Brunton, Acta Cryst. B27, 245 (1971).

THE CRYSTAL STRUCTURE OF $LiYbF_4$[1]

G. D. Brunton

Tetragonal $LiYbF_4$ has the space group $I4_1a$ with lattice constants a_o = 5.1335(2) and c_o = 10.588(2) Å. The calculated density is 6.0928 g/cm^3 and Z = 4. The Yb-F distances range from 2.217(3) to 2.270(3) Å and the Li-F distances range from 1.894(3) to 2.871(4) Å. The Li-rare earth-F_4 compounds are isostructural with scheelite, $CaWO_4$.

[1]R. E. Thoma, G. D. Brunton, R. A. Penneman and T. K. Keenan, Inorg. Chem. 9, 1096 (1970).

THE CRYSTAL STRUCTURE OF ERBIUM OXALATE TRIHYDRATE[1]

H. Steinfink and G. D. Brunton

The compound $Er(C_2O_4)(HC_2O_4)\cdot 3H_2O$ crystallizes in space group P4/n with a_o = 8.6664(3) Å and c_o = 6.4209(8) Å at 24°. The measured density is 2.8(1) g/cm^3 and the calculated density is 2.742 g/cm^3 so that there are two formula weights in the unit cell. The parameters were refined by least squares to R = 0.072 using anisotropic temperature factors for all atoms except for the water molecules. The erbium atom is coordinated to eight oxygen atoms at distances of 2.362(5)-2.418(5) Å and they form a distorted square antiprism around the cation. A water molecule forms the ninth near neighbor at 2.441(9) Å above the larger square face of the antiprism. The acid oxalate and oxalate anions occupy crystallographic sites at random. The "statistically averaged" oxalate group is centrosymmetric and planar with C--C = 1.529(11) Å, C--O equivalent to C==O equals 1.254(7) Å; the values of the angles are O(1)-C-O(2) = 125.9(5)°, O(1)-C-C = 116.8(7)°, and 9(2)-C-C = 117.3(6)°. Hydrogen bonding exists between $H_2O(1)$ and the oxygen atoms of the acid groups at distances of 2.73(7) Å. A very short hydrogen bond, 2.43(4) Å, is observed between two $H_2O(2)$ molecules but the physical significance is difficult to assess because $H_2O(2)$ is disordered in this structure. This compound occurs also for dysprosium, ytterbium, and yttrium analogs but could not be prepared for neodymium.

[1]H. Steinfink and G. D. Brunton, Inorg. Chem. 9, 2112 (1970).

ELECTROCHEMICAL STUDIES

THERMODYNAMICS OF MIXING IN THE MOLTEN SALT SYSTEM $LiF-BeF_2$ FROM ELECTROCHEMICAL MEASUREMENTS

D. D. Sood* and J. Braunstein

Electromotive force measurements of the molten salt concentration cells with transference

$$Be|LiF,BeF_2\ (X_1)\ \vdots\ LiF,BeF_2\ (X_2)|Be$$

have been employed in refinement of the liquidus of the $LiF-BeF_2$ phase diagram, determination of ionic transference numbers, and investigation of thermodynamics of mixing of LiF and BeF_2.[1] In order to extend these studies we are investigating the usefulness of lithium-bismuth alloy electrodes of composition 0.001 to 0.003 mole fraction lithium. Concentration cells without transference

$$Be|LiF,BeF_2\ (X_1)|Li,Bi\ LiF,BeF_2\ (X_2)|Be$$

have been measured with salt compositions between 0.20 and 0.33 mole fraction BeF_2 in the temperature range 500-800°C. The cell reactions for these concentration cells, with and without transference, are identical if, as has been reported,[2] the transference number of Li^+ is unity. Values of $(\Delta EMF/\Delta X)_T$ from both cells, at comparable temperature and composition, are in agreement.

The emf of individual cells

$$Be|LiF,BeF_2|Li,Bi$$

also have been measured. They are stable and reproducible within ± 1 mv, but the slopes of the EMF vs $\ln X_{Li}$ plots is about 8 mv below the theoretical Nernst slope, suggesting a mixed (but possibly reproducible) electrode reaction and are under further investigation.

*On assignment to ORNL from Bhabha Atomic Research Center, Bombay, India.

[1] D. D. Sood, K. A. Romberger, and J. Braunstein, MSRP Semiann. Progr. Rept. for Period Ending Feb. 28, 1971, ORNL-4676.

[2] K. A. Romberger and J. Braunstein, Inorg. Chem. 9, 1273 (1969).

A Ni-NiO REFERENCE ELECTRODE FOR MOLTEN FLUORIDES

B. F. Hitch and C. F. Baes, Jr.

Studies of the Ni-NiO electrode, an electrode of the third kind which may be represented as Be^{2+}/NiO, BeO, Ni, were completed.[1] The reliability of this electrode was established by measurement of the cell

$$Be|LiF\ (.667),\ BeF_2\ (.333)|NiO_{(c)},\ BeO(c),\ Ni$$

which the assumed cell reaction being

$$Be_{(c)} + NiO_{(c)} \rightleftarrows BeO_{(c)} + Ni_{(c)}$$

The measured potentials were least squared to the expression $E° = A + BT$ (with B assigned from available entropy and heat capacity data), giving

$$E° = 1.9075 - 0.000056T\ v\ (T = 780\text{-}980°K)$$

The average deviation from this expression was 2.1 mV.

The free energy changes derived from this expression are about 1.6 kcal/mole more negative than values calculated from the thermochemical data for BeO and NiO. The present results, combined with such data for NiO, give the formation heat of BeO as

$$\Delta H^f_{298}\ (BeO(c)) = -\ 144.7 \pm 0.2\ \text{kcal/mole}.$$

This value is well within the uncertainty range assigned[2] to the presently recommended value of -143.1 ± 4 and is quite close to our previous estimate of -145.3 kcal/mole[3] for ΔH^f_{298} of BeO.

The Be^{2+}|NiO, BeO, Ni° electrode thus appears to be a reliable and convenient reference electrode for use in LiF-BeF_2 mixtures. It is expected that analogous electrodes involving ThO_2 instead of BeO as the second saturating oxide will be usable in molten fluorides containing ThF_4.

[1] B. F. Hitch and C. F. Baes, Jr., Reactor Chem. Div. Ann. Progr. Rept., May 31, 1970, ORNL-4586, p. 13.

[2] H. L. Schick, "Thermodynamics of Certain Refractory Compounds," Vol. I, Academic Press, New York, 1966, p. 1-208.

[3] B. F. Hitch and C. F. Baes, Jr., Inorg. Chem. 8, 201 (1969).

EMF STUDIES IN $NaBF_4$-NaF MELTS

B. F. Hitch, D. Yarbrough,[1] C. E. Bamberger and C. F. Baes, Jr.

Potentiometric studies of the $NaBF_4$-NaF (92-8 mole %) eutectic were initiated to study various chemical equilibria in such melts. A cell which can be represented as

$$B|NaBF_4,NaF|H_2,\ HF,Pt.$$

was assembled to study the behavior of oxide and hydroxide species in molten fluoroborate solutions. It was found, however, that the boron reference electrode was insufficiently reversible in the temperature range of interest (400-600°C). Also, additions of protons to these $NaBF_4$ melts as boric acid or $NaHF_2$ could not be made quantitatively because both of these reagents formed gaseous reaction products. Nickel boride (Ni_3B) appeared to be more reversible in the cell

$$Ni,Ni_3B|NaBF_4,\ NaF|H_2,HF,Pt$$

which will be used to continue this study.

The half cell reaction corresponding to the $Ni,Ni_3B|BF_4^-$ electrode

$$3Ni^\circ + BF_4^- + 3e \rightleftarrows Ni_3B + 4F^-$$

defines the potential at which a fluoroborate melt will be reduced in the presence of nickel or a nickel-base alloy. Similarly, the recently discovered limited solubility of $NaNiF_3$[2] suggests that the half cell reaction

$$Na^+ + 3F^- + Ni^\circ \rightleftarrows NaNiF_3 + 2e^-$$

should define the potential at which, in the same system, nickel will be oxidized. These two half cells are being compared in measurements now in progress.

[1]Department of Chemical Engineering, Tennessee Technological University.

[2]J. H. Shaffer, Private communication.

OXIDE-FLUORIDE SYSTEMS

ABSENCE OF AN EFFECT OF OXIDE ON THE SOLUBILITY AND ON THE ABSORPTION SPECTRA OF PuF_3

C. E. Bamberger, R. G. Ross, C. F. Baes, Jr., J. P. Young*

The solubility of PuF_3 and its absorption spectra in molten $LiF-BeF_2-ThF_4$ (72-16-12 mole %) has been measured in the presence and in the absence of ThO_2 as a saturating oxide. The results showed that the presence of oxide had no effect on the solubility of PuF_3 or on its absorption spectra. This indicates that Pu(III) forms neither a stable solid oxyfluoride nor a stable oxy-species in solution.

The measured solubility of PuF_3 can be represented by

$$\log S_{PuF_3} \text{ (mole \%)} = (3.01 \pm 0.06) - (2.41 \pm 0.005) \times 10^3/T$$

which gives a heat of solution for PuF_3

$$\Delta H_S = 11{,}008 \pm 237 \text{ cal/mole.}$$

These results are nearly identical with those obtained by barton et al[1] for CeF_3 in the same solvent, thus confirming the suitability of CeF_3 as a stand in for plutonium. The spectrum of Pu^{3+} obtained is the first to be recorded in molten fluorides and is similar to that seen for Pu(III) in aqueous solution.[2] The most intense peak in the molten fluoride mixture used occurs at 563 nm with a molar absorptivity of approximately 20.

*Analytical Chemistry Division, ORNL.

[1] C. J. Barton, M. A. Bredig, L. O. Gilpatrick and J. A. Fredricksen, Inorg. Chem. 9, 307 (1970).

[2] W. T. Carnall and B. G. Wybourne, J. Chem. Phys. 40, 3428 (1964).

THE OXIDE CHEMISTRY OF Pa^{5+} IN MOLTEN $LiF-BeF_2-ThF_4$

R. G. Ross, C. E. Bamberger and C. F. Baes, Jr.

Among the several methods that have been proposed for the removal of protactinium from MSBR fuel, the precipitation with oxide[1] deserves further study because it is inherently simple and apparently is specific for protactinium. The present investigation was undertaken to identify the oxide phases that are precipitated under various conditions and to measure the related equilibria. Initial tests showed that the efficiency of the precipitation increased with increased oxidation of the system suggesting that the solid phase was a compound of Pa(V). In order to characterize the solid phase, protactinium was precipitated, with and without excess ThO_2, from concentrated solutions (3000 ppm Pa) in $LiF-BeF_2-ThF_4$ (72-16-12 mole %). The stoichiometry of the reaction

$$PaF_5(d) + \tfrac{5}{4}ThO_2(c) \rightleftarrows \tfrac{1}{2}Pa_2O_5(c) + \tfrac{5}{4}ThF_4(d) \qquad (1)$$

indicated the precipitate to be Pa_2O_5 and the equilibrium results permitted an estimate of the solubility product of Pa_2O_5 as well as of ThO_2 in the fluoride melt used. Combining these results with a previously measured equilibria between UO_2-ThO_2 solid solutions and UF_4 dissolved in the same solvent,[2] the following equilibrium was estimated

$$\tfrac{5}{4}UF_4(d) + \tfrac{1}{2}Pa_2O_5(c) \rightleftarrows PaF_5(d) + \tfrac{5}{4}UO_2(ss)$$

$$\log(X_{PaF_5}\, a_{UO_2}^{5/4}/X_{UF_4}^{5/4}) = 6.0\text{-}7.0\ (10^3/T) \qquad (2)$$

These results indicate the feasibility of precipitating only Pa_2O_5 from a proposed MSBR fuel ($X_{UF_4} \simeq 0.003$) by mild oxidation of a stream of the fuel, followed by the controlled addition of oxide. Work continues in order to demonstrate this.

[1] J. H. Shaffer, G. M. Watson, D. R. Cuneo, J. E. Strain and M. J. Kelly, Nucl. Sci. & Eng. 18, 117 (1964).

[2] C. E. Bamberger and C. F. Baes, Jr., J. Nucl. Mat. 35, 177 (1970).

THE STABILITY AND OXIDE CHEMISTRY OF Pa^{4+} IN MOLTEN $LiF-BeF_2-ThF_4$

C. E. Bamberger, R. G. Ross and C. F. Baes, Jr.

Since a Molten Salt Breeder Reactor (MSBR) fuel will presumably be maintained at relatively reducing conditions in order to minimize corrosion and to counteract the oxidizing effect of fission, it is important to estimate the redox potential of the couple Pa^{4+}/Pa^{5+} and to determine the behavior of Pa^{4+} in oxide-containing melts. The former was estimated by measuring the equilibrium partial pressures of HF in H_2 over a $LiF-BeF_2-ThF_4$ (72-16-12 mole %) melt saturated with Pa_2O_5 and ThO_2. The assumed equilibrium was

$$\tfrac{1}{2}Pa_2O_5(c) + \tfrac{5}{4}ThF_4(d) + \tfrac{1}{2}H_2(g) \rightleftarrows PaF_4(d) + \tfrac{5}{4}ThO_2(c) + HF(g) \qquad (1)$$

Combining this equation with eq. 1 of the preceding section we have obtained the equilibrium quotient for

$$PaF_5(d) + \tfrac{1}{2}H_2(g) \rightleftarrows PaF_4(d) + HF(g) \qquad (2)$$

$$\log Q = -13.1 + 11.2\ (10^3/T)$$

The result indicates that under the mildly reducing conditions that should prevail in a MSBR fuel, the protactinium should be in the tetravalent state.

The precipitation behavior of Pa^{4+} was studied by adding known amounts of ThO_2 to a melt containing 2400 ppm protactinium, while the 4+ state was maintained by flowing hydrogen through the system. The results obtained thus far indicate that Pa^{4+} is much less readily precipitated than Pa^{5+} and forms a PaO_2-ThO_2 solid solution. Work continues in order to determine the corresponding equilibria quotients between the melt and the solid solutions formed at various experimental conditions.

THE OXIDE CHEMISTRY OF NIOBIUM IN MOLTEN FLUORIDES

G. Ting[1], C. E. Bamberger, C. F. Baes, Jr., G. Mamantov[2]

In continued studies of the chemistry of niobium, an important fission product element, we have begun a series of experiments in which sparingly soluble Nb_2O_5 (labelled with ^{95}Nb) is equilibrated with molten $LiF-BeF_2$

(67-33 mole %) and excess BeO in an attempt to determine the position of the equilibrium

$$\tfrac{1}{2}Nb_2O_5(c) + \tfrac{5}{2}BeF_2(d) \rightleftarrows NbF_5(d) + \tfrac{5}{2}BeO(c)$$

and hence the stability of NbF_5 in such melts.

In some of the measurements, excess NiO, a mild oxidant, was added to minimize the contribution of NbF_4 to the solubility of Nb_2O_5. (Previous measurements[3,4] allow us to estimate that the amount of NbF_4 present in solution under such oxidizing conditions should be negligible.) The results obtained thus far give $\log X_{Nb(V)} = 2.20 - 6.68\ (10^3/T)$. This combined with available thermochemical data gives the tentative values

$$\Delta G^f\ (NbF_5(d)) = -439.97 + 53.73\ (T/10^3)$$

$$\log[X_{NbF_5(d)}/P_{NbF_5(g)}\ (atm)] = 0.15 + 5.01\ (10^3/T)$$

The high solubility estimated here for gaseous NbF_5 is consistent with our failure to detect the evolution of $NbF_5(g)$ from the mixture. It remains for us to determine that BeO and Nb_2O_5 were present at equilibrium with the melt and also whether or not oxy-ions of niobium are formed in solution.

[1]Visiting scientist from the Republic of China.

[2]ORNL Consultant, Professor of Chemistry, University of Tennessee.

[3]B. F. Hitch and C. F. Baes, Jr., Reactor Chem. Div. Ann. Progr. Rept., May 31, 1970, ORNL-4586, July 1970, p. 13.

[4]C. F. Weaver and H. A. Friedman, MSRP Semiann. Progr. Rept., Feb. 28, 1970, ORNL-4548, Aug. 1970, p. 124.

NOBLE METAL FLUORIDES

SYNTHESIS AND DISPROPORTIONATION OF NIOBIUM FLUORIDES

C. F. Weaver, J. S. Gill and J. D. Redman

Synthesis studies[1,2] of the lower valence niobium fluorides have been made to establish preparative methods analogous to those previously described for the molybdenum fluorides.[3] The reduction of NbF_5 and disproportionations of the lower fluorides have been reported in the literature but still not well understood.[4] Small (1 g) samples of niobium tetrafluoride were synthesized by the reduction of excess NbF_5 with niobium metal in quartz containers at 200°C. The product was identified by x-ray diffraction. Experiments conducted by heating NbF_4 in closed evacuated quartz tubes with one end at room temperature have suggested that the NbF_4 disproportionates in the temperature range 250 to 350°C under conditions which maintain an NbF_5 pressure of a few hundred microns. The disproportionation of NbF_4 at 350°C was found to produce NbF_5 and a compound identified by x-ray diffraction as NbF_3 (ASTM-9-168). This material was extremely sensitive to air, reacting to form a vapor and NbO_2F, identified by x-ray diffraction. The NbO_2F decomposed above 300° in a vacuum to form $NbOF_3$ vapor (identified with a mass spectrometer) and a residue of niobium oxides. Decomposition of both NbF_4 and NbF_3 at higher temperatures (up to 700°C) and lower pressures ($<10^{-5}$ torr) leave niobium metal as a residue. All such observations at temperatures above 350°C were made with a Knudsen effusion unit attached to a Time-of-Flight (TOF) mass spectrometer. In addition to the development of new procedures, several gram batches of high purity NbF_5, MoF_5, MoF_4, MoF_3, and NiF_2 were synthesized for use in the kinetic and mass spectroscopic studies described below and in other related projects such as Raman spectroscopy, absorption spectroscopy, and potentiometric studies.

[1] MSRP Semiann. Progr. Rept., Aug. 31, 1970, ORNL-4622, pp. 71-74.

[2] MSRP Semiann. Progr. Rept., Feb. 28, 1971, ORNL-4676, (in press).

[3]Reactor Chem. Div. Ann. Progr. Rept., May 31, 1970, ORNL-4586, pp. 17-20.

[4]F. Fairbrother, "The Chemistry of Niobium and Tantalum," Elsevier Publishing Company, New York, 1967.

STABILITY OF MOLYBDENUM AND NIOBIUM FLUORIDES IN MOLTEN Li_2BeF_4 SOLUTION

C. F. Weaver and J. S. Gill

Studies of the kinetics of the disproportionation MoF_3 solutions[1] in the temperature range of 500 to 700°C and in the concentration ranges of 1 to 1500 ppm were continued.[2,3] Our earlier work at 500°C showed that the Mo^{3+} left the Li_2BeF_4 solvent by a half-order process which was not significantly affected by the flow rate of helium, surface area of the copper container, the quantity of molybdenum metal produced by disproportionation, or the presence of 1-2 mole % UF_4.

We have shown that the addition of graphite to the solution at 500°C had no significant effect on the rate of loss of molybdenum. The behavior of similar solutions at higher temperature suggested that the mechanism of removal of Mo^{3+} differed in the 600 to 700°C range from that observed near 500°C. Experiments at 700° showed that the loss of molybdenum occurred more rapidly, the order of removal was variable and higher, and the removal rate was flow dependent.

The reaction

$$Nb + XHF \rightleftarrows NbF_x + \frac{x}{2}H_2$$

in molten $2LiF \cdot BeF_2$ was studied[1-3] over the temperature range 500 to 900°C and at concentrations up to 3,000 ppm. Instability was noted at 700 and 900°C but not at 500°C. Since there was no evidence of corrosion of the copper container it is assumed that the loss was a result of either disproportionation or evaporation of the niobium compound. The expected increase in nobility of the niobium with temperature was manifested by a value of $\approx 10^{-2}$ $atm^{\frac{1}{2}}$ for $P_{HF}/P_{H_2}^{\frac{1}{2}}$ at 900°C and 3,000 ppm of niobium in solution. This behavior with respect to reduction by hydrogen indicates

that niobium is only slightly more noble than chromium and much more reactive than iron in fluoride melts.

[1]Reactor Chem. Div. Ann. Progr. Rept., May 31, 1970, ORNL-4586, pp. 17-20.

[2]MSRP Semiann. Progr. Rept. Aug. 31, 1970, ORNL4622, pp. 71-74.

[3]MSRP Semiann. Progr. Rept. Feb. 28, 1971, ORNL4676, (in press).

