methanol, the extent of (*a*) solvent molecule immobilzation in the immediate vicinity of an ion, and (*b*) solvent structure disruption beyond the periphery of the ionic species, will determine the extent of any net structure-making or -breaking effect. In the presence of pyridine, (*a*) appears to offset (*b*) more than when nitromethane or benzene are present, or when no additive is present. The small reduction in mobility observed here in the presence of benzene is about the same as that observed at 25° C. (*1*).

The values of ΔH, ΔS^0, and ΔF^0 for the equilibrium of silver nitrate in methanol, and in the presence of the additives pyridine and benzene, are consistent with the exothermic nature of the solvation process. However, solvation in the presence of nitromethane appears to be an endothermic process. This is brought about by silver nitrate behaving as a much weaker electrolyte at 25° than at 30° C. At 25° C., there is much greater ionic mobility at infinite dilution in the presence of nitromethane than when either pyridine or benzene is present or in the absence of an additive (*1*); whereas at 30° C., only a small diminution in Λ_0 is observed. Thus the extent—and perhaps nature—of solvation has, in the course of a 5° rise in temperature, undergone a profound change. A number of explanations could be advanced for this, but only two will be mentioned here. The silver ion may, more or less, be permanently solvated mainly by nitromethane at 25° C., whereas at 30° C. methanol largely replaces nitromethane in this role. Also, the silver ion at 25° C. may not be permanently solvated by either nitromethane or methanol, whereas at 30° C. permanent solvation, mainly owing to silver ion-methanol interaction occurs. Both these suggestions imply that, in the presence of nitromethane, the effective bonding between solvent molecules, within the solvate sheath and those in the bulk of the solvent, is more important at 30° than at 25° C.—i.e., any dragging effect involving long range forces should be more pronounced at the higher temperature. However, more data are needed at other temperatures to make any explanation more conclusive.

NOMENCLATURE

Λ_0 = limiting equivalent conductivity of electrolyte, silver nitrate, at infinite dilution
Λ = equivalent conductivity of electrolyte, silver nitrate
K_A = association constant
ΔH = heat of dissociation in calories
ΔS^0 = entropy of dissociation, in calories, at unit activity
ΔF^0 = free energy of dissociation, in calories, at unit activity
c = concentration of electrolyte, silver nitrate, in moles per liter of solution

LITERATURE CITED

(1) Busby, R.E., Griffiths, V.S., *J. Chem. Soc.* **1963**, p. 902.
(2) Butler, J.A.V., "Chemical Thermodynamics," 4th ed., p. 459, Macmillan, London, 1949.
(3) Davies, C.W., "The Conductivity of Solutions," 2nd ed., p. 50, Wiley and Chapman, London, 1933.
(4) Frank, H.S., Evans, M.W., *J. Chem. Phys.* **13**, 507 (1945).
(5) Frank, H.S., Wen-Yang Wen, *Discussion Faraday Soc.* **24**, 133 (1957).
(6) Fuoss, R.M., Kraus, C.A., *J. Am. Chem. Soc.* **79**, 3304 (1957).
(7) Gillo, L., *Ann. Chim. Paris* 12, 281 (1939).
(8) Glasstone, S., "Textbook of Physical Chemistry," 2nd ed., p. 830, Macmillan, London, 1948.
(9) Griffiths, V.S., *J. Chem. Soc.* **1952**, p. 1326.
(10) Hartley, H., Barrett, W.H., *Ibid.*, **103**, 786 (1913).
(11) Rybicka, S.M., Wynne-Jones, W.F.K., *Ibid.*, **1950**, 3671.
(12) Shedlovsky, T., *J. Franklin Inst.* **225**, 739 (1938).

