CHAPTER 3

PROPERTIES OF AQUEOUS FUEL SOLUTIONS*

3–1. Introduction

The chemical and physical properties of aqueous fuel solutions are important because they affect the design, construction, operation, and safety of homogeneous reactors in which they are used. This chapter will discuss primarily those chemical and physical properties, except corrosion, which are important for reactor design and operation. Special attention will be given to the properties of solutions of uranyl sulfate, since such solutions have been the most extensively studied, and at present appear the most attractive for ultimate usefulness in homogeneous reactors.

Solubility relationships are discussed first, with data for uranyl sulfate followed by information concerning other fissile and fertile materials. The effects of radiation on water, the decomposition of water by fission fragments, the recombination of radiolytic hydrogen-oxygen gas, the decomposition of peroxide in reactor solutions, and the effects of radiation on nitrate solutes are then presented. Finally, tables of relevant physical properties are given for light and heavy water, for uranyl sulfate solutions, for other solutions of potential reactor interest, and for the hydrogen-oxygen-steam mixtures which occur as vapor phases in contact with reactor solutions.

3–2. Solubility Relationships of Fissile and Fertile Materials†

3–2.1 General. For the most part, studies of aqueous solutions of fissile materials for use in homogeneous reactors have dealt with hexavalent uranium salts of the strong mineral acids. Hexavalent uranium in aqueous solutions appears as the divalent uranyl ion, UO_2^{++}. Tetravalent uranium salts in aqueous solutions are relatively unstable, being oxidized to the hexavalent condition in the presence of air. Other valence states of uranium either disproportionate or form very insoluble compounds and have not been seriously proposed as fuel solutes.

Uranyl salts are generally very soluble in water at relatively low temperatures (below 200°C). At higher temperatures, miscibility gaps appear in the system. These are manifested by the appearance of a basic salt solid

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*By H. F. McDuffie, Oak Ridge National Laboratory.
†Taken from material prepared by C. H. Secoy for the revised AEC Reactor Handbook.

phase from dilute solutions and by the appearance of a uranium-rich second liquid phase from more concentrated solutions. In both the salt and the second liquid phase, the uranium-to-sulfate ratio is found to be greater than in the system at lower temperature; this suggests that hydrolysis of the uranyl ion is responsible for the immiscibility in each instance. Hydrolysis can be repressed effectively by increasing the acidity of the solution or, alternatively, by the addition of a suitable complexing agent for the uranyl ion. Even the anions of the solute itself may be considered to accomplish this to some degree, since very dilute solutions hydrolyze much more extensively than more concentrated solutions.

Primary emphasis has been placed on the study of uranyl sulfate solutions because of the superiority of the sulfate over other anions with respect to thermal and radiation stability, absorption cross section for neutrons, ease of chemical processing, and corrosive properties. Other uranyl salts which have either been used in reactors or studied for possible use include the nitrate, phosphate, fluoride, chromate, and carbonate. It has been found possible to improve the solubility characteristics of uranyl salt solutions at elevated temperatures by the addition of acids or salts of the chosen anion.

The marked differences between light water and heavy water with respect to moderating ability and thermal neutron absorption cross section make solutions in both solvents of interest for reactor use. Generally speaking, the upper temperature limit of solution stability occurs about $10°C$ lower in heavy-water solutions than in light-water solutions.

Tetravalent uranium can be stabilized by increasing the reduction potential of the solution. However, tetravalent uranium is more readily hydrolyzed at elevated temperatures than hexavalent uranium, and it probably cannot be kept in solution except by the use of otherwise excessively high concentrations of acid.

Plutonium, the other fissile material, also forms salts which can be dissolved in water. The possibility of using such solutions in aqueous homogeneous reactor systems has been examined, and limited experimental studies have been directed toward this goal but without substantial success (see Article 6–6.3).

Uranium–238 and thorium, the fertile materials, have been considered for use in converter or breeder reactor systems. The solubility of uranium is such that satisfactory aqueous solutions of uranium can be obtained for use in the conversion of U^{238} to plutonium. Substantial efforts have been made to develop solutions of thorium which could be used as a blanket in a two-region breeder reactor system.