MASS SPECTROSCOPY OF NIOBIUM FLUORIDES AND OXYFLUORIDES

C. F. Weaver and J. D. Redman

A TOF mass spectrometer was used[1-3] in conjunction with a Knudsen effusion unit to observe the gas species associated with the synthesis and solution studies described above. We have resolved the composite cracking pattern of the complex polymer mixture of pentavalent niobium fluorides. The individual cracking patterns for NbF_5 monomer and dimer were obtained. Use of this information to analyze the results of niobium fluorination with low pressure fluorine ($\approx 10^{-2}$ torr) indicated that the reaction yields essentially pure NbF_5 with a few percent Nb_2F_{10} between 150 and 600°C. At temperatures between 650 and 900°C the trifluoride also was present. Analysis of the gases produced by NbF_4 disproportionation showed that NbF_4 disproportionates above 100°C. That this temperature was somewhat lower than those used in the synthesis experiments described above is a reflection of the lower operating pressure and high sensitivity of the mass spectrometer. In the temperature range 100-300°C the vapor over disproportionating NbF_4 was nearly all NbF_5. Above 300°C the vapor contained NbF_3 in addition to NbF_5. The decomposition reaction

$$NbO_2F(s) \rightleftarrows Nb_3O_7F(s) + NbOF_3(g)$$

was observed to have a $\Delta H°$ of 30 ± 1.5 kcal per mole of $NbOF_3$ in the temperature range 623 to 823°K with a $NbOF_3$ pressure of 8×10^{-3} torr at 823°K.

[1]Reactor Chem. Div. Ann. Progr. Rept. May 31, 1970, ORNL-4586, pp. 17-20.

[2]MSRP Semiann. Progr. Rept. Aug. 31, 1970, ORNL-4622, pp. 71-74.

[3]MSRP Semiann. Progr. Rept. Feb. 28, 1971, ORNL-4676, (in press).

FLUOROBORATES

SOLUBILITY OF BF_3 GAS IN FLUORIDE MELTS

S. Cantor and W. T. Ward

The objectives of these measurements are to relate BF_3 solubility to changes in the thermodynamic properties of molten fluorides and to provide data relevant to the use of BF_3 as a burnable neutron poison for purposes of reactor control. This report is a continuation of last year's preliminary results.[1] We have modified our apparatus to saturate and to strip (BF_3 gas from) salt samples within the same vessel.

Solubilities of BF_3 have been determined in five molten $LiF-BeF_2$ solvents, varying in composition between 63 and 80 mole % LiF. Each solvent has been studied over a temperature interval of 200°C within overall limits of 470-866°C. BF_3 saturation pressures were varied between 1.3 and 3.0 atmospheres.

The chief results obtained thus far are:

1) the enthalpy of solution is exothermic and approximately the same (-16 kcal/mole) in each solvent; in qualitative terms, the higher the temperature the lower the BF_3 solubility, and plots of log Henry's law constant *versus* reciprocal temperature are linear and parallel for all five solvents;

2) at constant temperature and pressure, the BF_3 solubility increases with the concentration of LiF; further, the Henry's law constant appears to be linear with the thermodynamic activity of LiF. This linear behavior is consistent with BF_3 solubility associated with the formation of fluoroborate ions:

$$F^-(\ell) + BF_3(g) \rightleftarrows BF_4^-(\ell)$$

3) Henry's law is obeyed in almost all cases; however, where the

concentration of BF_3 in the melt approaches 1 mole % or greater, there are discernible positive deviations from Henry's law.

[1]S. Cantor and W. T. Ward, Reactor Chem. Div. Ann. Progr. Rept. May 31, 1970, ORNL-4586, p. 30.

SOLUBILITY OF HF IN $NaBF_4$-NaF EUTECTIC

H. W. Kohn and C. R. Benson

Preliminary and approximate values for solubility of HF in the $NaBF_4$-NaF eutectic (92-8 mole %) have been obtained by two relatively simple experimental methods. These values were obtained (1) by saturation of the molten salt with HF at 400°C followed by measuring the pressure increase (corrected for expansion of the gas phase and for the moderate increase in BF_3 pressure) of the closed system as the temperature was increased, or (2) by saturation of the molten salt at 400°C followed by titration for HF of portions of the cover gas after equilibrations at higher temperatures. These values agree reasonably well with a few measurements obtained by saturation of melts followed by stripping of the contained HF for analysis and with calculations using the correlation[1] obtained by Shaffer and Watson which relates the Henry's law constant to free fluoride ion concentration and temperature. (Free fluoride ion concentrations for this calculation were estimated from vapor pressure data determined by Cantor[2] for the $NaBF_4$-NaF system.) The Henry's law constant drops from 0.33 ± 0.03 equivalents per liter atmosphere at 400°C to about 0.09 ± 0.01 equivalents per liter atmosphere at 650°C. Further studies by a more sophisticated technique will be used to verify these values.

[1]Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1960, ORNL-2931, p. 32.

[2]S. Cantor, "Physical Properties of Molten-Salt Reactor Fuel, Coolant and Flush Salts," ORNL-TM-2316, Aug. 1968.

PHASE RELATIONS IN THE SYSTEM $RbF-RbBF_4$

L. O. Gilpatrick, C. J. Barton and H. Insley

An investigation of the equilibrium phase diagram for $RbF-RbBF_4$ was completed and a diagram presented in an earlier report.[1] Final revisions to the system as reported have resulted from measurements made with purer RbF than was previously employed. A new lot of RbF was purified by treatment with dry H_2 and HF at temperatures up to and above the melting point to remove water, hydroxide and carbonates. The resulting material had a melting point of 793°C in agreement with the literature value of 795°C. New compositions were prepared from this purified stock at 5 mole percent intervals ranging up to 20 mole % $RbBF_4$.

These compositions gave the expected higher temperatures in each case when examined by differential thermal analysis (D.T.A). Irregularities in the original study were eliminated by substituting this newer data based on the RbF of improved quality.

An improved calibration procedure for the D.T.A. has made it possible to determine the temperatures in this system to an accuracy estimated to be better than ± 2°C. At high RbF compositions the data fits the Schroder equation[2] to beyond 15 mole % $RbBF_4$ to within this temperature precision and the system, therefore, shows nearly ideal behavior. This work has been prepared for publication.

[1] L. O. Gilpatrick and C.J. Barton, MSRP Semiann. Progr. Rept. Feb. 28, 1970, ORNL-4548, p. 133.

[2] I. Schroder, Z. phsik. Chem. 11, 449 (1893).

MASS SPECTROSCOPY OF FLUOROBORATE MSR COOLANTS

C. F. Weaver and J. D. Redman

Mass spectrometric studies of the volatile species associated with the fluoroborate systems proposed for MSBR coolants was initiated.[1] Polymerization was not observed with BF_3. $NaBF_4$ was found to decompose yielding

BF_3 monomer as the only vapor species. Hydrogen-containing additives proposed as a means of tritium control by exchange were investigated. One of these materials, NaOH, behaved in a complex way. Polymerization, decomposition and reduction occurred. The most prominent of the reduced species was sodium vapor, attributed to the container corrosion reaction,

$$Na_2O + Ni \rightarrow NiO\downarrow + 2Na\uparrow \quad .$$

The possibility of adding hydrogenous material to the fluoroborate coolant as water either intentionally or accidentally as a steam leak suggested that the reaction of moisture with $NaBF_4$ should also be investigated. Steam was reacted with $NaBF_4$ over the temperature range, 25-270° at an approximate leak rate of 10^{-7} torr liter sec^{-1}. The extreme complexity of the reaction was apparent. Nevertheless, at 300°, reaction products of $NaBF_4$ and steam accounted for at least 30% of the total vapor pressure, most of which was HF.

A study of the thermal decomposition of $NaBF_3OH$[2] was made over the temperature range 25 to 800°C. The material started to decompose at 90°C with H_2O as the gaseous product by the reaction:

$$2NaBF_3OH(s) \rightleftarrows Na_2B_2F_6O(s) + H_2O(g)\uparrow \quad .$$

This reaction was followed isothermally at 100° to completion by constantly monitoring the effusing water vapor. The pressure was calculated to be $2.44 \pm 0.04 \times 10^{-5}$ atm. Heating of the reaction product to 800°C yielded only BF_3 and NaF vapors. The BF_3 effused over the entire temperature range 245 ± 5° to 800° the NaF appeared at 725°C and above.

[1] MSRP Semiann. Progr. Rept. Feb. 28, 1971, ORNL-4676, (in press).

[2] L. Kolditz and Cheng-Shou Lung, "Condensation of Fluorohydroborates," Z. Chem. 12, 496 (1967).

A NEW SYNTHESIS FOR $NaBF_3OH$

L. O. Gilpatrick and C. J. Barton

Laboratory studies are continuing in attempts to synthesize hydrogen containing species for the retention of tritium in the MSR coolant salt. One of these species is the first hydrolysis product of $NaBF_4$ in aqueous solution which has been reported to be $NaBF_3OH$.[1,2] Ryss and Slutskaya[3] have reported a successful synthesis of this compound in which boric acid is reacted at 0°C with a saturated solution of $NaHF_2$ according to:

$$2NaHF_2 + H_3BO_3 \xrightarrow[H_2O]{0°C} NaBF_3OH + NaF$$

This synthesis has the disadvantage that it produces a mixture of $NaBF_3OH$ and NaF and the product is further contaminated with some $NaBF_4$ produced by a side reaction when attempts are made to recrystallize it from water solutions.

A new synthesis has been devised for $NaBF_3OH$ which employs the following reactions in a saturated solution of $NaHCO_3$.

$$BF_3 + H_2O \xrightarrow[H_2O]{\sim 0°C} H\ (BF_3OH)$$

$$H(BF_3OH) + NaHCO_3 \xrightarrow[H_2O]{0°C} NaBF_3OH + CO_2 + H_2O$$

One mole of solid $NaHCO_3$ and BF_3 gas are added progressively to 5 moles of water at 0°C to produce a clear solution. Four volumes of cold 95% ethanol are then added. Storage at 0°C gives a good yield of product which has a better purity than that produced by Ryss's method.

[1] A. Travers and L. Malprade, Bull. Soc. Chim. 47, 788 (1930).

[2] C. A. Wamser, J. Am. Chem. Soc. 70, 1209 (1948).

[3] I. G. Ryss and M. M. Slutskaya, J. Gen. Chem. U.S.S.R. 22, 45 (1952).

PART II. CHEMICAL BEHAVIOR OF MOLTEN SALT REACTOR EXPERIMENT

FUEL, COOLANT, AND MODERATOR BEHAVIOR

CHEMICAL SUPPORT FOR THE MOLTEN SALT REACTOR EXPERIMENT

R. E. Thoma

A reference document, "Chemical Aspects of MSRE Operations," summarizing all of the results of laboratory analyses (except the mass of data on fission product and tritium distribution and transport) performed in surveillance of MSRE salt, water, gas and oil systems, has been completed. The report recapitulates conclusions derived from chemical analyses performed from 1965 to 1969 and modified by the results of postoperational examination of some of the reactor components. Surveillance results were evaluated with respect to their significance as indicators of the need and potential for development of specific in-line methods of analysis for molten salt power reactors.

As judged from chemical data, the MSRE was highly successful as a materials demonstration. The flowing salts did not wet their containment systems; fuel salt neither wetted nor penetrated the graphite moderator surface. In operations which employed successively ^{235}U, ^{233}U, and ^{239}Pu as sources of power in the reactor, the circulated fluids remained chemically stable, free of radiation damage, and free of contamination. Average full-power output of the reactor was computed from experimental results of isotopic dilution mass spectrometric analysis of fissile species to be 7.4 Mw(th).

Chemical analyses showed corrosion within the $2LiF \cdot BeF_2$ coolant system to be negligible. This has been borne out by subsequent examination of the salt side of the tubes from the air cooled radiator and of the coolant side of the primary heat exchanger. Similar but more numerous analyses suggested that corrosion within the fuel system was slight (but observable) in agreement with results of many engineering tests. However, postoperational examination by metallographic techniques done by scientists in the ORNL Metals and Ceramics Division has disclosed a curious grain boundary embrittlement or possibly an intergranular attack on the metal exposed to the MSRE fuel. This attack appears to have penetrated the metal to about the depth of a single grain and may be due to reaction with one or more fission

product species. This behavior, which may have serious consequences for a long-lived power reactor, is under careful examination in several Divisions of the Laboratory.

METAL TRANSFER IN THE MOLTEN SALT REACTOR EXPERIMENT

E. L. Compere and E. G. Bohlmann

Cobalt-60 is formed in Hastelloy N by neutron activation of the minor amount of Co-59 (.09%) put in the alloy with nickel; the detection of ^{60}Co activity in bulk metal serves as a measure of its irradiation history, and the detection of ^{60}Co activity on surfaces should serve as a measure of metal transport from irradiated regions. Cobalt-60 deposits were found on segments of coolant system radiator tube, heat exchanger tubing, and on core graphite removed from the MSRE in January 1971.

The activity found on the radiator tubing (which received a completely negligible neutron dosage) was $\sim$160 dpm/cm^2. This must have been transported by coolant salt flowing through heat exchanger tubing activated by delayed neutrons in the fuel salt. The heat exchanger tubing exhibited subsurface activity of about 3.7×10^8 dpm/cc metal, corresponding to a delayed neutron flux in the heat exchanger of about 1×10^{10}. If metal were evenly removed from the heat exchanger and evenly deposited on the radiator tubing throughout the history of the MSRE, a metal transfer rate at full power of about .0005 mils/yr is indicated.

^{60}Co activity in excess of that induced in the heat exchanger tubing was found on the fuel side of the tubing, (3.1×10^6 dpm/cm^2) and on the samples of core graphite taken from a fuel channel surface (5×10^6 - 3.5×10^7 dpm/cm^2). The higher values on the core graphite and their consistency with fluence imply that additional activity was induced by core neutrons acting on ^{60}Co after deposition on the graphite.

The reactor vessel (and annulus) walls are the major metal regions subject to substantial neutron flux. If these served as the major source of transported metal, and this metal deposited evenly on all surfaces, a metal loss rate at full power of about .11 mils/yr is indicated. Because deposition occurred on both the hotter graphite and cooler heat exchanger

surfaces, simple thermal transport is not indicated. Thermodynamic arguments preclude oxidation by fuel.

One mechanism for the indicated metal transport might have 10% (1.5 w/cc) of the fission energy in the annular fuel within a 30 micron range deposited in the metal, and a small fraction of the metal sputtered into the fuel. About .15% of the fission fragment energy entering the metal resulting in such transfer would correspond to the indicated reactor vessel loss rate of .11 mils/yr. If this is the correct mechanism, reactors operating with higher fuel power densities adjacent to metal should exhibit proportionately higher loss rates.

BINARY GAS DIFFUSION IN MSRE MODERATOR GRAPHITE

R. B. Evans III and J. L. Rutherford

Previous communications describe gas-flow properties of several MSRE moderator graphite specimens.[1,2] A combination of results of exhaustive counter-diffusion and permeability determinations covering a single sample revealed that the free-molecule or Knudsen effects dominate the diffusion mechanism for fission gas concentrations at reactor conditions.[1a] Our subsequent studies, therefore, emphasized careful permeability measurements. Under conditions obtainable in these experiments, however, the free-molecule and normal diffusion contributions were of equal importance.

An intriguing feature of a complete permeability survey was that the Knudsen coefficients varied from 10^{-7} to 10^{-4} cm^2/sec, while the open porosity remained constant at $\sim$10 vol %.[1b] Our initial reaction was to attribute this unusual behavior to wide variations in pore sizes. Thus, seven specimens, exhibiting divergent flow properties, were subjected to counter-diffusion tests which would afford a complete characterization of the material.[2] Results were startling -- relative contributions of free-molecule and normal diffusion coefficients remained constant. Variations in the flow-weighted pore radii, r_o, were not greater than a factor of two - a result which was consistent with earlier mercury porosimetry measurements. However, estimates of N/A, the number of channels engaged in flow per unit

area normal to flow, varied from 2×10^{-5} to 2×10^{2}. These variations, combined with those associated with various powers of r_o, accounted for the wide variations of the Knudsen coefficients.

In retrospect, the results are understandable since this material was treated with impregnants to plug flow channels. Graphites so treated exhibit unpredictable and nonuniform flow properties although their densities and porosities are constant.

[1] A. P. Malinauskas, J. L. Rutherford, and R. B. Evans III, Gas Transport in MSRE Moderator Graphite, I. Review of Theory and Counterdiffusion Experiments, ORNL-4148, (Sept. 1967), (b) II. Effects of Impregnation, III. Variation of Flow Properties, ORNL-4389 (May 1969).

[2] R. B. Evans III, L. D. Love, and E. A. Mason, "Graham's Laws: Simple Demonstrations of Gases in Motion, Part II. Experiments," J. Chem. Educ., 46, 423 (1969).

FISSION PRODUCTS

EXAMINATION OF A GRAPHITE STRINGER FROM THE MOLTEN SALT REACTOR

S. S. Kirslis and F. F. Blankenship

A graphite moderator stringer (2 in. x 2 in. x 64.5 in.) from near the center of the MSRE core was removed for careful examination in the hot cells about 1 year after shutdown of the reactor. Visual examination (with a Kollmorgen periscope) showed the graphite to be in good condition, as were the graphite surveillance specimens previously examined. The corners and edges of the stringer were sharp, the surfaces were generally very clean, and the original milling marks were clearly visible. The stringer had clearly not been wetted by the salt except for one small area (perhaps 0.1 square inch) when some grayish-white material may have wetted a section of the surface. A small area of a heavy, dark deposit (which seemed to be partly salt and partly carbonaceous material) was observed on the top surface of the stringer. Chemical and radiochemical analysis of this deposit showed some flush salt and relatively high concentrations of noble metal fission products.

Minute samples (ca. 0.1 mg) were collected from several areas of the graphite surface by light brushing with a small curved file. Attempts were made to identify by x-ray diffraction the chemical form of materials in these surface samples. Many weak lines were observed in the x-ray patterns. Since Mo, Te, Ru, Tc, Ni, Fe, Cr, and carbon were known to be present in significant concentration (by other analyses) in the graphite surface, these elements and their carbides and tellurides were searched for by careful comparison of their x-ray diffraction patterns with the observed patterns.

In all three of the graphite surface samples so far analyzed, most of the lines for Mo C and Ru metal were certainly present. For one sample most of the lines for Cr_7C_3 were seen. The expected chromium carbide in equilibrium with excess graphite was Cr_3C_2, but nearly half the diffraction lines for this compound were missing, including the two strongest lines. Five of the six strongest lines for $NiTe_2$ were observed. Fairly definite-

ly excluded by the observed patterns were Mo metal, Te metal, Tc metal, Cr metal, CrTe and $MoTe_2$. These observations (except for Cr_7C_3) are in general accord with expected chemical behavior. X-radiography of thin cross sections of the graphite stringer showed films of heavy material on graphite surfaces adjacent to the control rod thimble surface, and spotty deposits on one fuel channel surface.

CONCENTRATION PROFILES FOR FISSION PRODUCTS IN THE MSRE MODERATOR STRINGER

S. S. Kirslis and F. F. Blankenship

The graphite stringer described immediately above was sectioned and several specimens were milled and analyzed to determine profiles of fission product concentration vs distance from the surface. Since the stringer had aged for more than a year before these analyses, only long-lived fission products could be measured. However, analysis of some species (notably ^{125}Sb, ^{110}Ag, ^{134}Cs, and ^{90}Sr) was markedly eased by prior decay of interfering short-lived species.

^{125}Sb, ^{106}Ru, ^{110}Ag, ^{95}Nb, ^{127}Te, and ^{99}Tc all showed high concentrations at or near the surface; these values dropped rapidly with depth to values lower by several orders of magnitude in the interior of the specimen. This behavior, and the profiles, are very similar to those observed for ^{99}Mo, ^{132}Tc, ^{103}Ru, ^{106}Ru, and ^{95}Nb in previously studied surveillance specimens. The profile for ^{90}Sr (which has a 33 second ^{90}Kr precursor) was much steeper than those previously observed for ^{89}Sr (which has a 3.2 min. ^{89}Kr precursor) in the surveillance specimens. This difference is that expected if the Kr isotope diffuses in the moderator pores and the decay products ^{89}Rb, ^{90}Rb (both of which are short-lived), ^{89}Sr, and ^{90}Sr are relatively immobile.

Quite different profiles are shown by the long-lived species ^{137}Cs and ^{134}Cs which are produced, respectively, by decay of 4.2 min ^{137}Xe and by decay of 5.27 day ^{133}Xe followed by neutron capture by the resultant stable ^{133}Cs. The concentration of ^{137}Cs increases about 20% from its value at 1 mil depth to that at 20 mils and then decreases steadily to its value at 800 mils depth. The concentration of ^{134}Cs, however, increases from con-

trations equivalent to 4×10^6 disintegrations per minute per gram of carbon at 10 mils depth to about 3×10^8 dpm/g at 800 mils. ^{133}Xe, with its half-life of 5.2 days, should permeate the graphite so that its concentration is nearly uniform; ^{133}Cs should, accordingly, be produced at a nearly uniform rate throughout the moderator pore structure. Since Cs can diffuse with some ease in graphite at these temperatures and since the fuel salt is a sink for this element, the concentration increase of ^{134}Cs (and ^{133}Cs) with depth is plausible. ^{137}Xe, with its half-life of 4.2 min, should show a marked concentration profile diminishing with depth and ^{137}Cs would also show such a profile if it were immobile. Diffusion of this species should, however, modify the profile to resemble that observed.