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Phase Transition on Submicron Particles of ZrO_2

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Spherical submicron particles of ZrO_2 were a mixture of 50% monoclinic and 50% tetragonal ZrO_2. The metastable tetragonal phase transformed to the monoclinic phase when samples were heated to 820° C. for 2 hours. The transitions of the as-received ZrO_2 samples determined by high temperature x-ray diffraction and differential thermal analysis methods were from 1000° to 1190° C. (increasing temperature, endothermic) and 1040° to 300° C. (decreasing temperature, exothermic). The transformations for specimens preheated to 1450° C. were from 1110° to 1205° C. (increasing temperature) and from 980° to 895° C. (decreasing temperature)

POLYMORPHIC TRANSITION encountered in ZrO_2 has been studied by many investigators (*2, 5, 6, 7, 9*). Recently, the high temperature tetragonal phase was stabilized to room temperature by pressures of 15 to 20 kbars at temperatures of 1200° to 1700° C. (*8*). The reversible monoclinic-tetragonal transition of ZrO_2, which is associated with a destructive volume change makes its higher temperature applications very difficult. This transition occurs rapidly with increasing temperature at 1193° to 1205° C. and with decreasing temperature at 1050° to 1000° C. (*3, 4*). Baun (*1*) found by high temperature x-ray diffraction on spectrographic grade ZrO_2 (99.95% pure), a transition temperature range from 1000° to 1200° C. with increasing temperature, and from 980° to 750° C. with decreasing temperature.

EXPERIMENTAL

Spherical submicron particles of ZrO_2 (99.7% pure with 0.1% carbon as the major impurity), as-received from Vitro Laboratories with an average particle size distribution of 0.04 micron, were used in studying this transformation. These particles were prepared by a carbon arc vaporization - sublimation process using monoclinic ZrO_2 powders (325 mesh) as starting materials. Table I shows the principal impurities of a typical sample and the impurity distribution of a sample heated to 820° C. in air for 2 hours using a platinum boat.

Subsequent x-ray diffraction analysis using Co $K\alpha$ radiation indicated the particles to be a mixture of 50% monoclinic–50% tetragonal ZrO_2. The percentage of monoclinic

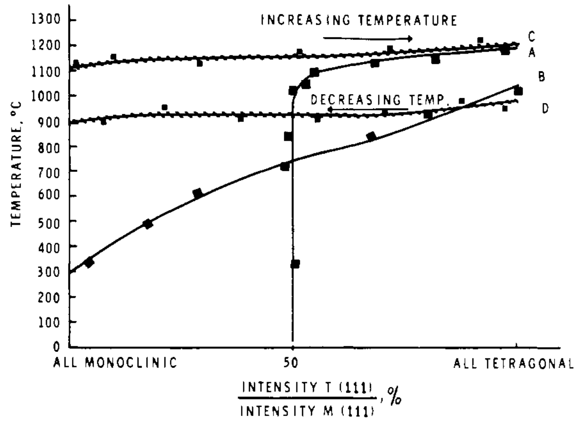

Figure 1. High temperature x-ray hysteresis of ZrO_2
As-received particles (curves A and B)
Pre-heated to 1450° C. particles (curves C and D)

and tetragonal phases present in samples was derived on the intensities of the (III) - reflections. To determine the thermal stability of the tetragonal phase, samples were placed in platinum boats and heated in air from 600° to 1450° C. for 2 to 6 hours using a standard resistance furnace. Specimens heated to 820° C. or above showed by subsequent x-ray analysis only the monoclinic phase. The high temperature x-ray studies were undertaken with a TEM-PRES X-ray Diffractometer. The samples were placed on a flat platinum holder in the form of a Duco cement–alcohol–zirconia paste, and heated by a Pt–20% Rh wound alumina furnace surrounding the sample holder arrangement. Copper Kα radiation was used for the high temperature x-ray study. The heating and cooling rates determined by two Pt, Pt–10% Rh thermocouples were about 600° C. an hour and are considered to be accurate within ±5° C. Figure 1 presents the x-ray hysteresis of the as-received ZrO_2 sample (curves A and B), and that of a sample, having an average particle size of 10 microns, preheated in air to 1450° C. for 2 hours (curves C and D). The transformations for increasing temperature of the 50% monoclinic–50% tetragonal ZrO_2 sample towards the all tetragonal phase started to increase at about 1000° C. and was completed at 1190° C. (curve A). For decreasing temperature, the tetragonal-monoclinic transition started at 1040° C. and was finished at 300° C. (curve B). The particle size, after this transition, had increased to about 6 microns. For the 1450° C. prefired ZrO_2 sample, the transformation ranged from 1110° to 1205° C. for the increasing temperature (curve C), and from 980° to 895° C. for the decreasing temperature (curve D). The final particle size of this specimen was about 12 microns.