Thorium appears to be stable in the tetravalent form but has a strong tendency toward hydrolysis at elevated temperatures. Insoluble thorium dioxide is ultimately formed as the hydrolysis product. Thorium nitrate
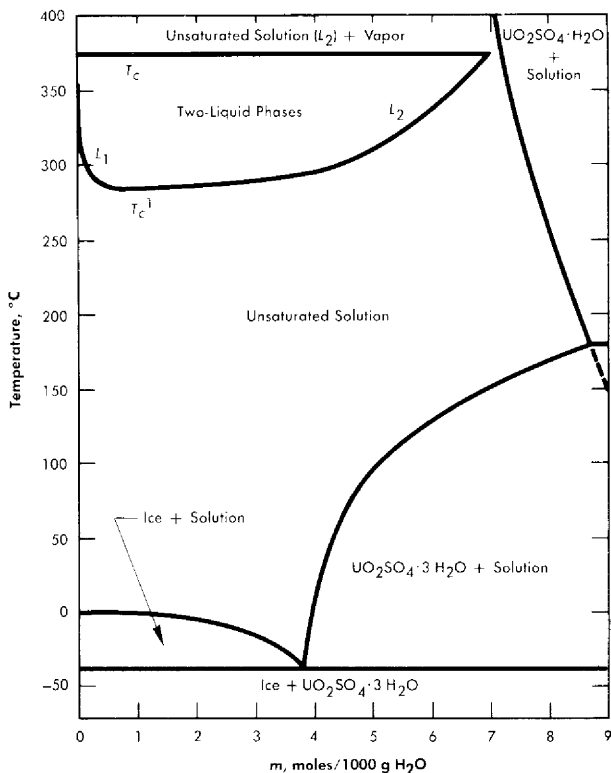
Fig. 3–1. Phase diagram for the system UO_2SO_4-H_2O.

and thorium phosphate can be maintained in solution at satisfactory concentrations by the use of substantial concentrations of nitric or phosphoric acids to inhibit hydrolysis. However, in the nitrate system an acceptable breeding ratio could only be obtained by using N^{15}. Thorium phosphate solutions containing the necessary amount of phosphoric acid are extremely corrosive to all but the noble metals.

Neptunium and protactinium complete the listing of fissile and fertile materials, since these are intermediates in the production of plutonium and U^{233} from U^{238} and thorium. Limited exploratory studies of their solubilities have been carried out primarily in connection with the development of processes for their continuous removal from blanket systems.

3–2.2 Uranyl sulfate. The solubility of uranyl sulfate in water and the characteristics of the phase relationships at elevated temperatures, displayed in the form of a binary system, UO_2SO_4–H_2O, are shown in Fig. 3-1 [1]. It is necessary, however, to study the ternary system, UO_3–SO_3–H_2O, in order to understand the hydrolytic precipitation of the

A = $UO_3 \cdot 2SO_3 \cdot 1.5H_2O$
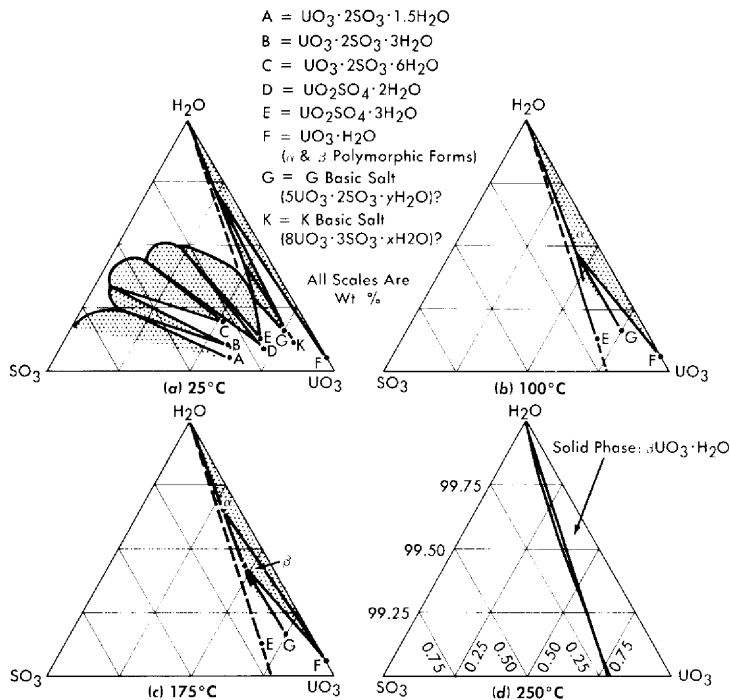B = $UO_3 \cdot 2SO_3 \cdot 3H_2O$
C = $UO_3 \cdot 2SO_3 \cdot 6H_2O$
D = $UO_2SO_4 \cdot 2H_2O$
E = $UO_2SO_4 \cdot 3H_2O$
F = $UO_3 \cdot H_2O$
(α & β Polymorphic Forms)
G = G Basic Salt
($5UO_3 \cdot 2SO_3 \cdot yH_2O$)?
K = K Basic Salt
($8UO_3 \cdot 3SO_3 \cdot xH_2O$)?