NOBLE METAL FISSION PRODUCT BEHAVIOR IN THE MSRE

E. L. Compere and E. G. Bohlmann

The noble metal fission product elements, including Nb, Mo, Tc, Ru, Ag, Sb, and Te, were deposited and concentrated on many surfaces removed from the MSRE. Salt samples taken from below the liquid surface in the pump bowl, exhibited activity levels which varied widely, suggesting pick-up of varying amounts of a separate phase rich in the noble metals. However, even the minimum concentrations were at least an order of magnitude too high to be composed of single atoms of noble metals, since these would be expected to diffuse to surfaces in a few minutes and thereby be at very low concentrations.

The transport paths and lags of the noble metal fission products have been examined using all available data on the activity ratio of two isotopes of the same element, 39.6 day ^{103}Ru and 367-day ^{106}Ru. Comparison of the observed ratio with the expected ratio based on fission yields and power history (inventory ratio) provides an estimate of the "age" of the observed material. Data (from the graphite and metal surveillance specimens, exposed for various periods and removed at various times, for material taken from the off-gas system, and for all salt and gas samples and other materials exposed to pump bowl salt), were compared with appropriate inventory ratios and with ratio values calculated for several assumed lags

in a simple compartment model, the equations for which were integrated through the MSRE power history. This model assumed a holdup phase, from which off-gas deposits were accumulated and which comprised the noble metal content of samples and specimens from the pump bowl. It also contributed appreciably to deposits on the graphite and metal surveillance specimens. Adequate agreement of observed data with indications of the model resulted when first order loss rates from the holdup phase corresponding to retention periods of 45-90 days were assumed.

EXAMINATION OF DEPOSITS FROM THE MIST SHIELD OF THE MSRE PUMP BOWL

E. L. Compere and E. G. Bohlmann

Examination of the sampler cage and mist shield excised from the MSRE pump bowl in January 1971 revealed that all surfaces were covered with generally gray-black deposited films over unattacked metal. These films contained carbon, fuel salt fluorides, structural metals, fission products (dominated by noble metal isotopes), ^{137}Cs, and tritium. Much but probably not all the structural metals could be debris from the excising operations. Tritium/carbon atom ratios of $\sim 1 \times 10^{-4}$ are consistent with nontrivial exchange with hydrogen in tars resulting from the cracking of lubricating oil which leaked into the pump bowl. A very high proportion, relative to calculated inventory per gram of fuel salt, was observed for all determinable noble metal fission product isotopes: ^{95}Nb, ^{99}Tc, ^{103}Ru, ^{106}Ru, ^{125}Sb and ^{127m}Te. The relative proportions of ^{103}Ru and ^{106}Ru isotopes, and the quantities of deposit suggest that these deposits were accumulated over a considerable period of time and that several percent of the reactor inventory of noble metal isotopes was deposited in the pump bowl. Thickest deposits were noted on the sample cage rods and inner mist shield walls below the surface. Appreciably thinner deposits at similar levels in the annulus and on the outer surfaces suggested that the more quiescent conditions within the shield permitted deposition of suspended material.

FISSION PRODUCT DEPOSITION FROM FUEL IN THE MSRE PUMP BOWL DURING SHORT INTERVALS

S. S. Kirslis and F. F. Blankenship

Our knowledge of fission product deposition in the MSRE was obtained almost exclusively from samples that had been exposed for many months under widely varying conditions. It was of interest to know whether initial rates and rates under known conditions were different from the long-term ones.

In early attempts to measure deposition from the fuel on samples immersed in the pump bowl, the results were obscured by deposition from the gas phase above the fuel. To remedy this a capsule was devised with a buoyancy activated window that opened only under the surface to expose graphite and Hastelloy N specimens. Exposures of 1/6, 1, 3 and 10 hours were made.

The rate of deposition of noble metal nuclides showed a definite but not very large variation with exposure time. The 10 and 3 hr exposures gave about 5 times as much deposition as the 1 hr and 1/6 hr exposures. In general, the initial rates were high, but after 10 hours the rate had decreased to that found with months long exposures.

Oddly, the ^{89}Sr on all specimens for all exposure times was about the same. We believe this was a result of permeation of the windowed capsule by the parent ^{89}Kr during the time the capsule was passing through the pump bowl gas. Evidently the stripped fuel was depleted in ^{89}Kr compared to the gas.

A POSSIBLE ORIGIN OF SMOKES AND MISTS EMITTED BY MSRE FUEL

F. F. Blankenship and S. S. Kirslis

The fact that fluoride fuels are strongly nonwetting toward clean metals is well established. The consequences of this type of interfacial behavior for very small metallic particles or even single atoms are curious.

A metallic particle which is at the surface is on rather than in the surface, as in more familiar cases, because the interfacial energy is less the smaller the area of contact. A particle at the surface is expelled from the surface, and work would be required to cause the particle to penetrate the surface. Formation of a new interface probably requires at least 200 erg/cm^2 which is the surface energy of the MSRE fuel. We suggest that as a particle moves from a higher potential energy in the liquid to a lower energy state, part of the potential energy difference is converted to kinetic energy.

If, when the liquid surface collapses as the particle is ejected, droplets are jetted (as when a gas bubble collapses) we have an explanation of both the smoke and the mist that arise from the fuel. Also, non-wetted particles on the surface of the molten fuel could, particularly if only a few atoms in size, be dislodged by Brownian motion.

SOME ASPECTS OF TRITIUM BEHAVIOR IN THE MSRE

S. S. Kirslis and F. F. Blankenship

Surprisingly high concentrations of tritium were found in moderator graphite from the center of the MSRE core. The tritium concentration decreased rapidly from about 10^{11} gpm/g at the surface to about 10^9 dpm/g at a depth of 1/16 in. and then decreased slowly to about half this value at the center of the stringer. If all of the graphite in the MSRE contained this much tritium, then about 15% of the tritium produced during the entire power operation had been trapped in the graphite. About half the total trapped tritium was in the outer 1/16 in. layer.

Similarly high concentrations of tritium were found in specimens of POCO graphite (a graphite characterized by large uniform pores) exposed to fissioning salt in the core during the final 1786 hr of operation. Surface concentrations as high as 4.5×10^{10} dpm/g were found, but interior concentrations were below 10^8 dpm/g, much lower than for the moderator graphite. This suggests that the graphite surface is saturated relatively quickly but that diffusion to the interior is slow.

If it is assumed that the surface area of the graphite (about $0.5m^2/g$) is not changed by irradiation (there was no dependence of tritium sorption on flux) there was one tritium per 100 surface carbon atoms. Since the MSRE cover gas probably contained about 100 times as much hydrogen (from pump oil decomposition) as tritium, a remarkably complete coverage by chemisorbed hydrogen is indicated.

PART III. MOLTEN SALT BREEDER STUDIES

REDUCTIVE EXTRACTION STUDIES

DISTRIBUTION OF SODIUM AND POTASSIUM IN THE METAL TRANSFER PROCESS AT 650°C

D. M. Richardson, W. P. Teichert, W. K. R. Finnell, and J. H. Shaffer

The metal transfer process for removal of rare earths and other fission products, along with some possible fuel contaminants, uses successive redox exchanges between four liquid phases. In the first step, the MSBR fuel solvent ($LiF-BeF_2-ThF_4$ from which uranium and protactinium have already been removed) is equilibrated with bismuth containing 0.2 atom % Li; some of the rare earth fission products (or other materials) are extracted with some thorium in this step. In the second step, this bismuth alloy is equilibrated with pure LiCl, the rare earths and some other materials (but not the thorium) pass into the LiCl. Finally, the LiCl is freed from the rare earths by equilibration with a concentrated solution (perhaps 5 atom %) of Li in bismuth. It was of interest to determine the distributions of the possible fuel contaminants, sodium and potassium, in this process. Measurements were obtained for both the fluoride/bismuth and chloride/bismuth extractants at 650°C. The four reductions were performed in 4-in. vessels with mild steel liners. The fluoride salts were $LiF-BeF_2-ThF_4$ (72-16-12 mole %) to which NaF (with ^{22}Na) or KF were added to make 1 mole %. The chloride salts were LiCl to which NaCl (with ^{22}Na) or KCl were added to make 1 mole %. Reductions were made by incremental additions of 0.5- or 1.0-g pieces of clean lithium metal; samples of salt and metal phases were taken after a minimum of five hours of argon sparging at one liter per minute. In the fluoride/bismuth experiments log $(D_{Na}/D_{Li}) = 1.080$, and log $(D_K/D_{Li}) = 0.899$. The separation factors, D_M/D_{Li}, were 30% to 70% smaller that for trivalent rare earths. In the chloride/bismuth experiments log $(D_{Na}/D_{Li}) = -0.168$, and log $(D_K/D_{Li}) = -1.104$. These results show that sodium and potassium would become concentrated in the chloride phase. At equilibrium with 100 ppm as metal in the MSBR fuel solvent there would be 3600 ppm sodium and 20,000 ppm potassium in the lithium chloride, respectively.

EXTRACTION OF RUBIDIUM AND CESIUM FROM MSBR FUEL SOLVENT INTO BISMUTH BY REDUCTION WITH LITHIUM AT 650°C

D. M. Richardson, W. P. Teichert, W. K. R. Finnell, and J. H. Shaffer

Equilibrium distribution of the fission products rubidium and cesium between the MSBR fuel solvent ($LiF-BeF_2-ThF_4$, 72-16-12 mole %) and molten bismuth with added lithium has been measured at 650°C. The salt mixtures initially contained 1.48×10^{-2} mole % RbF (traced with ^{86}Rb) or 0.95×10^{-2} mole % CsF (traced with ^{137}Cs) and had been carefully purified to insure the virtual absence of oxygen-bearing species and easily reducible metals. Reductions were performed by successive additions of small known quantities (0.5 to 1 gram) of clean lithium metal. Samples of salt and of the bismuth phase were taken after at least 5 hours of stirring of the system by sparging with clean argon at 1 liter per minute. Values obtained were: $\log (D_{Rb}/D_{Li}) = 0.936$, and $\log (D_{Cs}/D_{Li}) = 1.178$. Comparison of these values with those from other studies show that at 650°C the order of extractability of the alkali metals into bismuth from this solvent is cesium, sodium, rubidium, potassium. The relative values are, respectively, 1:0.80 : 0.57:0.53.

REDUCTIVE EXTRACTION DISTRIBUTIONS OF BARIUM AND THORIUM BETWEEN BISMUTH-LEAD EUTECTIC AND MSBR FUEL SOLVENT MIXTURE

D. M. Richardson, W. P. Teichert, and J. H. Shaffer

The eutectic mixture of bismuth and lead (56.3-43.7 mole %) offers the advantages of a low melting point (125°C) and zero volume change in freezing; it should also be less aggressive than pure bismuth toward container materials. These properties were sufficiently attractive to merit further examination. The distributions of barium and thorium between the eutectic melt and $LiF-BeF_2-ThF_4$ (72-16-12 mole %) were determined at 650°C in a 4-in. vessel with a mild steel liner. Barium fluoride (with ^{133}Ba) was added to the fuel solvent salt to make 9.1×10^{-3} mole %. Reductions were performed by successive additions of 0.25- to 0.5-grams of clean lithium metal; samples of salt and metal phases were taken after a minimum of five hours of argon sparging at one liter per minute. The equilibrium quotient for

barium with eutectic metal was: $D_{Ba}/(D_{Li})^2 = 9.81 \times 10^2$, 2.4 times less than for pure bismuth. The equilibrium quotient for thorium with eutectic metal was: $D_{Th}/(D_{Li})^4 = 6.64 \times 10^8$, 3.7 times greater than for pure bismuth. Thorium solubility in the eutectic was approximately 1500 ppm, at 650°C.

BISMUTH-MANGANESE ALLOYS AS EXTRACTANTS FOR RARE EARTHS FROM MSBR FUEL SOLVENT

D. M. Moulton and J. H. Shaffer

Bismuth-manganese mixtures have been used to extract cerium from LiF-BeF -ThF (72-16-12 mole %). From a study of the phase diagrams it seemed that adding manganese to the bismuth might raise the thorium solubility without precipitating any solids. An extraction was carried out at 600° with 24 and 32 mole % Mn in Bi and at 700° with 36.5 mole %, using Th metal as the reductant.

Thorium solubility increased substantially over that in bismuth alone, to 1.36 and 2.38 wt. % at 600° and 700°, and these did not seem to be saturated. The maximum distributions (0.075 and 0.13) were not correspondingly high because of the lower average atomic weight of the metal. Oddly, the distribution of cerium leveled off as if saturated, but its concentration was so low (0.1 wt. % in the salt) that it does not seem likely that it formed a primary solid phase.

The equilibrium constants are shown in Table below; they are not very different from the figures in pure bismuth. The two manganese concentrations at 600° gave the same results and are not distinguished. If the levelling off of the cerium turns out not to be real then it should be possible with this solvent to reduce the amount of liquid metal circulating in the reductive extraction process without much penalty in the separation.

Table Logs of Equilibrium Constants in Bi-Mn Solutions

T°C	D^3_{Li}/D_{Ce}	D^4_{Li}/D_{Th}	D^4_{Ce}/D^3_{Th}
600	-7.77 ± .18	-10.17 ± .19	+0.81 ± .09
700	-6.74 ± .15	- 8.90 ± .29	+0.26 ± .39

OTHER SEPARATIONS

REMOVAL OF FLUORIDE FROM MOLTEN-LITHIUM CHLORIDE

F. A. Doss, C. R. Benson, W. R. Grimes, and J. H. Shaffer

The reductive extraction process, as currently proposed for an MSBR fuel reprocessing plant, provides for the separation of fission products from thorium by back-extraction from molten bismuth into molten lithium chloride. If the molten chloride becomes contaminated with fluoride ion (i.e., by entrainment or finite solubility of the reactor fuel solvent in bismuth), then the separation process will become less effective. An experimental program has determined that fluoride ion can be effectively removed from molten lithium chloride by the reaction,

$$BCl_3(g) + 3LiF(d) \rightleftarrows 3LiCl + BF_3(g).$$

For these experiments boron trichloride admixed with hydrogen was bubbled through molten LiCl, at 650°C, to which known amounts of LiF had been added. Samples of the gas influent and effluent streams were periodically collected in water and analyzed for acid content by titration with standard caustic solutions. Filtered samples of the salt were also withdrawn at frequent intervals during the reaction period and analyzed for fluoride ion.

The results obtained from eight experiments demonstrated the effectiveness of this method. Initial concentrations of 5000 to 10,000 ppm by weight fluoride were rapidly diminished to low values (< 40 ppm) within the 4-hour reaction periods at low BCl_3 concentrations (0.8 millimoles/liter N_2 at 1.5 liters H_2/min) in the gas sparge stream. Material balance calculations showed that the exchange process was practically quantitative.

Where estimates of the BCl_3 concentration over the melt could be made, values calculated for the equilibrium relation,

$$K = \frac{N_{BF_2}}{N_{BCl_3}} \cdot \frac{1}{N_{LiF}^{3}} ,$$

approached $K = 10^{14}$ as a limit. During these experiments the boron content of the melt, used repetitively, remained below 200 ppm and corrosion of the nickel reaction vessel could not be detected from analyses of the salt samples.

DISTRIBUTION OF SOLUTES IN BISMUTH ON CRYSTALLIZATION

D. M. Richardson and J. H. Shaffer

In the course of numerous experiments on reductive extraction of metal species into bismuth alloys from molten mixtures of fluorides or from molten lithium chloride we have observed that several solute metals of interest are strongly concentrated near the surface of the samples of bismuth as they freeze. These samples were dipped directly from the pool of bismuth (under the salt and covered with an inert atmosphere) in small (0.2 ml) graphite ladles and were removed to a cool region (still under the inert atmosphere) and allowed to solidify before removal from the apparatus. Successive layers of the (ca 2 gram) pellets were dissolved in weakly acid aqueous solutions of chelating agent (Versene); this dissolution was markedly aided by stirring the system with a 28 kilohertz sonic scrubber. Analysis, by chemical or radiochemical techniques, of these solutions showed that the distribution of several dissolved species was far from uniform. The degree of concentration at the pellet surface decreased in the order: thorium, cerium, chromium, manganese, nickel, lithium, and cesium. For thorium, cerium, and chromium the average concentration in the outer 1% by weight of the pellet was 60 to 70 times the average concentration of the pellet; nearly 65% of each of these species was, accordingly, in this thin outer shell.

Since increasingly stringent attempts to insure that the graphite samplers were oxide-free had no effect on the phenomenon, it seems unlikely

that oxidation of the solutes played a role in this behavior. It is possible, though it appears unlikely, that carbide formation may be involved; no checks of this have been made.

GRAPHITE

GRAPHITE DEVELOPMENT FOR THE MOLTEN SALT REACTOR - THE USE OF HIGH TEMPERATURE CENTRIFUGATION.

R. A. Strehlow

Centrifugation of pitches, resins, and mixtures of these materials with filler materials has been explored in order to assist with development of improved isotropic graphites.[1] Micrographic examination of several types of coal tar pitch after centrifugation during thermal treatment to 500°C showed that the amount of distribution of fine grained material in various pitches did not parallel the results of solubility tests previously used to characterize the starting material. The micrographic examination of samples showed that apparent viscosity differences during final stages of polymerization affected strongly the development of anisotropic carbon structures. Flow of coalesced polymer was found to be important in the carbonization mode of these precursors.

Certain fabrication problems in the mixing of pitch with filler materials such as carbon black have been generally recognized as resulting from a lack of dispersion of the filler during a heat treatment cycle. The centrifugation technique has been used to screen possible additives for efficacy in minimizing this difficulty. Results indicate that dispersion may be effected by fatty acid additions to the mixture. This finding while not new in graphite fabrication technology shows that high temperature centrifugation combined with micrographic examination offers a new kind of information about carbon structure development.

[1] MSRP Semiann. Progr. Rept., Aug. 31, 1970, ORNL-4622, pp. 135-141.

TRITIUM BEHAVIOR

SOLUBILITY OF HYDROGEN IN MOLTEN FLUORIDES

A. P. Malinauskas, D. M. Richardson, and J. E. Savolainen

To understand, and ultimately to control, the behavior of tritium within a Molten Salt Breeder Reactor we need detailed understanding of several interrelated phenomena. One such is the solubility of tritium in the fuel salt of the MSBR. While the solubility of HF and of DF in molten fluorides is relatively well understood, as is the solubility of the rare gases, virtually no data exist on solubility of hydrogen or its isotopes in any molten salt. Furthermore, the ease with which H_2 and its isotopes permeate metals at elevated temperatures--the phenomenon which makes tritium control in the MSBR a real problem--greatly complicates determination of the solubility of these materials.

An apparatus has been designed and constructed for these solubility determinations, and measurements are currently being performed with H_2 as the solute and $2LiF \cdot BeF_2$ as the solvent. The experimental procedure involves saturating a quantity of molten salt with hydrogen in one region of the apparatus and transporting a known quantity of the salt to a separate region of the apparatus where the hydrogen is stripped from the fluid, collected, and the amount determined. Both regions of the apparatus are doubly contained, but for different purposes. In the saturating section, the salt is effectively suspended within a hydrogen-filled container to eliminate losses from the salt; the stripping section is contained within a vacuum chamber which is continuously pumped to collect the previously dissolved hydrogen which permeates the walls of the stripping section.

Preliminary checkout of the apparatus with helium as the solute showed the Henry's law constant at 630°C to be 1.9×10^{-7} moles/cm^3-atmosphere, a value nearly 50% higher than that found in earlier studies in this Laboratory. Further study is under way to resolve this appreciable (but not especially serious) discrepancy.

The preliminary values so far obtained for H_2 suggest a Henry's law constant of about 3×10^{-7} moles H_2/cm^3 salt-atmosphere at 620°C. This preliminary value, which is probably accurate to within a factor of 2, is appreciably higher than anticipated on the basis of molecular dimensions alone. Further measurements with H_2 are in progress to refine this value and to determine the temperature coefficient of solubility.

STUDIES OF HYDROGEN EVOLUTION AND TRITIUM EXCHANGE IN MOLTEN FLUOROBORATE

S. Cantor and R. M. Waller

This investigation seeks to determine the capacity of fluoroborate coolant salt (92-8 mole % $NaBF_4$-NaF) for retaining hydroxide. Any hydroxide remaining in the melt can serve to sequester tritium (produced in molten-salt reactors) via the isotope exchange reaction:

$$HT(g) + OH^-(\text{dissolved}) \rightleftarrows H_2(g) + OT^-(\text{dissolved})$$

The concentration of OH^-, however, is limited because of corrosion reactions with metals (which comprise the coolant circuit of the reactor), e.g.,

$$Cr(\text{in alloy}) + 3OH^-(d) \rightleftarrows Cr^{3+}(d) + 3O^{2-}(d) + \frac{3}{2}H_2(g).$$

In our experiments, evacuated nickel capsules, containing salt (fluoroborate with hydroxide impurities) and metallic coupons, are heated (usually at 600°C) within a silica vessel which is connected to gas-handling and pressure-measuring apparatus. Hydrogen (or tritium) gas permeating the nickel does not escape the apparatus because fused silica is virtually impermeable to hydrogen.