Table I. Impurities of Submicron ZrO_2

As-Received, %		Heated to 820° C., %	
Fe	0.03	Fe	0.02
Ni	0.005	Ni	0.004
Mn	0.001	Mn	0.001
Si	0.05	Si	0.05
Mg	0.02	Mg	0.02
B	0.005	B	0.005
Cr	0.01	Cr	0.01
Ca	0.04	Ca	0.04
Hf	0.05	Hf	0.05
C	0.1	C	0.01

Subsequently the transition was studied by differential thermal analysis on similar samples using a platinum wound furnace, a platinum cell, two Pt, Pt–10% Rh calibrated thermocouples, with alumina as a standard. The voltage difference between the thermocouple outputs from the standard and the ZrO_2 sample was amplified with a microvolt amplifier, and this difference was plotted as a function of temperature using a Moseley X-Y Plotter. Heating and cooling rates were about 450° C. an hour. Temperature measurements are reproducible within ±3° C. Figure 2 shows the transitions of the as-received ZrO_2 particles. The broad transformation of the starting material, as determined by differential thermal analysis, makes it difficult for a precise determination of the transition range. Figure 3, shows the transformation of a ZrO_2 sample preheated to 1450° C. for 2 hours, which is in good agreement with the transition of the similar sample studied by high temperature x-ray diffraction (Figure 1, curves C and D). Specimens heated in air to 820° C. for 2 hours (average particle size 0.15 micron), having only the monoclinic phase present as determined by room temperature x-ray diffraction, were also studied by high temperature x-ray diffraction and differential thermal analysis techniques. These transitions, when compared with the transformations of 10-micron starting particles (samples preheated to 1450° C.), showed good agreement (within ±10° C.) in the total transition temperature.

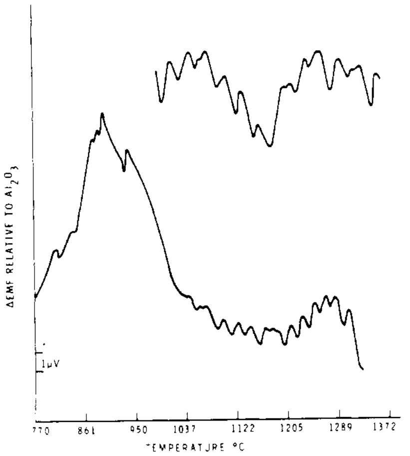

Figure 2. Differential thermal analysis curves of as-received submicron ZrO_2
Upper: increasing temperature (endothermic)
Lower: decreasing temperature (exothermic)

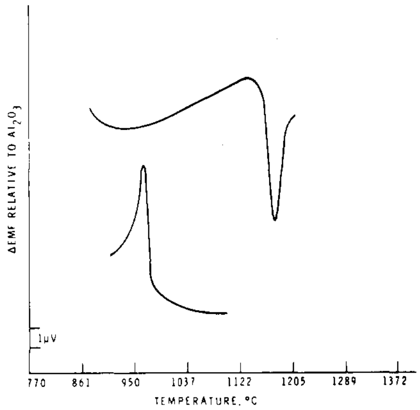

Figure 3. Differential thermal analysis curves of ZrO_2 preheated to 1450° C.
Upper: increasing temperature (endothermic)
Lower: decreasing temperature (exothermic)

CONCLUSIONS

These investigations have shown that particle size has little or no influence on the transformation temperature of monoclinic-tetragonal ZrO_2. The presence of metastable tetragonal ZrO_2, however, increased the transition range considerably. The thermal stability of the tetragonal phase present in the starting material seems to be related to the kinetics of the carbon arc preparation process and also may be due to impurities such as, primarily, carbon present. The 0.1% carbon present in the starting particles disappears gradually by heating them in air above 800° C., and it may be with this that the metastable tetragonal phase inverts back to the stable monoclinic phase of ZrO_2 upon cooling to room temperature.