All Scales Are
Wt %

FIG. 3-2. The system UO_3-SO_3-H_2O.

basic solid phase, β-$UO_3 \cdot H_2O$, which occurs in very dilute solutions at elevated temperatures, and the position of the tie lines in the liquid-liquid miscibility gap. Figure 3-2 shows portions of the ternary isotherms at 25, 100, 175, and 250°C [2,3]. A point of special significance in these diagrams is that the solubility of UO_3 in uranyl sulfate solutions decreases with increasing temperature to the extent that at 250°C excess acid is required to maintain homogeneity in solutions of low concentration. Excess acid also has a marked effect on the liquid-liquid miscibility gap, as shown by the curves in Fig. 3-3 [4]. In very dilute solutions the surface formed by these curves intersects the surface representing the liquid compositions in equilibrium with the hydrolytically precipitated solid phase, β-$UO_3 \cdot H_2O$. Figure 3-4 shows this intersection and three paths on the liquidus surface at fixed SO_3/UO_3 mole ratios [5].

Figure 3-5 shows, from the data of Jones and Marshall [6], how the two-liquid-phase separation temperature is lowered when the solvent is changed from light water to heavy water. Scattered experiments suggest that the temperatures for solid-phase separation through hydrolytic precipitation are also somewhat lower in heavy-water systems than in systems containing light water as the solvent.
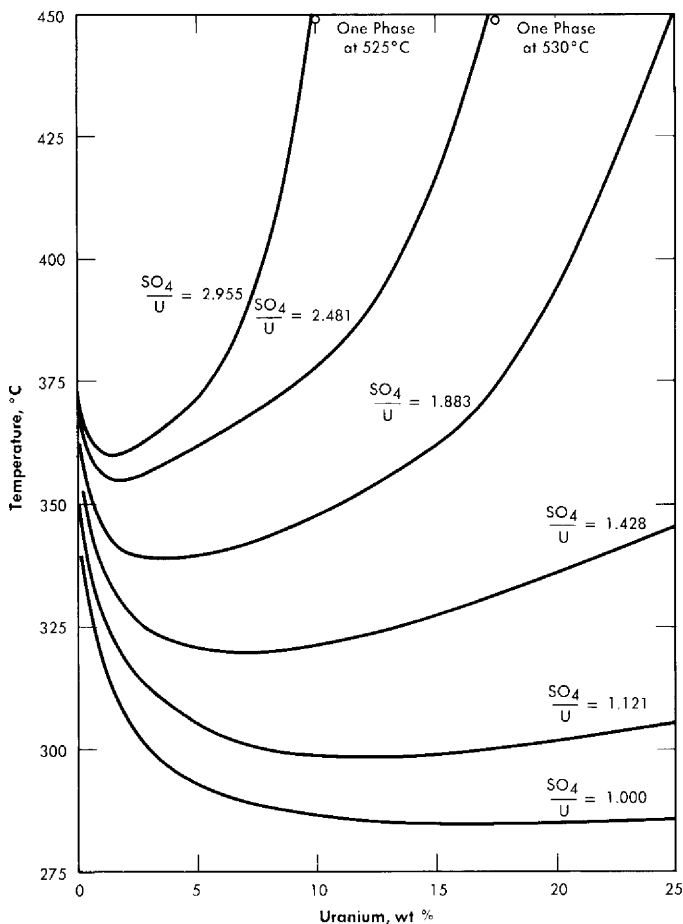
Fig. 3–3. Coexistence curves for two liquid phases in the system UO_2SO_4-H_2SO_4-H_2O.