The salient results of a series of such capsule experiments are: (1) in the presence of coupons of pure chromium, all the hydroxide reacted to form gaseous hydrogen which passed through the capsule; the amounts of evolved hydrogen were initially established by gas-chromatographic analyses; the loss of hydrogen from the salt was confirmed by tritium tracer analysis, (2) similarly, in the presence of coupons of Hastelloy N (a Ni-Mo base alloy with ∿7% Cr) all the hydroxide reacted to yield hydrogen but at a somewhat slower rate than was the case with Cr coupons, (3) in an all-nickel

system, low (0.5 microequivalent of H per gram of salt) but potentially useful concentrations of hydroxide were retained in the salt.

PERMEATION OF METALS BY HYDROGEN

J. H. Shaffer, W. Jennings, Jr., A. P. Malinauskas, and W. R. Grimes

This experimental program has been directed toward an evaluation of the dependence of hydrogen permeation rates through metals on hydrogen pressure. A Kovar metal tube (54% Fe, 28% Ni, and 18% Co) has been used in these experiments to facilitate the construction of an effective diffusion cell of Pyrex glass.

Changes in the hydrogen pressure, associated with the diffusion process, are related to the hydrogen pressure by the equations

$$q = -\frac{\partial P_a}{\partial t} \sum_i \frac{V_{a_i}}{RT_{a_i}} = [2\pi\ell DK/\ln \frac{b}{a}][P_a^n - P_b^n] \qquad (1)$$

for the decrease in pressure, P_a, diffusing into a volume at pressure P_b, and

$$q = \frac{\partial P_b}{\partial t} \sum_j \frac{V_{b_j}}{RT_{b_j}}[2\pi\ell DK/\ln \frac{b}{a}][P_a^n - P_b^n] \qquad (2)$$

for the increase in pressure, P_b, as hydrogen diffuses through the metal cylinder from pressure, P_a. Incremental system volumes and temperatures are denoted by V and T; ℓ is the length of the test section having inside and outside radii, a and b; D is the diffusion constant (cm^2/sec), q is the quantity of gas passed (moles/unit time), and K is the proportionality constant which relates dissolved gas concentrations in the metal to gas pressure, P^n.

The results of some 30 experiments conducted thus far at a cell temperature of 495°C have yielded a value of $n = 0.560 \pm 0.011$ and a value of $DK = 5.18 \times 10^{-11}$ (limits of standard error = 4.95 to 5.42×10^{11}) moles/torr-cm at pressures for P_a of 1.4 to 800 torr. These experiments were conducted under conditions where P_b was maintained at zero and where P_a was maintained constant. The direction of hydrogen flow through the test

cell did not significantly affect the experimental results.

HYDROGEN PERMEATION THROUGH OXIDE COATED METALS

R. A. Strehlow

The control of tritium flow in a molten salt reactor system involves a need for knowledge of both the permeation rates through steam generator heat exchanger material and of the extent to which permeation is decreased due to the oxide coatings in contact with the steam.

An experimental program was begun to study hydrogen permeation under conditions closely analogous to those which might be expected in a molten salt reactor steam generator heat exchanger.[1] Permeation rates of hydrogen have been measured using, for example, a 4% hydrogen argon gas mixture through two types of stainless steel and Hastelloy N tubing sections. A quadrupole mass analyzer is used as detector in these studies. The rates as measured agreed with literature values to within about 20%. The more interesting feature of the findings, however, is found in the time dependence of the permeation rate after the addition of water vapor to the gas mixture. For the steels an increase of hydrogen permeation has been observed followed by a very slow decline. This behavior is presumed due to a corrosion reaction with a slow development of a poorly protective oxide. In contrast to this Hastelloy N shows no increase under the same experimental conditions but shows a decrease in permeation rate to a value less than one-fifth of the initial value. Thermal cycling of the specimen and repetition of the experiment produced nearly identical results. One may conclude that a "self-healing" oxide forms on Hastelloy N, but that this oxide does not have a close enough thermal expansion coefficient. Further studies will include the effect of artificially deposited oxides and a study of the pressure dependence of hydrogen permeation at very low pressures.

[1] MSR Program Semiann. Progr. Rept. Feb. 28, 1971, ORNL-4676.

SPECIAL STUDIES

LIQUIDUS TEMPERATURE OF $LiF-BeF_2-ThF_4$ (70-15-15 mole %)

L. O. Gilpatrick, C. J. Barton, and H. Insley

Bauman and Chang[1] have recently recommended that the salt composition 70 mole % LiF, 15 mole % BeF_2, and 15 mole % ThF_4 be adopted as the optimum composition for coming studies of the permanent-core single-fluid MSBR. In view of its probable importance in future reactor design considerations, we thought it desirable to confirm the liquidus temperature and the primary phase assignment of this specific composition.

The composition was prepared from the pure components and carefully examined by the quench tube technique. It was found to have a melting point of 505°C ± 2°C; the primary phase was identified from its optical properties as $3LiF \cdot ThF_4$. The liquidus temperature was confirmed by an independent set of three differential thermal analysis (D.T.A.) measurements which averaged 506.3°C ± 1°C.

These results agree very well with the published phase diagram.[2]

[1] H. F. Bauman and S. I. Chang, MSR 70-42, p. 4, July 1, 1970.

[2] R. E. Thoma *et al.*, Nucl. Sci. Eng. 19, 408 (1964).

THE THERMODYNAMICS OF FORMATION OF INTERMETALLIC COMPOUNDS OF SOME ELECTROPOSITIVE METALS WITH PLATINUM

D. M. Moulton, W. R. Grimes, and J. Braunstein

Platinum forms intermetallic compounds of definite composition and great stability with the metals of the first five columns in the periodic table. A compound such as $ZrPt_3$, for example, is estimated to have a free energy of formation of 50-100 kcal. This stability is explained, on the Engel-Brewer theory of metallic bonding, by the transfer of one or more originally paired d-electrons from the platinum to unoccupied d-orbitals of the other metal, allowing the formation of both covalent and electrostatic bonds.[1] We have undertaken a study of the free energies of formation of some of these compounds.

Despite the stability of the oxides of the electropositive metals, so strong is the affinity for platinum that they can be reduced by hydrogen, as $Al_2O_3 + 3H_2 + 6Pt \rightarrow 2AlPt_3 + 3H_2O$ at temperatures of 1000° - 1500°C.[2] An apparatus has been constructed for observing this reaction: a hydrogen-inert gas mixture, to which variable amounts of water can be added, is flowed over a platinum-oxide mixture at elevated temperature. The partial pressure of water is monitored with a Panametrics moisture analyzer, which covers a range of 0.1 - 23000 ppm of water.[3] Since the solids appear as pure phases, the equilibrium depends only on the ratio H_2/H_2O. Measurement of this ratio in the inlet and outlet streams allows one to determine the point at which the reduction begins, and the free energy can be calculated from this figure and known quantities from the literature.

[1] L. Brewer, Science 161, 115 (1968).

[2] W. Bronger and W. Klemm, Z. anorg. allgem. Chem. 319, 58 (1962).

[3] Panametrics, Inc., Waltham, Mass.

PRODUCTION OF MOLTEN SALTS FOR THE MSR PROGRAM

F. A. Doss, W. Jennings, Jr., W. P. Teichert, C. R. Benson, W. K. R. Fennel, and J. H. Shaffer

The preparation of all fused salt mixtures required by the Molten Salt Reactor Program is a continuing responsibility of the Reactor Chemistry Division. During this fiscal year the production facility was operated on a part-time basis for the preparation of about 400 kg of fused fluoride mixtures in 11 batch operations and about 55 kg of $NaBF_4$-NaF mixtures in 4 batch operations. These materials were used within ORNL for the various chemical and engineering tests of the MSRP.

PART IV. AQUEOUS STUDIES

ELEVATED TEMPERATURE AND EQUILIBRIA

BORIC ACID-BORATE EQUILIBRIA AT ELEVATED TEMPERATURES

R. E. Mesmer, C. F. Baes, Jr., and F. H. Sweeton

Boric acid solutions are used as soluble neutron poisons in pressurized water reactors to replace some of the control rods. The pH of these solutions under operating conditions has been unknown because of the lack of acidity measurement capability. We have now studied the boric acid-borate equilibria by means of a hydrogen electrode concentration cell from 50° to 290°C. The equilibrium between the monomers in dilute solutions

$$B(OH)_3 + OH^- = B(OH)_4$$

was studied as a function of KCl concentration from 0.13 m to 1.0 m. A small ionic strength effect which decreases slightly with temperature was observed and the pressure dependence of the equilibrium is very small up to 2000 psi. At 50° the results are in excellent agreement with previous work and the equilibrium quotient is given to better than 0.01 log units by the expression

$$\log \underline{Q}_{1,1} = \frac{1573.21}{T} + 28.6059 + .0120787 - 13.2258 \log T$$
$$(.3250 - .00033T)\ I - .0912\ I^{3/2}$$

In more concentrated boric acid solutions the polyborates formed are $B_2(OH)_7^-$, $B(OH)_{10}^-$, and lesser amounts of $B_4(OH)_{14}^{2-}$ or $B_5(OH)_{18}^{3-}$. The trimer is needed to fit data at all temperatures studied. The dimeric species, not previously reported, is important at high temperatures and the fourth species (tetrameric or pentameric) contributes at low temperatures at high ratios of hydroxide-to-boric acid. The equilibrium quotients and thermodynamic parameters have been derived for all the equilibria in 1 m KCl and the equilibrium between the monomers at infinite dilution. The information is useful for establishing standard buffers to cover temperature ranges not previously covered as well as enabling us to generate plots representing the pH of boric acid solutions under conditions of interest in nuclear reactors.

POTENTIOMETRIC DETERMINATION OF THE DISSOCIATION OF WATER AT ELEVATED TEMPERATURES USING A FLOWING CELL

F. H. Sweeton, R. E. Mesmer, and C. F. Baes, Jr.

The flowing EMF cell previously described,[1] with minor modification, behaved satisfactorily when tested between 0 and 300°C with two solutions having different concentrations of HCl; the EMF readings indicated a ratio of HCl concentration that averaged within 7% of the correct value over the temperature range. Measurements at room temperature with a glass cell substituted for the high-pressure cell showed that the passages through which the solutions flow to the inside of the high-pressure cell should have a cross section smaller than about 0.01 mm^2 in order to keep electrolytic currents from causing appreciable errors in the EMF reading.

Successful dissociation measurements have been made with HCl and KOH concentrations down to below 0.001 m and with ionic strengths down to 0.02 m. Measurements are now being made in relatively concentrated solutions. Readings are routinely taken both at pressures slightly above steam pressure and at 1400 psi.

The relation

$$\frac{\partial \log Q_w}{\partial P} = -\frac{\Delta V}{2.3\ RT}$$

has been used to convert the observed pressure dependence of the dissociation product Q_w to the change in volume ΔV accompanying the dissociation of one mole of water. The following table summarizes the tentative values of log Q_w and ΔV that have been determined.

Ionic Strength (molal)	log K_w (molal)			ΔV (cc/mole)				
	100°C	200°C	300°C	0°C	50°C	100°C	200°C	250°C
0	-12.2_8	-11.3_2	-11.2_1	-25	-22	-25	-47	-72
0.7	-11.8_9	-11.6_9	-10.1_1	-20	-17	-22	-36	-48
2.7	-12.0_7	-10.6_3	-9.7_2	-20	-17	-	-26	-31

[1] F. H. Sweeton, R. E. Mesmer, and C. F. Baes, Jr., Reactor Chem. Div. Ann. Progr. Rept., May 31, 1970, ORNL-4586, pp. 75-76.

ELECTRICAL CONDUCTANCES AND IONIZATION BEHAVIOR OF SODIUM CHLORIDE IN DIOXANE-WATER SOLUTIONS AT 300°C AND PRESSURES TO 4000 BARS.[1]

L. B. Yeatts and W. L. Marshall

Electrical conductance measurements were made of dilute NaCl (0.0005-0.01 m) in dioxane-water solutions to study its ionization behavior in this solvent system at 300°C and pressures to 4000 bars. This conductance study is believed to be the first one made in an aqueous-organic solvent above 100°C. Shedlovsky's conductance equation was used to calculate the limiting equivalent conductances (Λ_o) and conventional ionization constants (K_d) of NaCl at various pressures and at solvent compositions varying from 35 to 75 wt % dioxane. With hydration of the electrolyte species in solution considered an essential part of the ionization process, the complete ionization constant (K°) is represented by $NaCl(aq) + k\ H_2O \rightleftarrows Na(aq)^+ + Cl(aq)^-$, where $K° = K_d/C^k_{H_2O}$, C_{H_2O} is given in moles/liter as the solute concentration approaches zero, and dioxane is assumed to be non-solvating. A plot of log K_d vs log C_{H_2O}, which was a straight line over the entire ranges of pressure and solvent composition, produced a value of K° of $10^{-16.0}$. The net change on ionization in the number of solvating water molecules (k) is 10.0. These two values at 300°C for NaCl in dioxane-water are shown to be consistent with earlier results for this electrolyte both in water (400 to 800°C)[2] and in dioxane-water (25-100°C)[3] at pressures to 4000 bars.

[1]Abstract of paper submitted for publication (1971).

[2]A. S. Quist and W. L. Marshall, J. Phys. Chem. 72, 684 (1968).

[3]L. B. Yeatts, L. A. Dunn, and W. L. Marshall, ibid. 75, 1099 (1971).

SOLUBILITY OF CALCIUM SULFATE DIHYDRATE AND ASSOCIATION EQUILIBRIA AT 25°C IN SEVERAL AQUEOUS MIXED-ELECTROLYTE SALT SYSTEMS[1]

L. B. Yeatts and W. L. Marshall

Some correlations have been considered for the solubility of calcium sulfate dihydrate at 25°C among several mixed-electrolyte systems (a) Na_2SO_4-NaCl-H_2O, (b) Na_2SO_4-$NaNO_3$-H_2O, (c) Li_2SO_4-LiCl-H_2O, and (d)

Li_2SO_4-$LiNO_3$-H_2O.[2] For any single system, the proposed association equilibria for calcium sulfate[3] indicate an apparent invariance of activity coefficients for Ca^{2+}, SO_4^{2-}, and $CaSO_4^0$ at constant ionic strength (I). This behavior was observed in each of the four systems at I(molal units) = 0.5, 2, and 6 over a wide range of the ratio, molality of added sulfate/molality of 1-1 electrolyte. A modified Harned's rule could also be applied under these same conditions but it would require evaluating three constants instead of the two equilibrium quotients needed for the above approach. The differences in solubility among the four systems, at both constant ionic strength and molality of SO_4^{2-}, can be correlated fairly well in terms of the "free" or unsolvated water which is present in 1-1 salt solutions at I = 0.5, and 2, but not at I = 6. The fact that the actual ionic strength of a solution is less than the formal ionic strength at the high concentration is considered a possibility and qualitatively related to the solubilities.

[1]Submitted for publication in J. Chem. Eng. Data.

[2]L. B. Yeatts and W. L. Marshall, Reactor Chem. Div. Ann. Progr. Rept., Dec. 31, 1968, ORNL-4400, pp. 77-79.

[3]L. B. Yeatts and W. L. Marshall, J. Phys. Chem. 75, 1099 (1971).

A FURTHER DESCRIPTION OF COMPLETE EQUILIBRIUM CONSTANTS[1]

W. L. Marshall

A complete equilibrium constant (K°), in which solvent species are included to reduce the number of parameters needed for describing solute ionization equilibria, is derived from a multistep solvation treatment of a conventional ionization constant (K). The previously assumed average net change (k) in the number of solvent molecules in the reaction process[2] is shown to have this mathematical form both for single and multiple solvent systems. The usefulness of K° and k originates from their experimental, isothermal constancy over wide ranges of solvent concentration (where the solute concentration always approaches zero). In the present derivation, neither term is found to be exactly constant. Therefore, the experimental

invariance of k and K° is proposed to result from only a very few solvated species of major concentration for each class of solute species, and thus the usefulness of the concept is unhindered. No additional parameters are needed for application. The use of fugacity of the solvent and the Gibbs-Duhem relation are considered in connection with this description. In an example of application, the aqueous ionization behavior of $MgSO_4$ is predicted in dioxane-water solvents at saturation vapor pressure and in water to 2000 bars by combining solvent separated ion-pair theory (six constants required) with the complete constant approach, using results in water at saturation vapor pressure only. Reasonable agreement with experiment is observed, although better agreement is obtained by applying just a complete constant concept, which requires only the two constants, K° and k.

[1]Abstract of paper submitted for publication (1971).

[2]W. L. Marshall and A. S. Quist, Proc. Natl. Acad. Sci. 58, 901 (1967); A. S. Quist and W. L. Marshall, J. Phys. Chem. 72, 1536 (1968).

ASSOCIATION EQUILIBRIA OF Cd^{2+} WITH Cl^- OR Br^- IN MOLTEN $Ca(NO_3)_2 \cdot 4H_2O$

J. Braunstein and H. Braunstein*

Stepwise association constants of dilute solute species in concentrated aqueous electrolytic solvents and their comparison with equilibria in anhydrous molten salt solvents have provided useful information on competitive ion-ion and ion-water interactions.[1,2] Since an anomalous structural effect has been hypothesized recently[3] for $CdBr_2$ in molten $Ca(NO_3)_2 \cdot 4H_2O$, on the basis of inconclusive evidence for the absence of the species $CdBr_2$ in solution, an accurate redetermination of association constants in this system, as well as additional measurements in related systems, was needed.

New potentiometric measurements were made of the association constants, tabulated below, of $CdCl^+$, $CdCl_2$, $CdBr^+$ and $CdBr_2$ in molten $Ca(NO_3)_2 \cdot 4H_2O$ at 50°C. Carefully prepared Ag-AgCl and Ag-AgBr indicator and reference electrodes were stable to ± 0.001 mv and ± 0.01 mv respectively, and showed

Nernst behavior over two decades of halide concentration.

Association Constants of Cd(II) With Cl^- or Br^- in Molten $Ca(NO_3)_2 \cdot 4H_2O$ At 50°C (moles/mole Ca)$^{-1}$

$K_1(CdCl^+)$	$K_2(CdCl_2)$	$K_1(CdBr^+)$	$K_2(CdBr_2)$
1070 ± 50[1]	340 ± 50[1]	3900 ± 200[1]	1400 ± 100[1]
		(3900 ± 200)[2]	(1500 ± 200)[2]

The new chloride results and accurately confirmed bromide results give ratios of K_1/K_2 of about 3, similar to values found for anhydrous molten salts[2] and revealing no anomalous effects in the stepwise equilibria.[3]

*Oak Ridge Graduate Fellow from the University of Maine under appointment from Oak Ridge Associated Universities.

[1]Chemical Communications, in press, 1971.

[2]J. Braunstein, A. R. Alvarez-Funes and H. Braunstein, J. Phys. Chem. 70, 2734 (1966); J. Braunstein, "Statustical Thermodynamics of Molten Salts and Concentrated Aqueous Electrolytes," in Ionic Interactions: From Dilute Solutions to Molten Salts, ed. S. Petrucci, Academic Press, New York (1971).

[3]D. G. Lovering and D. J. Alner, Chem. Comm. 1970, 570. D. G. Lovering, Ph.D. Thesis, City University, London (1969).

ISOPIESTIC STUDIES OF VERY CONCENTRATED AQUEOUS ELECTROLYTES

H. Braunstein* and J. Braunstein

Thermodynamic properties of aqueous salt solutions show marked changes when the water content is reduced below 4-8 moles H_2O per mole salt, reflecting the gradual transition between aqueous electrolytes and molten salts.[1] Water activities at high concentrations have been calculated at 100°C from our isopiestic measurements of LiCl, $LiNO_3$, LiBr, $Ca(NO_3)_2$ and of several mixtures including $(Li,K)NO_3$ using water activity data for LiCl solutions.[2] All show a region in which the Stokes and Robinson - B.E.T. adsorption model of hydration can be fitted with physically reasonable energy parameters. For the system $(Li,K)NO_3$-H_2O, vapor pressure data extend to low concentrations of water in molten salt, permitting a

comparison of the model parameters with independent measurements of thermodynamic properties. The difference between the energy of adsorption and energy of liquefaction, calculated with the model from isothermal activity data, is 0.7_1 kcal mol^{-1}, while the difference between the enthalpies of vaporization of water at infinite dilution in molten salt and of pure liquid water is 0.7_3 kcal mol^{-1}. Henry's law constants for water in molten salt may be estimated from the model equation. For $(Li,K)NO_3$ the estimated value at 100°C is 0.219, compared with the experimental value 0.229 (moles salt - moles $water^{-1}$).