LITERATURE CITED

(1) Baun, W.L., *Science* **140**, 1330 (1963).
(2) Curtis, C.E., Doney, L.M., Johnson, J.R., *J. Am. Ceram. Soc.* **37**, 458 (1954).
(3) Kofstad, P., Ruzicka, D.J., *J. Electrochem. Soc.* **110**, 181 (1963).
(4) Lynch, C.T., Vahldiek, F.W., Robinson, L.B., *J. Am. Ceram. Soc.* **44**, 147 (1961).
(5) Mumpton, F.A., Roy, Rustum, *Ibid.*, **43**, 234 (1960).
(6) Ruff, O., Ebert, F., *Z. Anorg. Allgem. Chem.* **180**, 19 (1929).
(7) Teufer, G., *Acta Cryst.* **15**, 1187 (1962).
(8) Vahldiek, F.W., Robinson, L.B., Lynch, C.T., *Science* **142**, 1059 (1963).
(9) Wolten, G.M., *J. Am. Ceram. Soc.* **46**, 418 (1963).

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Vapor Pressure of Hafnium (IV) Iodide

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Vapor pressures of the hafnium (IV) iodide system were measured between 263 and 406° C. by a metal diaphragm technique. Three stable forms of the HfI_4 were identified (α, β, and γ modifications), in addition to a metastable form which transforms slowly at temperatures in the vicinity of 300° C. to the α-modification. Enthalpies of sublimation, ΔH°_T, were found to be 28.37 ± 0.04 (263 to 401° C.), 48.9 ± 1.3 (302 to 324° C.), 33.7 ± 0.6 (325 to 372° C.), and 28.2 ± 0.5 (375 to 405° C.) kcal./gram mole for the mestastable, α, β, and γ modifications, respectively. The transition temperatures were measured by thermal analysis to be 329 ± 3° C. and 375 ± 2° C. for the ($\alpha - \beta$) and ($\beta - \gamma$) transitions, respectively.

INTEREST in the separation of hafnium from zirconium and the subsequent purification of hafnium has stimulated a study of the thermodynamic properties of their halides. Hafnium (IV) iodide currently plays an intermediate role in the purification of hafnium by the van Arkel crystal bar method. Very little experimental data are available in the literature on the hafnium (IV) iodide system, and up to the present time no information on its vapor pressure. The heat and entropy of sublimation (ΔH° and ΔS°), however, were estimated by Brewer (*1*) to be on the order of 28 kcal./gram mole and 40 eu., respectively. Sublimation pressures and other thermodynamic properties are reported for HfI_4 (solid and gas), as estimated by Kelley and King (*7*) and are substantially based on Brewer's estimates. Krause and coworkers (*8*) isolated a small quantity of hafnium (IV) iodide in capillaries for study of the x-ray diffraction pattern. Hampel (*4*) gives a brief description of the preparation of pure hafnium by the iodide process. However, no data are given on the properties of hafnium (IV) iodide.

EXPERIMENTAL

Hafnium (IV) iodide was prepared by direct combination of the elements within an evacuated reaction tube at 400° to 500° C. Anhydrous iodine was supplied to the reaction zone by decomposition of chromium (III) iodide which had been prepared by the method of Gregory and Handy (*3*). These two steps are represented by Equations 1 and 2:

$$2CrI_3 \rightarrow 2CrI_2 + I_2 \qquad (1)$$

$$Hf + 2I_2 \rightarrow HfI_4 \qquad (2)$$

The vapor pressure sample was prepared by subliming the HfI_4 from the reaction tube to a sample capsule, which was afterwards sealed under vacuum. Details of the HfI_4 preparation have been given (*10*). Metallic impurities in the hafnium were in the p.p.m. range, except for zirconium which was 3.8% Zr/(Zr + Hf). The principal impurities were, by spectroanalysis: Al, 60 p.p.m.; B, 0.3 p.p.m.; Cd, < 0.5 p.p.m.; Cr, 10 p.p.m.; Cu, 15 p.p.m.; Fe, 10 to 50 p.p.m.; Mg, 5 to 80 p.p.m.; and Mo, 10 p.p.m. Chemical analysis indicated that the Zr iodated to ZrI_4 along with the Hf and remained with the HfI_4 sample. The absence

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