Figure 3–6 shows the liquidus composition isotherms from 150 to 290°C for dilute sulfuric acid solutions saturated with UO_3 [7].

Study of the data leads to the following general conclusions with respect to the stability of uranyl sulfate solutions of reactor interest:

(1) Stoichiometric uranyl sulfate solutions in light and heavy water are unstable at temperatures of 280°C and above because of hydrolysis.

(2) Stability up to approximately 325°C is provided at uranium concentrations up to 2.5 w/o by the addition of a 50 mole % excess of sulfuric acid.

(3) Stability up to as high as 400°C is provided at uranium concentrations above 20 w/o by the addition of a 100 mole % excess of sulfuric acid.
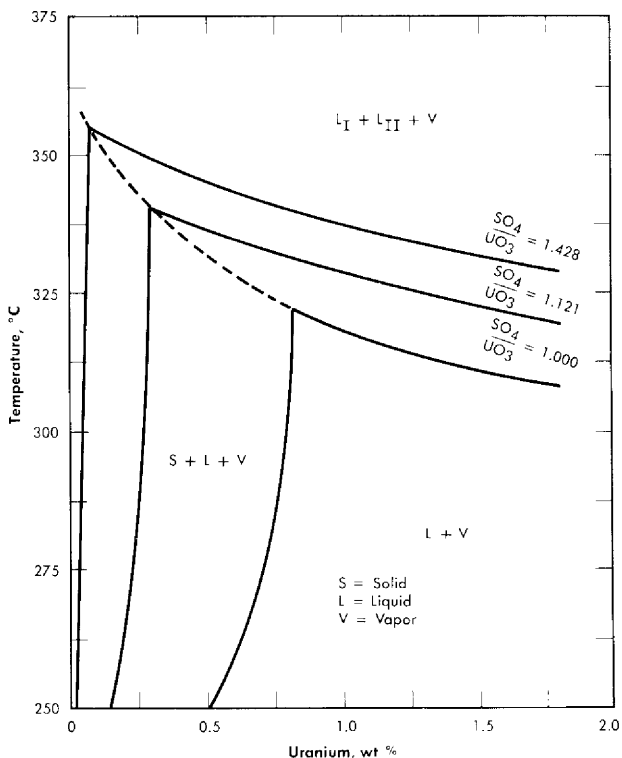
FIG. 3-4. Effect of excess H_2SO_4 on the phase equilibria in very dilute UO_2SO_4 solutions.
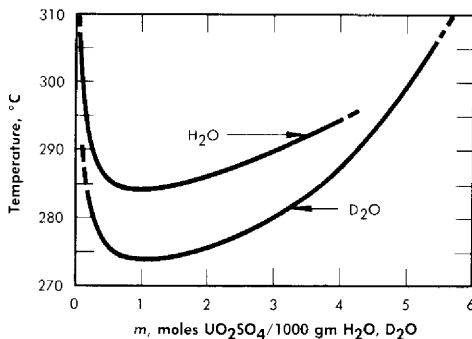