A new shaft seal for rotary and reciprocal motion under vacuum or pressure was designed, installed and tested on the isopiestic apparatus. Measurements of isopiestic ratios with D_2O are in progress.

*Oak Ridge Graduate Fellow from the University of Maine under appointment from Oak Ridge Associated Universities.

[1]Journal of Chemical Thermodynamics, in press, 1971.

[2]H. F. Gibbard, Jr., Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass. 1967.

SELF-DIFFUSION OF Na^+ IN MEMBRANES AND MEMBRANE MODEL SOLUTIONS BY A RADIOMETRIC POROUS-FRIT METHOD

A. J. Shor and H. O. Phillips*

Salt transport through organic-water solutions which act as models for hyperfiltration membranes or through the membranes themselves has been investigated to improve our understanding of the process of salt removal. We have measured the self-diffusion of Na^+, D_{Na}, in ion-exchange membranes and in solutions by the rapid radiometric porous frit method.[1] Membranes, or porous gold frits of flat or cylindrical shape, are equilibrated for a suitable period in a solution of desired salt and polymer concentration also containing radiotracer Na^{24}. After mounting the membrane or frit in a cylindrical tube in a carefully characterized geometry, a tracer free solution of identical composition is pumped past the equilibrated specimen. The rate of elution (which depends on the self-diffusion constant of the

tracer and the character of flow past the surface of the specimen) is measured by recording the gamma-ray activity of the specimen as a function of time. The method has been used to measure self-diffusion coefficients of Na^+ in aqueous polyelectrolyte solutions (polyacrylic acid), glycerol triacetate solutions, and AMF-C-60 ion-exchange membranes at various equilibrium salt concentrations.

Preliminary measurements for D_{Na} in polyacrylic acid solutions as a function of water content and molecular weight were carried out at a sodium chloride concentration of 0.1 M. These results show that, as expected, D_{Na} is an insensitive function of the molecular weight and of the viscosity and is principally dependent on the water content of the solutions. Thus D_{Na} in 25% polyacrylic acid (molecular weight about 50,000) is about half its value in 5% solution while the bulk viscosity is a factor of 70 higher in the 25% solution.

Measurement of the rate of elution of Na^+ from an American Machine and Foundry Company AMF-C-60 ion-exchange membrane at various velocities (.04 to 280 cm/sec) and lengths has shown a linear dependence on the inverse one-third power of the linear velocity of solution flowing past the membrane, as predicted by theory.[2] Ready extrapolation to infinite flow velocity is thereby permitted. The extrapolated value of elution time at infinite flow velocity past the membrane may be converted to the self-diffusion coefficient, since in theory the liquid film contribution of resistance to transport of the ion into a flowing stream from the membrane surface is thereby eliminated. Self-diffusion coefficients may thus be directly computed from diffusion theory for slabs or cylinders by classical methods. The order of magnitude of D_{Na} measurements in the membrane (e.g., 1.1×10^{-6} cm^2/sec at 0.1 M NaCl, 0.95×10^{-6} for 1.0 M and 0.38×10^{-6} at 5 M) are consistent with previous measurements of the self diffusion of Na^+ in similar cation exchange resins.[3]

The system glycerol triacetate-sodium perchlorate-water has been studied as an approximate model for cellulose acetate membranes. D_{Na} and viscosity were measured for several solutions, 95 volume % glycerol triacetate-5% water. These varied in NaCl concentration from 0 to 1.5 M. The perchlorate ion is included because it improves the mutual solubility

of glycerol triacetate-water mixtures and is considered a beneficial additive to casting solutions in the fabrication of cellulose acetate desalting membranes.

It was found that between 0.1 m and 1.56 m sodium perchlorate, the self-diffusion coefficient decreases by a factor of 5 and the relative viscosity increases by a factor of 20. From these and prior studies,[4] it appears that Na^+ self-diffusion behavior is similar (i.e., the self-diffusion-viscosity product is constant within a factor of four) to that observed in other low-molecular-weight organic water mixtures such as glycols and alcohols.

*Chemistry Division, ORNL.

[1] A. E. Marcinkowsky, F. Nelson, K. A. Kraus, J. Phys. Chem. 69, 303 (1965).

[2] L. Dresner, Theory of the Porous-Frit Method of Measuring Self-Diffusion Constants, ORNL-4667 (Mar. 1971).

[3] R. Schlögl, Z. Elektrochem. 57, 195 (1953).

[4] A. E. Marcinkowsky, H. O. Phillips, K. A. Kraus, J. Phys. Chem. 72, 1201 (1968).

SURFACE

INTERACTION OF GASES WITH LUNAR MATERIALS[1]

E. L. Fuller, Jr., H. F. Holmes, R. B. Gammage,[2] and K. Becker[2]

Adsorption of carbon monoxide, nitrogen, oxygen and argon at -196°C shows the surfaces of lunar fines to be quite nonpolar. There is no evidence of inherent porosity in the range of 20 to 500 Å and the specific surface area is slightly greater than 1 m^2/gm. Water vapor appears to be specifically oriented in the monolayer region and penetrates the surface at $P/P_o = 0.9$. This penetration is reversed at $P/P_o = 0.8$. Repeated and prolonged treatment with water vapor increases the capacity for water vapor adsorption but does not alter the capacity for nitrogen adsorption. This suggests a rather unique surface structure. The observations seem to be related to the amorphous, radiation damaged, silicious surface region. Water vapor adsorption seems to be an informative means of probing the latent radiation damage tracks. Exposure to elevated temperatures in vacuo results in an initial decrease in the amount of water penetration, with no surface area loss at 500-600°C. The surface area shows a marked decrease at 800°C due to sintering. These results are for a single sample and full credence as to their representative nature awaits studies of other materials from different lunar environs.

[1]Modified abstract of paper from Geochim et Cosmochim Acta (in press).

[2]Health Physics Division, ORNL.

ADSORPTION ON POROUS THORIUM OXIDE MODIFIED BY WATER[1]

R. B. Gammage,[2] E. L. Fuller, Jr., and H. F. Holmes

A sample of thorium oxide containing pores in the micro (widths less than 20 Å), transitional (widths of 20 to 200 Å), and macro (widths greater than 200 Å) size ranges was subjected to various outgassing temperatures up to 500°C in a vacuum microbalance system. Equilibrium water vapor adsorption isotherms were determined at each temperature. The adsorptions of nitrogen and argon (on the water equilibrated surface) were used to

investigate the pore structure. Changes in the pore structure of the solid and the nature of the irreversibly adsorbed water were observed to alter significantly the energetics and extent of nitrogen and argon adsorption. These results emphasize the difficulties involved in characterizing an active solid of this type. An outgassing temperature as high as 400°C was required to remove water blocking entry to the micropores. As expected, nitrogen was able to penetrate the partially hydrated fine pore structure better than argon. Comparison (by means of t-plots) of nitrogen adsorptions showed the importance of carefully selecting the temperature of outgassing and the standard reference isotherm.

This study culminated in the following recommendations for comparing adsorption data:

1. The oxide used to obtain the reference isotherm should preferably be of the same type as the experimental oxide and, of course, be nonporous.

2. The adsorptions should be of comparable energy, some control of which can be obtained by varying the state of hydration of the oxide surface.

3. To ensure empty micropores, the oxide should be outgassed at as high a temperature as it can withstand without sintering.

[1]Modified abstract of a paper accepted for publication in J. Coll. Interfac. Sci., 1971.

[2]Health Physics Division, ORNL.

THE HEAT OF IMMERSION OF THORIUM OXIDE IN WATER AT ELEVATED TEMPERATURES

H. F. Holmes and E. L. Fuller, Jr.

Prior to this study there were no calorimetric data for the interaction of insoluble oxide surfaces with liquid water at elevated temperatures. Because of the general complexity of water-oxide interactions it was judged advisable to obtain such data. Data have now been taken for five thorium oxide samples whose specific surface areas ranged from 3 to 80 m^2/g. Pretreatment of the samples consisted of outgassing at 500°C for 24 hours. An adiabatic calorimeter was used to measure the heat of immersion in liquid water over the temperature range of 25 to 200°C.

Confusingly, heats of immersion were found to increase decrease, or remain constant with increasing immersion temperature. An increase with increasing immersion temperature was perhaps the usual behavior. For example, the heat of immersion of one sample increased from -1220 ergs/cm^2 at 25°C to -1850 ergs/cm^2 at 200°C. There is no obvious interpretation of the data nor is there a correlation with specific surface area. Samples recovered after an immersion experiment were found to have unchanged specific surface area. Lack of a correlation with specific surface area rules out solubility effects. Perhaps a plausible explanation lies in the structural effects which occur when an oxide surface interacts with liquid water. These would determine the change in heat capacity associated with the reaction which, in turn, would dictate the temperature dependence of the heat of reaction. It is hoped that further experiments will provide a sound basis for interpretation of the results.

THE HEAT OF IMMERSION OF SOL-GEL THORIUM OXIDE

H. F. Holmes and E. L. Fuller, Jr.

Oxides prepared by the sol-gel technique are useful in nuclear fuel production. Prior to the present study there were no calorimetric data for the interaction of these oxide surfaces with liquid water. The subject of the present study was a sol-gel thorium oxide having a specific surface area of 83 m^2/g. The heat of immersion of this sample in liquid water at 25°C was measured calorimetrically after outgassing the sample at selected temperatures in the range of 25° to 500°C. The heat of immersion as a function of outgassing temperature varied in an almost linear manner from -157 ergs/cm^2 for an outgassing temperature of 25°C to -712 ergs/cm^2 for an outgassing temperature of 500°C. These values are much lower than the corresponding quantities (-325 to -1300 respectively) for high-area thorium oxide prepared from the oxalate.[1,2] From the unusually low value obtained after outgassing at 25° one can estimate that the average net heat of adsorption of water on such a surface is only 600 cal./mole. This estimate, however, may be seriously in error

due to complicating factors such as loss of gas-solid interfacial area due to irreversibly adsorbed water. However, from the weight loss difference between outgassing at 25° and 500°C and the heats of immersion corresponding to these temperatures, one estimates that the average net heat of adsorption for the water lost between 25° and 500°C is 10.4 kcal/mole. Since this is an average value, it means that a substantial fraction of this water is interacting chemically with the oxide surface.

[1] H. F. Holmes and C. H. Secoy, J. Phys. Chem. 69, 151 (1965).

[2] E. L. Fuller, Jr., H. F. Holmes, C. H. Secoy, and J. E. Stuckey, J. Phys. Chem. 72, 573 (1968).

CORROSION

THE CORROSION OF COPPER AND ITS ALLOYS IN SODIUM CHLORIDE SOLUTIONS*

J. C. Griess, A. L. Bacarella, and E. G. Bohlmann

The mechanism for the anodic dissolution of pure copper in chloride solutions over the temperature range of 25 to 155°C has been established, and experiments with 70-30 cupronickel are in progress. As with pure copper the anodic dissolution of the 70-30 alloy is diffusion controlled and has essentially the same functional dependence on chloride concentration ($[Cl^-]^2$) and temperature. However at the potential where Ni_3O_4 and Cu_2O become thermodynamically stable, passivation occurs. (The potentials at which Ni_3O_4 forms from NiO and Cu_2O from copper are the same and have the same pH dependency.) The formation of Cu_2O on pure copper does not produce passivation. At lower potentials NiO is thermodynamically stable but has no detectable effect on the anodic process. Preliminary examinations of films formed on 70-30 cupronickel using photoelectron spectroscopy have shown the presence of nickel oxide, but identification of specific oxides formed at different potentials has not yet been made. Although NiO on the 70-30 alloy appears to have no effect on the anodic process, its presence has a large effect on cathodic processes. Details of the cathodic processes have yet to be determined.

In addition to the mechanistic studies specimens have been exposed to flowing 1m NaCl in titanium pump loops. Long-term tests at 3 to 15 fps in N_2-sparged (30 to 50 ppb O_2) 1 m NaCl at 125, 150, and 175°C showed that the corrosion rates of nickel-containing alloys (90-10 and 70-30 cupronickel and Monel 400) increased with increasing temperature whereas the corrosion rates of Admiralty brass, CDA-194 (∿ 2.5% Fe, bal. Cu), and copper decreased. At 125°C the complete removal of oxygen by addition of 10 to 20 ppm Na_2SO_3 resulted in lower corrosion rates for all alloys, but the effect was greatest for Admiralty brass and CDA-194; copper was not tested. In other experiments solution velocity in the range of 20 to 100 fps produced no significant localized attack on 90-10 or 70-30 cupronickel either at 60 or 125°C; only light uniform attack was noted at all velocities.

*Research sponsored by the Office of Saline Water, U.S. Department of the Interior.

PERFORMANCE OF MATERIALS IN SALINE WATER DISTILLATION EQUIPMENT

S. A. Reed

A report was prepared for the Office of Saline Water on the performance of the major materials of construction which are used in saline water distillation equipment and on experimental materials which have been exposed in the Office of Saline Water test facilities.

Carbon steel components have suffered rapid deterioration at temperatures above 200°F in areas of high turbulence and where there have been directional flow changes in equipment. Inleakage of air into the equipment and inadequate venting have also been major factors in accelerating the corrosion of steel and other materials in the plants.

Copper-base alloys used as heat transfer tubing may be ranked in the following relative order of corrosion resistance, 70/30 and 90/10 cupronickels, aluminum brass, Admiralty metal. The cupronickles have displayed excellent resistance to corrosion in both clean and mildly polluted feedwaters. Copper-2.3% iron alloy also appears to perform well in hot seawater brine, although it has only been tested for relatively short periods of time. The brasses have been subject to season cracking in some environments when impurities such as ammonia or hydrogen sulfide are present.

Type 316 stainless steel has performed satisfactorily in moving seawater and brine in applications such as pump and valve internals and in experimental exposures as heat transfer tubing. Type 304 stainless steel suffered rapid pitting attack in comparable service.

Sound castings of properly heat treated ductile Ni-Resist have given good performance as pump and valve components in most applications.

Unalloyed titanium has been subject to crevice corrosion attack in some applications when proper precautions have not been taken to avoid crevices.

Very few organic protective coatings systems or plastic materials which have been tested appear to be promising candidates for long term service in distillation plant environments, particularly at temperatures above 200°F. Cement mortar linings used to protect carbon steel components appear to be highly resistant to attack in most distillation plant environments in which they have been tested.

The report will be issued as ORNL-TM-3421.

STABILIZATION OF PRODUCT WATER FROM SEAWATER DISTILLATION PLANTS*

C. D. Bopp and S. A. Reed

Untreated product water from a seawater distillation plant will rapidly attack the construction materials that are commonly used in municipal storage and distribution systems. The pure distillate will dissolve the free lime in concrete and cause it to deteriorate rapidly. Similarly, it will remove the protective film from steel water lines that have been in service for many years and prevent protective film formation on new mains, leaving bare metal surfaces which can corrode at rates in excess of 10 mils per year.

To inhibit corrosion and reduce contamination by metal pickup, treatment of the product water from distillation plants is required. A report was prepared on the subject for the Office of Saline Water. The literature was reviewed for corrosion inhibition methods suitable for potable water. Previous work at the Office of Saline Water test facilities was reviewed and a survey of product water treatment for several privately owned plants in the Caribbean was conducted. It was concluded that calcium carbonate stabilization is generally the most satisfactory corrosion inhibitor. The costs of several methods of achieving a stable water containing 30 to 80 ppm of calcium alkalinity expressed as calcium carbonate, and a minimum of 5 ppm of dissolved oxygen were examined. If naturally hard water is unavailable for blending, the cheapest method for large plants (> 10 Mgd) at most localities is blending with a calcium carbonate solution prepared by absorption of carbon dioxide in a lime slurry. The estimated costs for calcium carbonate stabilization of product water from distillation plants are approximately 1.8¢/Kgal for a 10 Mgd plant and 1.4¢/Kgal for a plant producing 50 Mgd.

*The report will be issued as ORNL-TM-3459. It will also be issued as a Research and Development report by the Office of Saline Water.

MISCELLANEOUS WORK FOR THE OFFICE OF SALINE WATER

S. A. Reed

A number of tasks were carried out during the year at the request of the Office of Saline Water. This work was reported directly to the OSW by informal memoranda, letters or by verbal presentations in Washington, D. C.

1. Materials Surveillance Programs for the VTE-X - A detailed materials inspection program was prepared for the Vertical Tube Evaporator Experiment (VTE-X) test facility at Chula Vista, Calif. The program included ultrasonic thickness measurements of the major vessels, probologging of the evaporator tubing, measuring the resiliency of the silicone rubber protective cover on tube sheets, extensive photographing and visual inspection of the plant internals and installation of corrosion coupon assemblies. The program was initiated and resulted in our making two plant inspections during the year.

2. Shutdown Procedures for the VTE-X - Recommendations were prepared for procedures which could be used to protect the VTE-X vessels and their internals from corrosion during prolonged shutdown periods. The procedures included chemical cleaning and treatment using a commercial Butterworth jet-spray system, chemical solutions for flooding the vessels and inert gas blanketing. The latter method was chosen and is being used.

3. Plant Inspections - In addition to the VTE-X we also assisted OSW contractors in materials inspections of the Clair Engle multistage flash test bed at Chula Vista, Calif., and the advanced vertical tube evaporator test bed at Freeport, Texas.

MATERIALS INFORMATION CENTER

J. L. English and S. A. Reed

The Materials Information Center, operated for the Office of Saline Water, U. S. Department of the Interior, by Oak Ridge National Laboratory, became operative during 1969. Purpose of the Center is to collect, index, abstract, store, retrieve and disseminate information on corrosion and performance of materials used in all types of processes concerned with desalination of seawater and brackish waters. Four bibliographic reports,[1-4] each containing approximately 50 abstracts, were issued during the year. A topical report on corrosion of materials in distillation processes has been prepared also.[5] Abstracts in the bibliographic reports are accompanied by appropriate keywords for retrieval of specific types of information from the computerized storage system. The thesaurus of keywords developed by the Center currently numbers about 800 terms. Nearly 600 entries are presently contained in the storage system.

A total of 649 Office of Saline Water research and development reports has been reviewed; of these 426 contained pertinent information and were therefore processed. In addition, related open literature has been processed as time permitted.

A computerized program for storage and retrieval of information on equipment behavior from Materials Performance Reporting System (MPRS) inspection-type report forms was made operable. More than 1700 forms from Freeport (Texas), Senator Clair Engle (California) and Roswell (New Mexico) have been processed. Thirty-five search questions made on the system have aptly demonstrated its flexibility and capabilities.

Personnel from the Center assisted in the inspection of a number of test-bed plants and experimental facilities operated for the Office of Saline Water during the year.

[1] Indexed Bibliography on Corrosion and Performance of Materials in Saline Water Conversion Processes - 7, OSW-MIC-7 (June 1970).

[2] Indexed Bibliography on Corrosion and Performance of Materials in Saline Water Conversion Processes - 8, OSW-MIC-8 (Sept. 1970).

[3] Indexed Bibliography on Corrosion and Performance of Materials in Saline Water Conversion Processes - 9, OSW-MIC-9 (Dec. 1970).

[4] Indexed Bibliography on Corrosion and Performance of Materials in Saline Water Conversion Processes - 10, OSW-MIC-10 (Mar. 1971).

[5] S. A. Reed, Performance of Materials in Saline Water Distillation Equipment, ORNL-TM-3421 (to be issued).

THE EFFECT OF SOLVENT ON THE ELECTROCHEMISTRY OF IRON AND TITANIUM

A. L. Bacarella and A. L. Sutton

We have found that in the active to passive transition for titanium, i_{max}, the critical current for passivation, decreases with increasing ethyl alcohol content of the 0.5m H_2SO_4 in EtOH - HOH solvent. This is contrary to expectation since in aqueous solvent i_{max} increases with increasing acidity; and, since the addition of EtOH increases the activity of the proton, i_{max} should increase with EtOH content of the solvent. However, as in our studies with iron, H_2O is involved in the reaction sequence and consequently must play an important role in the passivation of titanium. The detailed role of H_2O and proton in the reaction sequence leading to passivation is being studied.

The basic data presented last year concerning the corrosion of pure iron in ethanol-water-sulfuric acid systems was refined by conducting additional experiments and by a detailed analysis of all the data. We have found,

$$\log ({}^{s}i_{+})_{E_{Fe}} - \log ({}^{w}i_{+})_{E_{Fe}} = \Delta pA + 2 \log \frac{{}^{s}M_{H_2O}}{{}^{w}M_{H_2O}} \qquad (1)$$

$${}^{s}E_{Fe(corr)} - {}^{w}E_{Fe(corr)} = \Delta pA - 0.03 \log \frac{{}^{s}M_{H_2O}}{{}^{w}M_{H_2O}} \qquad (2)$$

$$\log({}^{s}i_{(corr)}) - \log ({}^{w}i_{(corr)}) = \frac{5}{4} \log \frac{{}^{s}M_{H_2O}}{{}^{w}M_{H_2O}} - 1/2\ \Delta pA \qquad (3)$$

where i_+ is the anodic current density at constant potential E_{Fe} versus the standard hydrogen electrode in water $(SHE)^w$, and superscript s refers to ethanol-water solvent and w to pure water; ΔpA is the difference between the "absolute acidity"[1] in solvent s and in water, with $pA \equiv pH$ in pure water; and M_{H_2O} is the molarity of water in s $({}^sM_{H_2O})$, and pure water w, $({}^wM_{H_2O})$. Equation (2) represents the change in the corrosion potential of iron, $E_{Fe(corr)}$, as a function of pA and the molarity of water; and Eqn. (3) relates the solvent dependence of the corrosion current, i_{corr}.

[1]A. L. Bacarella and A. L. Sutton, Reactor Chemistry Division Ann. Progr. Rept., May 31, 1970, ORNL-4568, pp. 85-86.

ELECTROCHEMISTRY OF URANIUM AND URANIUM ALLOYS IN AQUEOUS SOLUTIONS

G. H. Jenks

Experimental measurements and literature type studies which were aimed at characterizing the electrochemistry of U and U alloys in aqueous solutions at room temperature were completed, and a report of the work was published.[1]

Many of the significant results of this work were summarized in the previous annual report.[2] Other results, not previously reported, showed that the pitting-behavior of the alloy, U-7.5Nb-2.5Zr, in solutions containing chloride ions is similar to that reported by others for other materials such as stainless steels. That is, it is characterized by a pitting potential below which pit growth does not take place and by a more positive, breakthrough, potential required to initiate pit growth on passive surfaces. The pitting potential was found to be dependent upon (Cl^-); in solutions of either 0.1M HCl or 0.1M KCl (pH 8.7), this potential was between -325 and -275 mv (SCE); in solutions of .01M KCl (plus 0.1M K_2SO_4), this potential was between 0 and -100 mv. The breakthrough potential depended, as expected, upon (Cl^-), upon the presence or absence of K_2SO_4 in the solution, and upon the type and amount of film on

a specimen. In general, this potential decreased with increasing (Cl^-) and with decreasing (K_2SO_4) at a given (Cl^-). The presence of a passive film had the effect of increasing the breakthrough potential.

An important conclusion which was drawn from these and other experiments with chloride is that the film on the alloy can be protected from Cl^- attack by maintaining a sufficiently low potential. With < 0.1M Cl^-, the film on unstressed specimens would not be attacked at potentials < -325 mv (SCE). Stressed specimens were not tested, but it appears likely that they would be protected from Cl^- attack at comparable potentials.

[1] G. H. Jenks, Electrochemistry of Uranium and Uranium Alloys in Aqueous Solutions, ORNL-4651, In Press.

[2] G. H. Jenks, "Electrochemistry of U and of U-Alloys in Aqueous Solutions," in Reactor Chem. Ann. Prog. Rept. for Period Ending May 31, 1970, p. 84.

THE CORROSION OF MATERIALS IN PRESSURE-SUPPRESSION AND IODINE-ABSORBING SPRAY SOLUTIONS

J. C. Griess and G. E. Creek

The resistance of a number of materials to alkaline borate spray solutions (pH = 9.3) was summarized in last year's report, and the results of similar exposure of various protective coatings have also been reported.[1,2,3] Since that time additional tests have been completed in boric acid solutions (3000 ppm B) at pH 4.5, 6.5 and 7.5. Many of the solutions also contained chloride ions (5 to 200 ppm) to determine the susceptibility of types 304 and 316 stainless steel to stress corrosion cracking. These tests were conducted over the temperature range 141 to 82°C and the results have also been reported.[4] The principal conclusions were: (1) both alloys undergo cracking but type 304 is more susceptible than type 316; (2) cracking frequency increases as the chloride concentration increases from 5 to 50 ppm, but additional chloride is without significant effect; (3) sensitization increases the susceptibility of both alloys to cracking; (4) pickling of sensitized alloys to remove thin oxide

films decreases the cracking tendency; (5) both alloys are much more susceptible to cracking at a pH of 4.5 than at higher pH's; (6) cracking is transgranular in all cases.

The corrosion rates of aluminum alloys, and other materials in containment systems, and the low probability of stainless steel cracking at pH's of 6.5 and 7.5, indicated that neutral borate solutions would be acceptable containment spray solutions, provided adequate iodine absorbing capacity can be achieved.

Additional long-term tests of stainless steel, aluminum alloys, and a number of protective coatings are being conducted in static 3000 ppm boric acid solutions (pH 4.5) at 4, 32, and 66°C. Preliminary results indicate very low corrosion rates (< 0.1 mpy) for all alloys, and a number of types of protective coatings seem to be stable under these conditions.

[1] J. C. Griess and A. L. Bacarella, "Design Considerations of Reactor Containment Spray Systems, Part III. The Corrosion of Materials in Spray Solutions," ORNL-TM-2412, Part III. (December 1969).

[2] J. C. Griess, T. H. Row, C. D. Watson and G. A. West, "Design Considerations of Reactor Containment Spray Systems, Part V. Protective Coating Tests," ORNL-TM-2412, Part V (October 1970).

[3] T. H. Row and J. C. Griess, "Evaluation of Burgess Fobes Paint Company Protective Coatings for Nuclear Plant Applications," ORNL-TM-3104 (January 1971).

[4] J. C. Griess and G. E. Creek, "Design Considerations of Reactor Containment Spray Systems, Part X. The Stress Corrosion Cracking of Types 304 and 316 Stainless Steel in Boric Acid Solutions," ORNL-2412, Part X (May 1971).

THE CORROSION OF MATERIALS IN IODEX PROCESS SOLUTIONS

G. E. Creek and J. C. Griess

The Iodex Process is being developed by the Chemical Technology Division for the removal and fixation of the total iodine released during the dissolution of fast reactor fuel elements. Gaseous elemental iodine and methyl iodide are contacted with the vapors above refluxing 68-70%

HNO_3 to form a higher valence iodine compound. Also in the proposed flow sheet there will be regions where dilute nitric acid solutions (∿ 4m) containing elemental iodine will contact container materials where such solutions will be heated to temperatures that may be as high as 200°C.

An investigation of the corrosion resistance of materials that could be used in the process was recently begun, and the preliminary results are summarized below. Titanium, Zircaloy-2, and tantalum were essentially unaffected in boiling 68-70% HNO_3 and in the reflux region where low concentrations of elemental iodine were continuously added. In the same environments the behavior of the austenitic stainless steels was very erratic; very little attack was observed in some tests, but catastrophic attack occurred in others. In all cases, however, the attack on the stainless alloys was greater in the vapor than in the solution.

In 4m HNO_3 containing 0.025m I_2 at 200°C titanium corroded at 40 to 50 mpy and at 150°C, about 10 mpy. At 200°C both Zircaloy-2 and tantalum developed only thin oxide films and showed weight gains of < 0.1 mg/cm^2 during several hundred hours of test.

Iodine crystals placed on the surfaces of austenitic stainless steel specimens in the vapor above 4m HNO_3 at room temperature produced severe pitting whereas iodine crystals resting on the same alloys submerged in the nitric acid caused no attack. Titanium, Zircaloy-2 and tantalum were completely resistant to both environments.

PART V. CHEMICAL SUPPORT FOR HIGH TEMPERATURE GAS-COOLED REACTORS

CESIUM AND STRONTIUM RELEASE FROM BONDED BEDS OF BISO COATED UO_2 PARTICLES DURING POSTIRRADIATION ANNEALS AT 1250°C

M. T. Morgan, O. Sisman and R. L. Towns

The fuel elements for high-temperature, gas-cooled, nuclear reactors will consist of bonded beds of coated fuel particles contained within a graphite moderator. The individual coated fuel particles will be 400 to 800 microns in diameter; the coatings will be pyrolytic carbon (PyC) or a combination of pyrolytic carbon and silicon carbide. Not all of the metallic fission products are retained by the PyC coating and, even if a SiC layer is also used, failure of the SiC coating would leave only the PyC coating to retain the fission products.

We are conducting annealing experiments on small bonded beds of BISO-type pyrolytic carbon coated particles to study the retention of Sr and Cs after burnups up to 20% FIMA. The bonded beds (1/4" long x 1/4" diam, containing UO_2 and ThO_2 coated with 40 microns of porous carbon followed by 64 microns of dense isotropic carbon) were irradiated at temperatures less than 800°C. (At 800°C essentially all of the fission products remain in the fuel.)

After a 2500-hr anneal at 1250°C, 25% of the Cs and 31% of the Sr were released from the coated particles.[1] The matrix of the bonded bed retained 0.3% of the Cs and 8.7% of the Sr which were released from the coated particles. Of the fission products remaining in the coated particles after the anneal, 45% of the Cs, 0.7% of the Sr, and 3% of the Ce were found in the coating.

Diffusion coefficients for Cs in pyrolytic carbon, determined on two specimens, were 5.6×10^{-12} and 6.8×10^{-12} cm^{-2}/sec respectively.

[1] C. D. Baumann, M. T. Morgan, R. L. Towns, "Fission-Product Release from High Burnup Coated Fuel Particles by Postirradiation Anneals," Gas-Cooled Reactor Program Semiann. Progr. Rept. Sept. 1970, Oak Ridge National Laboratory, to be published.

DIFFUSION OF CESIUM IN BISO COATED FUEL PARTICLES

M. T. Morgan, O. Sisman, and R. L. Towns

The diffusion of cesium and strontium through pyrocarbon (PyC) coatings is being studied by postirradiation anneals of BISO coated fuel particles.[1,2] The BISO coating consists of a porous carbon inner layer and a dense isotropic pyrocarbon outer coating. The coated particles were irradiated at temperatures below 800°C. In order to determine the characteristic coefficients for diffusion, it was assumed that no fission products diffused into the outer coating during irradiation, that there were no significant uranium contamination in the outer coating, and that the porous PyC is transparent to cesium and strontium. Diffusion coefficients were then calculated from the annealing time required for the fission products to penetrate the outer coating.

Diffusion coefficients for ^{137}Cs obtained on low temperature, propylene-derived, isotropic pyrocarbon coated particles irradiated to 10% FIMA and low fast fluence were 2×10^{-12} cm^2/sec at 1250°C, 9×10^{-11} cm^2/sec at 1400°C, 7×10^{-10} cm^2/sec at 1500°C, and 2×10^{-9} cm^2/sec at 1600°C. The value at 1400°C is about ten times that reported by Gethard and Zumwalt[3] for pyrolytic carbon deposited from methane at 2200°C. The activation energy calculated on the basis of our data is 109 kcal/mole; this is more than double the 42 kcal/mole reported by Gethard and Zumwalt.

[1] C. D. Baumann *et al*. "Fuel Integrity and Fission-Product Release," pp. 107-110, Nuclear Safety Program Ann. Progr. Rept. Dec. 31, 1970, USAEC Report ORNL-4647, Oak Ridge National Laboratory.

[2] C. D. Baumann, M. T. Morgan, R. L. Towns, "Fission-Product Release from High Burnup Coated Fuel Particles by Postirradiation Anneals," Gas-Cooled Reactor Prog. Semiann. Progr. Rept., Sept. 1970, Oak Ridge National Laboratory, to be published.

[3] P. E. Gethard and L. R. Zumwalt, "Diffusion of Metallic Fission Products in Pyrolytic Carbon," Nucl. Appl., 3, 679 (1967).

MEASUREMENT OF THE THERMAL CONDUCTIVITY OF URANIUM DIOXIDE DURING IRRADIATION

R. M. Carroll, R. B. Perez,* and O. Sisman

The thermal conductivity of UO_2 was determined during irradiation of a specimen along with measurements of fission-gas release from the same sample. The method of measurement involved making a step increase of fission power in the specimen and then measuring the resultant rate of temperature rise. By this method it is necessary to know only the temperature at the center of the specimen accurately. However, the method of calculation is difficult.[1] We have made some preliminary calculations in which radiant heat transfer has been neglected.

On the basis of these preliminary results, we find that simultaneous fissioning causes an increase in thermal conductivity. This is in disagreement with the results obtained previously by other researchers. We can interpret our results in terms of point-defect creation-annihilation processes,[2] and a correlation of the thermal conductivity with the fission-gas release mechanism has been found which appears to confirm this interpretation.

*Neutron Physics Division.

[1] R. B. Perez, R. M. Carroll, O. Sisman, "The Theory of a Time-Dependent Heat Diffusion Determination of Thermal Diffusivities with a Single Temperature Measurement," USAEC Report ORNL-4478, Oak Ridge National Laboratory, February 1971.

[2] R. M. Carroll, R. B. Perez, and O.Sisman, Release of Fission Gas During Fissioning of UO , J. of Am. Ceram. Soc., 48, 55-59 (1965).

HEATS OF TRANSPORT OF IDEAL GASES AND GAS MIXTURES[1]

A. P. Malinauskas and E. A. Mason*

Heats of transport or heats of transfer are employed within the framework of the thermodynamics of irreversible processes to describe thermo-osmosis and various thermo-chemical effects. However, unless kinetic theory expressions are available, these coefficients must be determined by direct experimental measurement. In this study the kinetic theory expressions for thermal transpiration were translated into the semantics of non-

equilibrium thermodynamics to provide a detailed description of the heat of transport in terms of gas properties.

For a pure monatomic gas, the heat of transport decreases from a constant value in the Knudsen limit to zero in the continuum region, the variation being an inverse quadratic function of pressure. For this case the heat of transport depends markedly on temperature. Inelastic collisions involving rotational degrees of freedom, as occur in polyatomic gases, result in small but nonetheless measurable deviations from monatomic gas behavior. With binary monatomic gas mixtures, interactions between the different species cause appreciable deviations from simple mixing rules.

[1]Trans. Faraday Soc., accepted for publication (1971).

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THERMAL TRANSPIRATION IN BINARY GAS MIXTURES[1]

A. P. Malinauskas, B. K. Annis, and R. E. Fuson*

Thermal transpiration data were obtained for the binary gas mixtures Ne-Ar, Ar-N_2, and N_2-CO_2 as a function of composition at an (assumed) characteristic temperature of 504°K. Although the Ne-Ar data could be correlated quite accurately using a simple empirical modification of the dusty-gas expression for pure gases, the extension to mixtures involving polyatomic molecules became complicated because of effects arising from inelastic collisions. It was also observed that a simplified theoretical approach, based upon the methods of irreversible thermodynamics, in general yields a poor description of the composition dependence of the phenomenon; this is primarily due to the neglect of unlike-molecule interactions in the theoretical formulation.

[1]Presented at the Fall Meeting of the American Physical Society, New Orleans, 23-25 November 1970.

*Physics Department, Tennessee Technological University.

MOTION OF AEROSOL PARTICLES. DRAG ON NEUTRAL OR CHARGED SPHERES[1]

B. K. Annis, A. P. Malinauskas, and E. A. Mason*

The frictional force between a spherical object and a gas in relative motion varies with the Knudsen number, that is, the ratio of the mean free path of the gas to the radius of the sphere. For very small values of this quantity, ordinary hydrodynamic methods permit evaluation of the drag force, whereas for large values, free molecule theory can be used. In the intermediate range of Knudsen numbers however, the drag force is not amenable to standard methods of analysis, thus a new approach is necessary. An expression for the Knudsen number dependence of the drag exerted on a spherical aerosol particle by a flowing gas has been derived by dividing the problem into two parts, one which is concerned with viscous effects and another which is concerned with diffusion effects. The latter part was treated in terms of classical gas kinetic theory by assuming the aerosol to be mathematically equivalent to a binary gas mixture. The resulting expression yields results which are in good agreement over the entire range of Knudsen number with the classical oil-drop data of Millikan and the accurate numerical results obtained recently by Cercignani and co-workers through the use of the mathematically elaborate Bhatnagar-Gross-Krook model.

[1]Submitted for publication in J. Aerosol Science.

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TEMPERATURE DEPENDENCE OF ROTATIONAL COLLISION NUMBERS FROM THERMAL TRANSPIRATION[1,2]

B. K. Annis and A. P. Malinauskas

The exchange of energy between rotational and translational degrees of freedom of gas molecules affects the manner in which the gas conducts heat, propagates sound, and scatters light. The efficiency of this type of energy exchange can be characterized by a parameter known as the rotational collision number, which is, in turn, related to asymmetries in the molecular interaction potential.

The temperature dependence of the rotational collision numbers for O_2, N_2, CO and CO_2 was investigated in the range 475-676°K by a thermal transpiration technique with the use of a novel apparatus design. In all cases the collision number was found to increase with temperature. For O_2 and N_2, where some comparison with theory is possible, the experimentally determined rate of increase with temperature was found to be greater than the predicted behavior. The results for CO and CO_2 were in general agreement with other transpiration measurements and with acoustic absorption results which were obtained at lower temperatures.

[1]J. Chem. Phys. 54, 4763 (1971).

[2]Presented at the Fall Meeting of the American Physical Society, New Orleans, 23-25 November 1970.

STRESS INDUCED DIFFUSION IN MONATOMIC GASES AND GAS SUSPENSIONS[1]

B. K. Annis

The interaction between viscous stress and diffusion was examined through the use of the Chapman-Enskog kinetic theory of gases, and the result for a general binary mixture of monatomic gases was obtained. It was demonstrated that the kinetic theory calculation provides a first iteration to the form of the diffusion equations predicted by statistical mechanics. The case of diffusion due to a pressure gradient, or "barodiffusion", was considered; the resulting barodiffusion coefficient was found to be in more general agreement with the results of the alternate 13-moment method of gas kinetic theory than had been indicated in previous calculations.

Experiments by other workers have suggested separation in the radial direction in various flowing fluid mixtures, including gases and gas suspensions. It was found, however, that the gas kinetic theory predicts separation in the direction opposite to that observed. Finally, the general equations were modified to permit the description of a dusty gas or aerosol of fine particles; the result was found to differ significantly from a calculation based on the methods of stochastic processes.

[1]Phys. Fluids 14, 269 (1971).

PART VI. NUCLEAR SAFETY

FAILURE OF SiC COATINGS AT TEMPERATURES ABOVE 1800°C

C. D. Baumann, M. T. Morgan, O. Sisman, and R. L. Towns

Postirradiation annealing experiments with coated fuel particles were performed to study the fission-product retention of various coatings.[1,2] Coatings consisting of a combination of pyrocarbon and silicon carbide layers were found to release cesium, but not krypton, at temperatures above 1800°C, thus indicating that the SiC coating had failed, but not the pyrocarbon coating. Studies were then made to determine if the failure of the SiC layer to contain the cesium was due to porosity, cracking, or some other mechanism.

Optical micrographs of SiC layers, which were exposed by burning off the outer pyrocarbon coating, failed to show any cracks in coated particles which had released cesium, but photomicrographs of sectioned coated particles did indicate cracks in the SiC layers, and electron micrographs of replicas of exposed SiC surfaces also showed cracks.

Stress calculations were made for these coated particles; these calculations indicated that the SiC layers would have failed during irradiation (unless abnormally high SiC tensile strength values were assumed) while the outer PyC coating would survive. It was thus concluded that cracking of the SiC layers caused the release of cesium.

[1] C. D. Baumann, M. T. Morgan, R. L. Towns, "Fission-Product Release from Coated Fuel Particles and Bonded Bed Fuels During Postirradiation Anneals," Nuclear Safety Prog. Ann. Progr. Rept., Dec. 31, 1970, USAEC Report ORNL-4647, Oak Ridge National Laboratory.

[2] C. D. Baumann, M. T. Morgan, R. L. Towns, "Fission-Product Release from High Burnup Coated Fuel Particles by Postirradiation Anneals," Gas-Cooled Reactor Prog. Semiann. Progr. Rept., Sept. 1970, Oak Ridge National Laboratory, to be published.

THE CONSEQUENCES OF RADIOACTIVE DECAY OF FISSION PRODUCT IODINE ADSORBED ON A CHARCOAL BED

R. J. Davis, R. A. Lorenz, and R. P. Shields

The problem of calculating temperature rise in a charcoal bed as a consequence of heating by radioactive decay of the iodine adsorbed on the bed has been organized in a versatile way to allow inclusion of mechanisms which limit the iodine loading on the filter. The method also clarifies the heat transfer parameters which characterize a charcoal bed.[1]

Two computer codes have been developed[2] to estimate the rate of increase of temperature after the initiation of a severe reactor accident. One code considers heat transfer in the air flow direction only, whereas the other considers heat loss out the sides of the charcoal bed as well. Calculations based on the codes indicate that the air velocity and the chronology of the transport of iodine from the reactor core to the charcoal bed are the most important parameters. In addition several sample calculations for conditions possible in a power reactor containment adsorber were performed; in these cases the maximum calculated temperature rise was less than 400°F above ambient.