FIG. 3-5. Two-liquid phase region of uranyl sulfate in ordinary and heavy water.
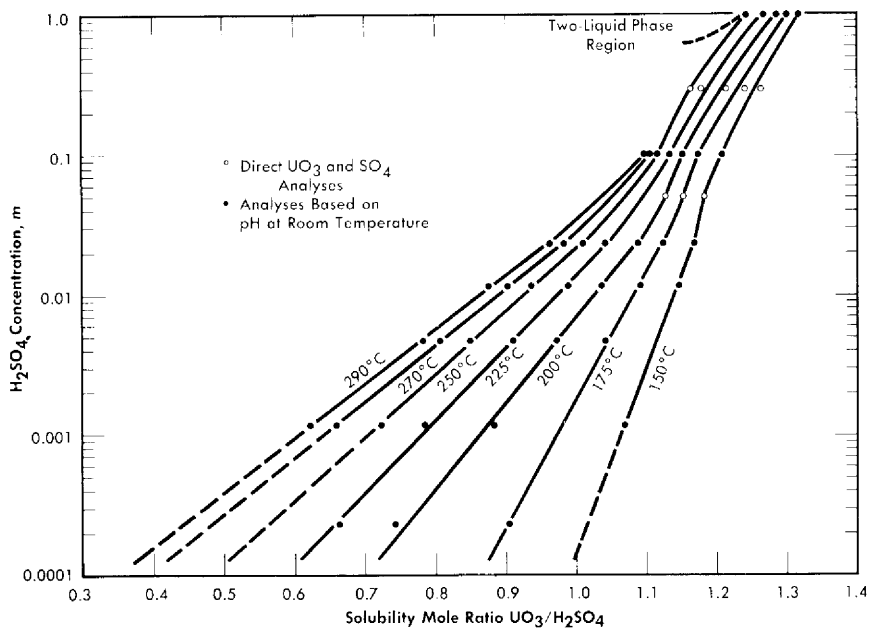
FIG. 3–6. Solubility of UO_3 in H_2SO_4-H_2O mixtures.
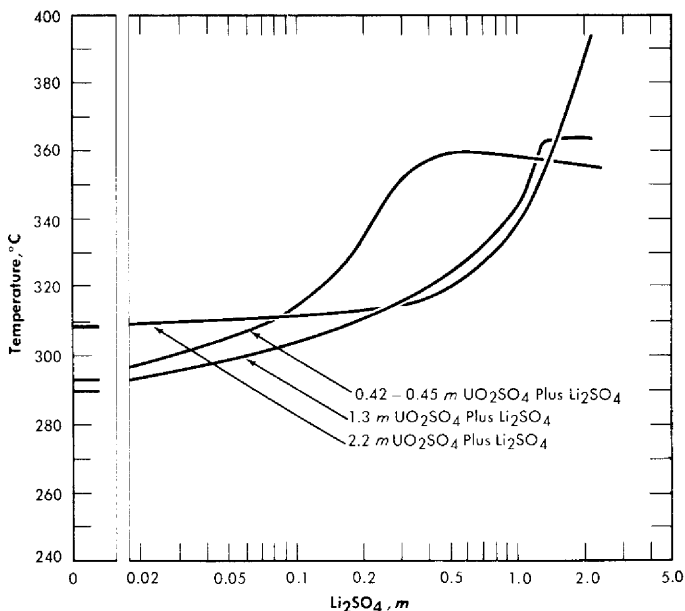
FIG. 3–7. Second-liquid phase temperature of UO_2SO_4-Li_2SO_4 solutions. Concentrations are uncorrected for loss of water to vapor phase at elevated temperatures.
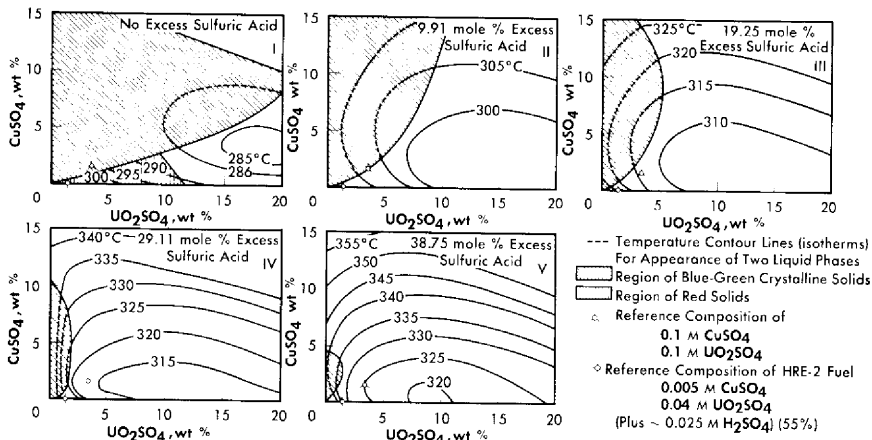
FIG. 3–8. Phase transition temperatures in solutions containing cupric sulfate, uranyl sulfate, and sulfuric acid.
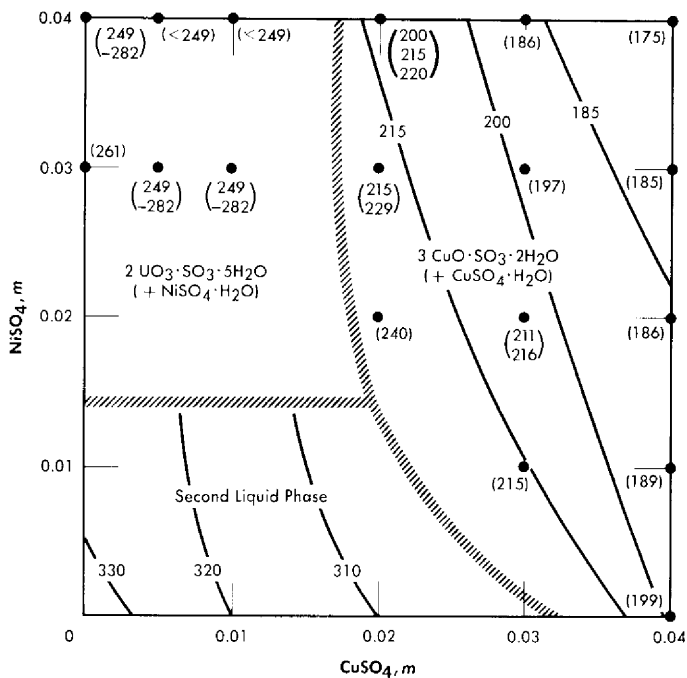