An experiment is being developed in which temperature rise due to iodine decay heating and the ultimate consequence of decay heatup (i.e., presumably iodine desorption or ignition) will be observed. It is anticipated that about 0.5 g of ^{129}I, in the form of PdI_2, will be irradiated to produce enough ^{130}I to generate about 8.5 watts of heat. The PdI_2 will then be decomposed and the I_2 thus formed will be deposited at a high air velocity on an instrumented, 1" diameter, 2" long charcoal bed. Temperature rises (up to about 150°C) will be observed at low air velocities. In a final test in each experiment, the temperature will be allowed to continue upward until either ignition (i.e., a sharp increase in the rate of temperature rise) or iodine desorption occurs.

[1] R. P. Shields, "Ignition of Charcoal Adsorbers by Fission Product Decay Heat," Proceedings of the 11th AEC Air Cleaning Conference, Richland, Wash., Aug. 31-Sept. 3, 1970, CONF-700816.

[2] R. P. Shields and M. Siman-Tov, "The Effect of Iodine Decay Heat on Charcoal Adsorbers," ORNL-4602, April 1971.

THE FUNCTION OF CONDENSING STEAM IN AEROSOL SCRUBBERS

R. J. Davis and J. Truitt

The ultimate objective of this program[1] is the development of a wet scrubber which efficiently and economically removes fine particles and which functions via three mechanisms in sequence: (1) particle growth by condensation of steam, (2) further growth by turbulent agglomeration, and (3) deposition by impaction. The immediate objective is to show that steam does efficiently condense on particles over a wide range of particle size, particle substance and particle concentration.

In the experimental apparatus, particle growth is made to occur by steam condensation, whereas deposition occurs by thermophoresis. The probability that a particle will deposit has been quantitatively related[1] to the amount of growth; hence the extent of particle growth is indicated by the observed fractional penetration of the aerosol particles through the experimental device.

A series of tests have been performed in which the fractional penetration was measured as a function of steam condensation rate for nine aerosol substances, including samples of hydrophobic, hydrophillic and hygroscopic substances. Particle concentration ranged from a hundred to two million per cubic centimeter, whereas particle sizes ranged from 0.05 to 2.7 microns diameter.

The results have been correlated on the basis of three growth mechanisms, one mechanism each for hydrophobic, hydrophillic and hygroscopic particles. From these three models, three equations were derived to relate the fraction of particles penetrating the device to the steam condensation rate and the incoming particle concentration. The calculated fractional penetrations approximately fit the observed values. Future experiments are planned to study the effect of water vapor supersaturation on growth by condensation and particle growth by turbulent agglomeration.

[1] R. J. Davis and J. Truitt, "The Function of Condensing Steam in Aerosol Scrubbers," ORNL-4654, May 1971.

THE EFFECT OF VELOCITY ON THE FILTRATION EFFICIENCY OF HIGH EFFICIENCY FILTER MEDIA

R. J. Davis and J. Truitt

Many containment systems depend, at least in part, on high efficiency fibrous (HEPA) filters to contain radioactive smoke particles. The nominal filter efficiency of commercial media is 99.97% at the recommended velocity of 5 ft/min. The objective of this program is to determine, as a function of velocity, the efficiency of filtration of tiny, metal oxide, agglomerate particles, such as anticipated in reactor accidents.

An electric arc generated, stainless steel oxide-UO_2 aerosol was employed.[1] This test aerosol contains a wide size distribution, the mean size being very small (about 0.02 microns diameter). The filter efficiency of samples of a dozen commercial filter media were determined in the velocity range 3.5 to 35 ft/min. The filter penetration values varied with filter media by about a factor of two. The general trend was toward a maximum penetration of about 0.05% (or an efficiency of 99.95%) at 10 ft/min; penetration values were less at either higher or lower velocities. This behavior was shown to be consistent with approximate theory.[1]

[1] R. J. Davis, J. Truitt, J. S. Gill and R. E. Adams, "Removal of Radioactive Aerosols on High Efficiency Fibrous Filter Media," ORNL-4524, June 1970.

IODINE TRAPPING ON SOLID ADSORBERS FOR LMFBR FUEL REPROCESSING PLANT OFF-GAS SYSTEMS

R. J. Davis, R. D. Ackley, Z. Combs, and W. H. Hinds

The object of this research is to find solid adsorbers which have, and will maintain, a high decontamination factor (i.e., 10^2 or greater) for all airborne iodine species under all conditions expected to be encountered in treating off-gases from liquid metal fast breeder reactor fuel reprocessing systems. Prior tests surveyed the CH_3I and C_4H_9I trapping capabilities of several metal zeolites and of a silver treated alumina. None of the materials tested seemed to offer advantages to challenge silver zeolite as an adsorber.

Most tests during the past year have been made with 13X (Linde) Molecular Sieve which had either been treated to replace 25% of the cation sites with silver (25% AgX) or to replace 90% of the cation sites with silver (90% AgX). Some tests were also done with GX135, a silver-salt-treated mixture of alumina and silica (commercially obtained from North American Carbon, Inc.).

The 90% AgX provides high decontamination factors (i.e., greater than 10^4) with either CH_3I or I_2, when operated at 100°C or 200°C, up to iodine loadings of at least 12 mg/cm^3. The 25% AgX and GX135 give higher decontamination factors at 200°C than at 100°C, and have a smaller capacity, but they both offer high decontamination factors up to practical loadings (i.e., $\sim$5 mg/cm^3). These adsorbers also have high trapping efficiencies at room temperature provided the relative humidity is low.

The 200°C and 100°C CH_3I trapping efficiencies were correlated on the basis of simple models. It was assumed that the rate of adsorption was proportional to the fraction of unoccupied adsorption sites and to the gas phase concentration of CH_3I. For the 200°C data it was assumed that every silver cation was an adsorption site. For the 100°C data, the same assumption was still applied for the GX135 adsorber, but for the silver zeolites it was assumed that the silver ions were randomly distributed among the three types of sites present in Linde 13X Molecular Sieve and that only the most readily available sites (44% of the total number) were available for adsorption. These assumptions led to equations which described the data accurately.

AQUEOUS TO GASEOUS PARTITION OF IODINE

R. J. Davis and Zell Combs

The objective of this program is to organize information pertaining to the function of caustic scrubbers which might be used to contain fission product iodine from liquid metal fast breeder reactor fuel reprocessing plants. Specifically, the objective is to be able to predict the overall partition of iodine, i.e., the ratio of the sum of the concentration of

aqueous species to the sum of concentration of gaseous species.

We improved on previous[1,2] calculations of the overall partition of iodine from equilibrium constants. Our code, although simple, calculates overall iodine partition, without limiting assumptions, from values of total iodine concentration, gas to liquid volume ratio, pH and reduction potential.

At fairly high iodine concentration, the calculated partition is in reasonable agreement with experiment.[3-5] At these concentrations the main uncertainty seems to be the aqueous solubility of HOI. There is thus a need to establish a value for this quantity.

At low iodine concentration, on the other hand, the calculated partition does not appear to be in agreement with observation.[6,7] Possible causes of the anomalous behavior at this concentration may be usefully categorized in terms of: (1) equilibria between known iodine species and dissolved oxidizing or reducing agents which do not contain iodine atoms, (2) equilibria which include additional iodine-containing species, and (3) slow or irreversible reactions between iodine species and dissolved or colloidal substances. The first of these can be characterized by reduction potentials, the second, by an additional equilibrium constant value for each additional iodine-containing specie, whereas the third is difficult to characterize.

We have designed an experiment in which air is bubbled through I_2-NaI-NaOH solutions and the effluent gas stream led through a gas analyzer which has the purpose of separating molecular I_2, particulate iodine, HOI and CH_3I. The pH and reduction potential of the solution are to be measured. The objectives of the experiment are to estimate the solubility of HOI and to characterize the anomalous behavior at low iodine concentration.

[1] A. E. J. Eggleton, "A Theoretical Examination of Iodine-Water Partition Coefficients," AERE-R-4887, 1967.

[2] L. F. Parsly, "Design Considerations of Reactor Containment Spray Systems, Part IV, Calculation of Iodine-Water Partition Coefficients," ORNL-TM-2412, Part IV, January 1970.

[3] R. F. Taylor, Chem. Eng. Sci. 10, 68-79 (1959).

[4]C. S. Patterson and W. T. Humphries, "Design Considerations of Reactor Containment Spray Systems, Part II, Removal of Iodine and Methyl Iodide from Air by Liquid Solutions," ORNL-TM-2412, Part II, Aug. 1969.

[5]Y. Nishizawa, Y. Kigoshi, O. Oshima, Y. Ozawa, T. Maekawa, "Vapor-Water Partition Coefficient of Iodine and Organic Iodides," ORNL-tr-2255.

[6]L. C. Watson, A. R. Bancroft and C. W. Hoelke, "Iodine Containment by Dousing in NPD-II," CRCE-979, Chalk River, Ontario, 1960.

[7]L. Devell, R. Hesbol and E. Bachofner, "Trapping of Iodine in Water Pools at 100°C," Symposium on Containment and Siting of Nuclear Power Plants," IAEA, Vienna, April 3-7, 1967.

IODINE TRAPPING FOR REACTOR OFF-GAS SYSTEMS

R. J. Davis, R. D. Ackley, and W. H. Hinds

This program pertains to iodine adsorbers on ORNL facilities. Until recently the objectives were to: (1) compare the changes in CH_3I trapping efficiencies with service life of a KI_3 and a triethylenediamine (TEDA) impregnated charcoal, (2) compare the CH_3I-trapping efficiencies measured via laboratory tests[1] with those done in-place[2], and (3) determine the causes of poisoning (i.e., loss of trapping efficiency with service time). Recently the program has been reoriented to a consideration of the desorption of iodine from charcoal beds.

Measurements of CH_3I trapping efficiency of a reactor containment charcoal adsorber were made, in-place, by the Inspection Engineering Department. Laboratory measurements were also made on samples previously exposed in a by-pass stream of the same reactor containment off-gas air. The results indicated: (1) that a TEDA impregnated charcoal maintained a higher trapping efficiency for CH_3I than did a KI_3 impregnated charcoal, and (2) that the laboratory and in-place CH_3I trapping efficiencies did not agree well with each other. It is suspected, but not proven, that the differences between the laboratory and in-place results were due to the CH_3I test loading. The laboratory tests employed a high loading and probably measured trapping efficiency resulting from an isotopic exchange mechanism (on the KI_3 charcoal) or chemical reaction (on the TEDA charcoal). The in-place test used a low loading and may be indicative of trapping due to physical adsorption.

A variety of tests were made which demonstrated that adsorbed organic molecules can decrease the trapping efficiency of charcoals for CH_3I, hence poisoning of the adsorbers may be due to organic contaminants in the air.

It has previously been demonstrated at ORNL[3] and elsewhere that iodine desorbs from charcoal at elevated temperature. We recently showed that desorption occurs slowly at room temperature. R. G. Pope (ORNL Inspection Engineering) demonstrated that the room temperature desorption is very significant in relation to the ORNL allowable penetration values (i.e., 0.1%) from a charcoal which had seen about one year of service. Other unpublished results[4] show that a radiation field (such as would be present in a charcoal bed after a severe accident), enhances this desorption. We are therefore planning a program to obtain information, not available elsewhere, which will make it possible to estimate iodine release due to desorption.

[1] R. E. Adams, R. D. Ackley and Z. Combs, Nuclear Safety Program Annual Prog. Rept. for Period Ending Dec. 31, 1968, ORNL-4374, p. 95.

[2] R. E. Adams, R. D. Ackley and Z. Combs, Nuclear Safety Program Annual Prog. Rept. for Period Ending Dec. 31, 1967, ORNL-4228, p. 110.

[3] J. H. Swanks, "In-Place Iodine Filter Testing," Proceedings of the 9th AEC Air Cleaning Conference, Boston, Mass., Sept. 13-16, 1966, CONF-660904, p. 1092.

[4] G. F. Merz et al., unpublished work.

AEROSOL BEHAVIOR IN CONTAINMENT STRUCTURES

R. J. Davis and J. S. Gill

Previously, we devised a simple calculation[1] of airborne particle concentration in a reactor containment as a function of time after an accident. The calculation assumed that the particle size distribution could be adequately described by a steady-state particle size distribution function,[2,3] and a sharply defined minimum particle size.

Experiments were performed[4] to demonstrate that the distribution function adequately describes an electric-spark-generated, stainless-steel-oxide aerosol, and to indicate the dependence of minimum particle size on

such environmental parameters as age, initial concentration and Reynold's number. In the experiment, an aerosol which was generated from an electric spark between stainless steel electrodes was blown down a tube (4" diameter). The tube length and air flow rate were varied, from experiment to experiment, and the particle size distribution measured.

The results indicated that the steady-state size distribution function from a sharply defined minimum size is an adequate description of the highly agglomerated aerosol tested (and presumably of any highly agglomerated aerosol). Furthermore, the minimum sizes could be correlated with only one parameter, the aerosol age (i.e., the time from particle generation to the time of sampling for size analysis).

[1] R. J. Davis, "A Simple Model for the Estimation of Aerosol Concentration in a Closed Vessel," American Industrial Hygiene Assoc. J. (in press).

[2] S. K. Friedlander and C. S. Wang, J. Coll. Int. Sci. 22, 126-132 (1966); 24, 170-179 (1967).

[3] B. Y. H. Liu and K. T. Whitby, J. Coll. Int. Sci. 26, 161-165 (1968).

[4] R. J. Davis and J. S. Gill, "Estimation of Aerosol Concentration in a Nuclear Reactor Containment After an Accident," Proceedings of the 11th AEC Air Cleaning Conference, Richland, Wash.. Aug. 31-Sept. 3, 1970, CONF-700816.

HIGH TEMPERATURE RUPTURE STUDIES OF IRRADIATED ZIRCALOY FUEL RODS

M. F. Osborne and G. W. Parker

The swelling and rupture of the Zircaloy-clad UO_2 fuel rods could significantly reduce the efficiency of emergency cooling systems in a loss-of-coolant accident in a water-cooled power reactor. Consequently, the effects of irradiation on the properties of Zircaloy were investigated through rupture tests of single rods under conditions simulating such an accident.

Twenty fuel rods, irradiated to 3,000-7,000 MWd/T, were ruptured in flowing steam in a remotely-operated induction furnace. A similar number of unirradiated rods were tested for comparison. Each fuel rod was pres-

surized with argon (in the range 50-1000 psig) to simulate fission gas release at high power and high burnup. The tests included linear heating rates of 10, 25, and 50°F/sec, starting from 600°F to rupture. Cladding ruptures occurred between about 1500°F for 1000 psig tests and about 2500°F for 50 psig tests. Maximum swelling varied from less than 20% to greater than 70%, with the smaller expansions occurring in the two-phase $\alpha + \beta$ region (1500 - 1780°F). Some embrittlement and strengthening was caused by steam oxidation in the higher temperature (> 2100°F) tests. The only indicated effect of irradiation on the swelling and rupture properties was a small (30% average) reduction in expansion.

These data were compared with a failure model based on a secondary creep equation, developed by White,[1] and with the results of tube burst tests conducted in inert atmospheres by Hobson.[2] In view of some experimental differences, such as methods of heating and test atmospheres, the data correlation is good. Our tests indicate that in a loss-of-coolant accident the irradiated rods will swell less than would unirradiated rods, and that coolant channel blockage may be less extensive than has been predicted by laboratory tests of unirradiated Zircaloy.

[1] E. F. Juenke and J. F. White, "Physical-Chemical Studies of Clad UO Under Reactor Accident Conditions," USAEC Report, GEMP-731, General Electric Co. (1970).

[2] D. O. Hobson, M. F. Osborne, and G. W. Parker, Nucl. Tech. 11, 2 (1971).

FISSION-PRODUCT BEHAVIOR EXPERIMENTAL PROGRAM FOR LOFT

G. W. Parker, W. J. Martin, and G. E. Creek

Commercial nuclear power plants presently are designed with emergency core cooling systems for maintaining core integrity in the event of a loss-of-coolant accident. Activation of the emergency core cooling system is expected to reduce the quantity of fission products released from the core; however, use of this engineered safety feature does not eliminate the possibility of limited fission-product release. Once fission products escape across the fuel pin cladding barrier, a fraction will be transported

through the primary system to the containment. The fission products which remain airborne in the containment atmosphere represent the potential source available for leakage from the containment to the environment through any leakage path in the containment shell and its penetrations.

The ORNL-LOFT assistance program was directed toward a demonstration of the release and transport processes that define the amount of fission products which escape from vented or ruptured fuels. The experimental work in the program consisted of release of actual and simulated fission products under various accident conditions in the containment research installation (CRI). This facility consists of a primary vessel simulator and a 125-ft^3 containment vessel which may be fitted with liners of different materials to simulate different surfaces within a reactor containment. In the most recent series of tests, the inherent deposition behavior of radioiodine has been compared over a wide range of concentrations for both the stainless steel system and a typical epoxy-base organic surface of Amercoat-66.

Over a 1000-fold range of iodine mass concentration released in the Amercoat-lined CRI, the fraction converted to organic alkyl iodine varied inversely by the same magnitude. This suggests that in the application to a real reactor accident any release of radioiodine will result in the production of a constant quantity of methyl iodide (CH_3I) instead of a constant fraction of that released.

FUEL ROD FAILURE IN SIMULATED LOSS-OF-COOLANT ACCIDENTS

R. A. Lorenz and G. W. Parker

Large water-cooled power reactors provide emergency cooling systems to prevent excessive fuel rod temperatures in case of loss of the primary reactor coolant. Two experiments have been performed with seven-rod bundles of Zircaloy-clad fuel rods in the Transient Reactor Test Facility (TREAT) where fissioning in the UO_2 pellets provided realistic simulation of a loss-of-coolant accident.

Helium pressures between 65 and 215 psia (at 25°C) simulated accumulated fission gas, and the reactor transients were sized to yield maximum

cladding temperatures of 1000°C and 1300°C in the two experiments. All of the rods swelled and ruptured; the swelling of the low pressure rods was equivalent to blockage of 91% of the coolant channel area of a modern boiling water reactor. The amount of swelling and the stress at rupture agreed well with data from laboratory-scale experiments.

Fission product release from the irradiated center rod of each experiment was between 0.1 and 0.5% of inventory for iodine, cesium, xenon, and krypton. The release of the low volatility fission products (Ru, Sr, Ce, and Zr) was 0.001% in the low temperature experiment, and almost a factor of ten lower in the second experiment because of a small rupture opening and a chemically reducing hydrogen-rich atmosphere.

The rate of swelling of the Zircaloy cladding was calculated from continuous measurements of temperature and pressure. We further calculated that the swelling (and therefore coolant channel blockage) of a full scale reactor fuel rod could be significantly reduced by the use of a check valve to confine fission gas to the rod plenum during an accident. A conventional fuel rod containing 75 psia of fission gas (at 25°C) would rupture at 1030°C but with a check valve would not rupture until 1350°C.

KINETICS OF THE STEAM-GRAPHITE REACTION

A. P. Malinauskas and C. M. Blood

Studies of the chemical kinetics characteristic of the steam-graphite reaction relate directly to an assessment of the consequences of steam inleakage in a high-temperature, gas-cooled, nuclear reactor. As is typical of many gas-solid reactions of commercial interest, a complicating feature is introduced in the kinetics studies owing to the fact that the solid surface undergoes continual alteration as a result of chemical reaction. The investigations thus far are therefore concerned with both the usual aspects of reaction kinetics and with the geometrical changes, on the micro scale, which result from reaction as well. For example, in one instance we have observed an approximate two-fold increase in the apparent rate of reaction of a specimen after about 10% of the original sample had been removed due

to exposure to steam. Over the same interval, the surface area, as determined by nitrogen adsorption, was observed to increase from 5 m^2 to 39 m^2.

In addition, we have observed a tendency for heavy metal impurities to agglomerate within the graphite. Furthermore, the sites of these agglomerates appear to be areas of extremely high reactivity, so much so that some graphite samples of relatively high metal impurity content were severely pitted after only brief exposures to steam at 1000°C.

THE REACTION OF STEAM WITH HTGR FUEL ELEMENTS DURING IRRADIATION

S. H. Freid, W. H. Montgomery, H. J. de Nordwall, and O. Sisman

The objectives of this program are to demonstrate that rate constants measured out-of-pile can be used to describe the way carbon is removed from an operating HTGR fuel element, and to study the behavior of the fuel element in the presence of steam.

The experimental facility has been described previously.[1] Three experiments in this series have been performed. The first experiment (SG-1) employed SiC coated microspheres and was designed as a test of the facility. Due to impurities in the H-327 graphite used for the fuel element casing, a high oxidation rate was observed. Oxidation occurred by a pitting mechanism. Also, we did not observe the expected superior resistance of SiC coated particles to steam, and this was probably due to the migration of the iron impurity from the graphite to the SiC layer. The experiment did however demonstrate that at higher temperatures the oxidation of the fuel binder material is dependent almost entirely on the properties and temperature of the outer graphite casing which functions as a sacrificial protective envelope.[2] All three experiments showed marked increases in the rates of gas release following the addition of steam.

[1] S. H. Freid, H. J. de Nordwall, B. F. Roberts, O. Sisman, and W. H. Montgomery, Reactor Chemistry Division Ann. Prog. Rept. Dec. 31, 1968, ORNL-4400 (1970), p. 120.

[2] H. J. de Nordwall and G. M. Watson, Nuclear Safety Program Ann. Progr. Rept. Dec. 31, 1969, ORNL-4511 (1970), p. 89.

ADSORPTION AND DESORPTION OF IODINE FROM Fe_3O_4

E. Hoinkis*

The adsorption of iodine on Fe_3O_4 has been measured between 250°C and 450°C at iodine partial pressures between 10^{-10} and 10^{-5} atm. Use of ^{131}I tracer permits the adsorption to be followed continuously. Following an adsorption experiment, samples of the iodine-loaded Fe_3O_4 were transferred in vacuo to a desorption apparatus, and the rate of desorption under vacuum conditions was measured as the specimen temperature was raised.

Iodine adsorption was slow, indicating an activated process. For example, a surface concentration of about 0.01 monolayers was reached only after 20 hours exposure to iodine at 10^{-9} atm at 450°C.

Desorption spectra[1] were obtained by plotting rate of desorption against temperature. For high iodine loadings a complex desorption spectrum was obtained, suggesting occupancy of sites of many different energies. However, at low concentrations (less than 0.025 monolayers), the desorption spectra contained only a single peak at about 420°C whose position appeared to depend onoy on iodine loading, or the energies of occupied sites, rather than on the loading temperature.

Analyses of desorption spectra and studies of peak displacement as a function of heating rate are being made to elucidate the order of reaction and a rate constant.

The activation energy characteristic of the predominant desorption process for iodine adsorbed at low pressure is approximately 40 kcal/mole.

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[1]A. W. Smith and S. Aranoff, J. Phys. Chem. 62, 684 (1958).

FISSION PRODUCT SURVEILLANCE STUDIES IN THE PEACH BOTTOM HTGR

F. F. Dyer,* J. O. Kolb,** and H. J. De Nordwall

The concentrations of fission products and other solid impurities present in the coolant circuit of the Peach Bottom HTGR are being measured us-

ing γ-spectroscopy and gas sampling techniques. The information obtained will be used to evaluate the applicability of current mathematical models of fission product behavior in a real plant, and to provide a body of fact for utilities and HTGR vendors to use in licensing and siting arguments.

The concentrations of rare gases with half-lives down to 33 sec were measured in a small duct during reactor operation and in the presence of deposited and circulating impurities.

The surface concentrations of γ-emitting isotopes have been determined at several places in the primary coolant circuit, both upstream and downstream of the steam generator. The principal activities were ^{134}Cs, ^{137}Cs, and ^{60}Co; ^{131}I was not detected.

We have deduced from the ratios of $^{95}Zr/^{95}Nb$, $^{103}Ru/^{106}Ru$ and $^{141}Ce/^{144}Ce$ which were observed that traces of fuel that entered the coolant during Core I have not circulated through the core during Core II.

We are currently evaluating what information may be obtainable by γ-analysis of the contents of the large inlet and outlet ducts of an 1100 MW HTGR.

Microscopic examinations of samples of dust supplied by Gulf General Atomic Inc. have confirmed previous estimates of dust composition and revealed that carbon deposition did occur on a diffusion probe body which was maintained at about 700°C.

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VII. SALT MINE REPOSITORY

GAS FLOW CHARACTERIZATION OF UNCONSOLIDATED BEDS

R. B. Evans III and J. L. Rutherford

Burial of highly radioactive waste in bedded salt[1] presents an important problem with respect to the behavior of the crushed salt used to cover waste casks in storage holes. Initially the crushed salt will comprise an unconsolidated bed; however, a combination of heat and moisture will induce consolidation, and finally, partial solidification of the salt. An ultimate objective is the investigation of this metamorphic process as influenced by steam-air transport phenomena.

Present activities involve the flow and diffusive behavior of helium and argon in unconsolidated beds comprising various grades of crushed salt obtained from the Carey Mine at Hutchinson, Kansas. Grades investigated were medium, fine, medium-fine mixture (50-50 wt %), and truncated run-of-the-mill. Average grain diameters were 0.41, 0.08, 0.17, and 0.056 cm respectively; bed porosities were 37.5, 37.7, 26.8, and 34.4 vol % respectively. Viscous flow and counter-diffusion coefficients decreased in the same order as the grade listing above. For example, the argon permeability coefficient at 1 atm for the mixture was 1.6×10^3 cm^2/sec while truncated run-of-the-mill was 9×10^2 cm^2/sec.

Results obtained for the mixture dramatically demonstrated the importance of porosity reduction, since the low value for this parameter counterbalanced the effects of the high average particle size. The low porosity value resulted from the wide range of particle sizes involved. When the porosities range about 35 vol %, it appears that the best way to decrease the gas parameters is to decrease the average grain size.

[1]National Research Council, "Disposal of Solid Radioactive Wastes in Bedded Salt Deposits," USAEC Report AT (30-1)-4155, Nov. 1970.

VOLATILITY ENHANCEMENT OF FISSION PRODUCT OXIDES IN THE PRESENCE OF WATER VAPOR

A. P. Malinauskas

The calcined radioactive waste encapsulated within one of the containers within the high-level facility of the radioactive waste repository will undergo a change in chemical environment in the event of a containment breach. Should such an incident occur prior to reconsolidation of the surrounding salt mass, volatile species which might form as the result of the change in chemical environment could possibly be transported unacceptably rapidly through the facility. As a result, a program of investigation has been initiated to ascertain whether or not volatile forms of radioactive waste can in fact exist under the conditions stipulated.

This study began with a consideration of the effects of water vapor, since this species is expected to be the major component of the new environment in the event of a containment breach, and because it is well known that a rather broad class of oxides undergoes vapor pressure enhancement in a moist atmosphere.[1] As a result of this investigation, it was concluded that although significant enhancement in the volatility of oxide species can result from an interaction with water vapor, the temperatures and oxides of concern to radioactive waste disposal in the repository are such that the phenomenon is not an important mechanism for gas-phase transport. Should transport via a surface diffusion mechanism prove significant, however, the effect of water vapor on this type of migration ought to be investigated.

[1] A. P. Malinauskas, J. W. Gooch, Jr., and J. D. Redman, Nucl. Appl. Tech. 8, 52 (1970).

SURFACE DIFFUSION OF OXIDES ON SODIUM CHLORIDE

B. K. Annis

Since the time scale necessary for safe storage of high level wastes in the radioactive waste repository is essentially infinite, a number of otherwise trivial physical processes may provide significant loss mechan-

isms for the stored radioactive material. One of the possibilities that has not been sufficiently evaluated is that of surface diffusion.

It was anticipated that the waste materials would be primarily in the form of oxides, and a subsequent literature study indicated that no relevant data for molecular diffusion on a sodium chloride substrate existed. Furthermore, diffusion coefficients inferred from film deposition data by a standard calculation indicated that, at least in the case of atomic diffusion, surface transport could be surprisingly large. Consequently an experimental program was begun in which lanthanum oxide was used as a simulant for plutonium.

Layers of the oxide were deposited upon portions of a number of salt crystals, and a diffusion anneal of approximately two days was carried out. An electron microprobe was used to determine the whereabouts of the oxide, and the presence of a diffusion-like concentration profile was indicated. Analysis of the results yielded a surface diffusion coefficient of approximately 10^{-10} cm^2/sec; this is several orders of magnitude less than that expected on the basis of the literature survey.

Further, more detailed examination with the microprobe indicated that lanthanum oxide, in amounts just at the detection threshold, had spread considerably farther over the crystal than previously indicated. These observations were corroborated by subsequent analyses based on Auger electron emission. This type of behavior does not appear to fall within the framework of diffusion theory and may be an artifact of the deposition process.

SOLID STATE DIFFUSION OF PLUTONIUM IN SODIUM CHLORIDE

G. M. Watson

In support of a demonstrational repository for radioactive wastes in an underground salt mine,[1] a literature survey was made in an effort to estimate the rate of solid state diffusion of plutonium in rock salt at temperatures less than 300°C.

The results of several types of investigation were considered: (1) Self-diffusion of Na^+ in NaCl; (2) interdiffusion of various metal ions in NaCl; (3) interdiffusion of some metal ions through a similar but larger lattice such as KCl; (4) self-diffusion of various ions in a variety of inorganic salts; and (5) interdiffusion of metal ions in various inorganic salts.

The calculations showed that at the temperatures of interest, the rates of solid state diffusion of a variety of ions through inorganic salts are extremely slow. For example the calculated root mean square displacement of Na^+ in NaCl in one million years is only 25 cm at 350°C. In addition, the diffusion and interdiffusion of various metal ions in a variety of salts is also quite slow. In general, root mean square displacements of less than forty meters are expected in one million years at temperatures around 350°C.

Due to other factors, such as surface and grain boundary diffusion, it is not possible to guarantee, on the basis of this brief study, that plutonium diffusion will not be a problem in the salt mine repository. It is recommended that some experimental work be done using lanthanum as a stand-in for plutonium.

[1]National Research Council, "Disposal of Solid Radioactive Wastes in Bedded Salt Deposits," USAEC Report AT (30-1)-4155, Nov. 1970.

RADIOLYSIS AND HYDROLYSIS OF SALT MINE BRINES

G. H. Jenks

Salt deposits of the type to be used for radioactive waste disposal contain a small volume-fraction of brine inclusions (∿ 0.5%). Some brine from these inclusions will enter the open and unconfined spaces around a waste can[a] due to the migration of the inclusions which occurs as the result of thermal gradients in the salt, and due to salt-fracture which takes place at high temperatures, starting at about 250°C.[1] In addition to the high temperatures involved, the brine, vapors and salts around a can will be exposed to high γ-ray intensities and doses. Accordingly, they will be

subject to radiolysis and to other changes in composition brought about thru thermally-induced reactions.

We made a detailed review and analysis of literature information bearing on the radiation and thermal chemistries of the salt and brines within the vicinity of a buried waste can, with the objective of providing information on the identities of the final radiolysis- and thermal reaction-products and of the amounts formed and released into the spaces around a can. Important radiolysis products which were identified included H_2, O_2 and possibly ClO_3^-, and BrO_3^-. Most of the ClO_3^- and BrO_3^- will decompose to halides and O_2 at the high temperatures around a can; $Mg(BrO_3)_2$ if present may give rise to some Br_2. Nearly all of the H_2, and the accompanying oxidized species, are formed within the migrating brine inclusions by the radiations absorbed within the brine and by dissolution of the interstitial chlorine and trapped electrons from the irradiated solid salt.

The brine is rich in $MgCl_2$ (2.3 to 3M), and hydrolysis of the $MgCl_2$ around a can will produce HCl. No serious problems arising from radiolytic or thermal effects have been recognized, but additional considerations of the radiolysis and the flammability of gases and vapors around a can are required.

[a]As presently planned,[1] solidified wastes will be canned in a metal container. The container will then be lowered into a vertical hole within the bedded salt, and the hole back-filled with some unspecified material. The heat output of the wastes within a given can will be as high as 5 kw at burial.

[1]W. C. McLain and R. L. Bradshaw, Nuclear Safety, 11, 130 (1970).

VIII. SPECIAL RESEARCHES

ECONOMIC ASPECTS OF ENVIRONMENTAL DEGRADATION

D. M. Moulton

In a perfectly functioning market economy, the net demand for goods and services (total desire minus total cost) is optimally satisfied because of feedback into the competitive system. However, there are phenomena which, by their nature, lie outside this mechanism. Pollution is an example of such an "externality"; a buyer is injured only negligibly by the pollution arising from the manufacture of a certain item, so the price he is willing to pay does not depend on whether pollution actually did occur. (If he suffered finite and identifiable damage he would pay that much less). Since pollution, unlike product deficiencies, is not automatically reduced by the market mechanism, it is possible that the damages resulting from it may substantially exceed cleanup costs. In this study a survey was made of the damage costs resulting from various types of pollution.

The data for air pollution are the most complete. In this instance there is abundant evidence of damage to health and property, and in many cases rough dollar values have been assigned. There are several classes of damage: soiling, deterioration of materials, injury to living creatures (including man), and esthetic and sensory damage (which has a considerable cost component). Damages are substantial for rubber, textiles, metals (especially galvanized iron), paint, and concrete and limestone. There is also considerable damage to commercial agriculture and of course to human health. Estimates of the cost vary but center around $15 billion per year in the United States alone. Water and solid waste costs are harder to assign; these are mainly esthetic, but they are true costs because people are willing to pay to eliminate the problem. By this measure they are of the same order of magnitude as the air pollution costs. Consideration was also given to ways to introduce these costs into the market mechanism, thereby allowing minimization of the function (pollution damages + cleanup costs), which is not now being done.

PARTICIPATION IN PLOWSHARE ACTIVITIES

C. J. Barton and M. J. Kelly

Initial studies of the hypothetical consequences of using natural gas or its byproducts containing radionuclides introduced by the use of nuclear explosives were performed in connection with the Gasbuggy project, the first of two experiments on gas stimulation completed with industrial participation. Doses that would result from the introduction of Gasbuggy gas into El Paso Natural Gas Company's distribution system and that of its customer companies, particularly in Los Angeles and San Francisco, were calculated. At tritium levels expected to be achieved in large scale exploitation of the nuclear stimulation concept, doses in these metropolitan areas were estimated to be less than 3 millirem/year.

An experiment was conducted in a small natural gas processing plant near Barnhardt, Texas, in cooperation with El Paso Natural Gas Company, to study the distribution of tritium among plant products and doses to plant personnel during the processing of gas containing radionuclides. Analyses of samples are not complete but it appears that the tritium distribution followed the predicted pattern. A sufficient number of atmospheric moisture samples was collected and analyzed so that tritium concentration contour lines could be drawn. These were in accord with the known plant sources of gas combustion products and with the average wind direction during the test.

RADIATION-INDUCED REACTIONS OF HYDROCARBONS

Ruth Slusher and W. W. Parkinson

The possibility of utilizing radiation for the hydrogenation and alkylation of aromatics, such as those in coal, is currently being studied by irradiating solutions of naphthalene in n-hexane as model compounds. The major portion of the radiation products consist of compounds of greater molecular weight than hexyl naphthalene and are unsuitable for gas chromatographic analysis.[1] However, this portion of the radiation product could be resolved into four fractions by gel permeation chromatography.[2] The

fraction of lowest molecular weight could not be separated further by thin-layer chromatography, but the higher molecular weight fractions were each resolved into four to six constituents on silica gel chromatographic plates. Mass spectrometric analysis of these fractions from the thin-layer chromatographic separation proved inconclusive because of background peaks either from the silica gel or from the developer solvent.[3] The mass spectrometric analyses are now being performed on the four gel permeation fractions themselves, without further separation.

[1]W. W. Parkinson, Ruth Slusher, and W. K. Kirkland, Reactor Chem. Div. Ann. Progr. Rept. May 31, 1970, ORNL-4586, p. 123.

[2]N. J. Williams, private communication.

[3]W. T. Rainey, private communication.

THE DEVELOPMENT OF RADIATION-RESISTANT INSULATORS

W. W. Parkinson, H. H. Stone, M. J. Kelley, and Ruth Slusher

Previous work under this program had indicated that for personnel dosimeters the radiation-induced conductivity in the critical capacitor dielectric must decay to about 10^{-19} mhos/cm within 10^4 seconds after irradiation. In the only available insulator suitable for such use, it was found that sulfate end groups on the polymer chain produced a rapid decay of conductivity after irradiation.[1,2]

The sulfate groups are incorporated at the chain ends as initiator residues during the polymerization process in an aqueous emulsion. The emulsifier residues, largely alkly benzene sulfonate, were shown to be ineffective in the decay of conductivity. This was done by measuring the conductance of polystyrenes synthesized without the sulfate end groups but with the emulsifier residues.

Under the assumption that the polar sulfate end groups act either as traps or as recombination centers for the charge carriers, various groups of differing degrees of polarity have been incorporated into styrene polymers and copolymers under a related contract with Monsanto Research Corp.

Mercaptan chain transfer agents incorporate sulfur-containing groups and are useful for controlling molecular weight. The end groups $C_{12}H_{25}S$- proved inactive electrically both when present in non-polar polymers and when inserted along with sulfate end groups. Initiation with H_2O_2 yielded -OH end groups in a polystyrene with sodium stearate emulsifier, and the decay of conductivity approached the rate with sulfate end groups. On the other hand, the strongly polar methacrylic acid side group in a polymer without emulsifier was ineffective. The possibility that strongly ionized positive species, i.e., metallic or ammonium ions, serve as traps or recombination centers is now being pursued.

[1]M. J. Kelly, W. W. Parkinson, W. K. Kirkland, and C. W. Linsey, Reactor Chem. Div. Ann. Progr. Rept. May 31, 1970, ORNL-4586, p. 123.

[2]M. J. Kelly and W. W. Parkinson, "The Development of Radiation-Resistant Insulators," ORNL-TM-2986 (1970).

FAST-NEUTRON IRRADIATION EFFECTS ON ELECTRICAL INSULATORS[1]

G. W. Keilholtz, R. E. Moore, and H. E. Robertson

The effects of fast neutrons on four commercial polycrystalline alumina products of high density were investigated. These materials have been considered for use as electrical insulators in nuclear-powered thermionic converters. Fast-neutron fluences up to 5.8×10^{21} neutrons/cm^2 (>1 MeV) were achieved; irradiation temperatures ranged from 60 to 1230°C.

At temperatures below 100°C, there was very little damage, as is usually manifested by gross fracturing, volume increase, and separation at grain boundaries. Damage was much worse, however, at temperatures from 570 to 1070°C, which is the range of greatest interest for thermionic applications. At about 1100°C and above, in-reactor thermal annealing was rapid enough to reduce damage significantly, but at much higher temperatures ($\sim$ 1230°C), damage again increased.

Based on the irradiation results, the following conclusions and recommendations were made for the use of polycrystalline alumina in thermionic converters: (1) the alumina should be of high purity to minimize gross

fracturing, and it should be of small grain size to minimize the effects due to separation at grain boundaries, (2) the thermionic device should be designed for continuous operation because thermal cycling apparently promotes separation at grain boundaries, (3) the design should allow for an increase in volume of the alumina insulators of about 3%, and (4) alumina of high purity and small grain size can withstand fast neutron fluences up to about 3×10^{21} neutrons/cm^2 in an ETR type neutron spectrum and up to about 2×10^{21} neutrons/cm^2 in an EBR-II type spectrum for those neutrons with energies greater than 1 MeV.

Four other electrical insulators were investigated in a preliminary manner as possible alternatives to polycrystalline alumina for thermionic applications. These are: (1) single-crystal Al_2O_3, (2) single-crystal MgO of high purity, (3) transparent polycrystalline Y_2O_3, and (4) silicon oxynitride (Si_2ON_2). The preliminary results were very encouraging. More comprehensive investigations of these materials appear to be warranted.

[1] G. W. Keilholtz, R. E. Moore, and H. E. Robertson, "Effect of Fast Neutrons on Polycrystalline Alumina and Other Electrical Insulators at Temperatures from 60 to 1230°C," ORNL-4678 (May 1971).

HELIUM RELEASE EXPERIMENTS

G. W. Keilholtz, R. E. Moore, and D. A. Dyslin*

A gas pycnometer which can measure the swelling of B_4C specimens during irradiation has been evaluated in an out-of-pile system. In its proposed use, the specimen chamber in the reactor core would be connected by a capillary tube to a bellows volume changer which is located outside the reactor. An accurate pressure gage would be located near the bellows. In practice the specimen will be at 700°C in-pile, whereas the capillary tube and bellows will be near room temperature.

A preliminary error analysis of the system, including temperature variations, has shown that the volume of a one cubic inch specimen could be determined within $\pm$ 0.7%. This predicted error is due to inaccuracies in pressure and temperature measurements as well as the initial volume of the system. It is desirable to detect specimen swelling of 5% during a

a three-month irradiation; therefore, an error of ± 0.7% on a daily reading is undesirable.

A bench test of the proposed gas pycnometer method has been completed, first with the entire system at room temperature, and then with the specimen chamber at temperatures between 500°C and 700°C, with the remainder of the system at room temperature. The results of the room temperature tests demonstrate that the volume of a one cubic inch specimen can be determined within ± 0.3%. The 500°C to 700°C tests show that the system is more sensitive to temperature changes than to specimen volume changes however. Data points of specimen volume versus pressure ratio for specimens between 0.0 and 0.015 cubic inches, with the specimen chamber between 700°C and 710°C, showed no change in pressure ratio. Other data at 540°C and 650°C resulted in appreciable change in pressure ratio with change in temperature. Thus the above system would be useful in measuring volume changes in a room temperature system where the temperatures were uniform and well known, but will not be practical in a high temperature system.

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