FIG. 3–9. The effect of $CuSO_4$ and $NiSO_4$ on phase transition temperatures $(0.04 \ m \ UO_2SO_4; \ 0.01 \ m \ H_2SO_4)$.

The addition of lithium sulfate or beryllium sulfate to uranyl sulfate solutions has been found to elevate the temperatures at which the second liquid phase appears [8]. Figure 3–7 shows the effect of Li_2SO_4 additions on the second liquid phase temperature for three uranyl sulfate solutions. In very dilute uranyl sulfate solutions excess acid must also be added to prevent hydrolytic precipitation.·

The solubility relationships in uranyl sulfate solutions containing cupric copper are also of interest (see Article 3–3.4). Copper sulfate solutions, like uranyl sulfate, undergo hydrolytic precipitation at elevated temperatures [9]. Even though the required concentration of cupric ion may be quite low, its presence influences the phase relationships. This influence is most significant in dilute uranyl sulfate solutions. A complete phase diagram for the four-component system, $CuO–UO_3–SO_3–H_2O$, has not been determined, but regions of special interest have been studied. Figure 3–8 shows the phase transition temperatures in solutions containing copper sulfate, uranyl sulfate, and sulfuric acid. The solid phase which appears at the higher $CuSO_4$ concentrations has been shown to be at least in part the basic copper sulfate, $3CuO \cdot SO_3 \cdot 2H_2O$ [10].

In uranyl sulfate solutions in contact with austenitic stainless steels it is important to know the effect of the corrosion products upon the solubility relationships. Under most conditions iron and chromium appear as insoluble hydrolytic products, but nickel appears as a soluble contaminant of the solution. Studies have been made of the precipitation temperatures for dilute solutions in the system $UO_2SO_4–CuSO_4–NiSO_4–H_2SO_4–H_2O$, and the solid phases have been identified [11]. Figure 3–9 summarizes the information for systems having compositions approximately that of the fuel solution of the HRE–2. In this preliminary study the tests were limited to short time intervals (15 minutes or less of exposure to the elevated temperatures). When solutions containing 0.01 m $CuSO_4$ plus 0.01 m $NiSO_4$, or 0.02 m $CuSO_4$ with no $NiSO_4$ were heated for longer periods of time at 300 to 310°C (just below the temperature for the formation of two liquid phases) green solids were deposited. Thus the results pictured in Fig. 3–9 should be applied to practical situations with considerable reservation until experiments with the exact composition of interest have been conducted.

3–2.3 Other uranium compounds. *Uranyl nitrate.* A phase diagram for the system uranyl nitrate-water [12] is shown in Fig. 3–10. Although uranyl nitrate remains very soluble at the elevated temperatures of interest for power-reactor operation, the nitrate group in such solutions decomposes to yield oxides of nitrogen which appear in the vapor phase. Although this situation is reversible with the lowering of temperature, it does introduce corrosion problems with respect to the vapor phase. The
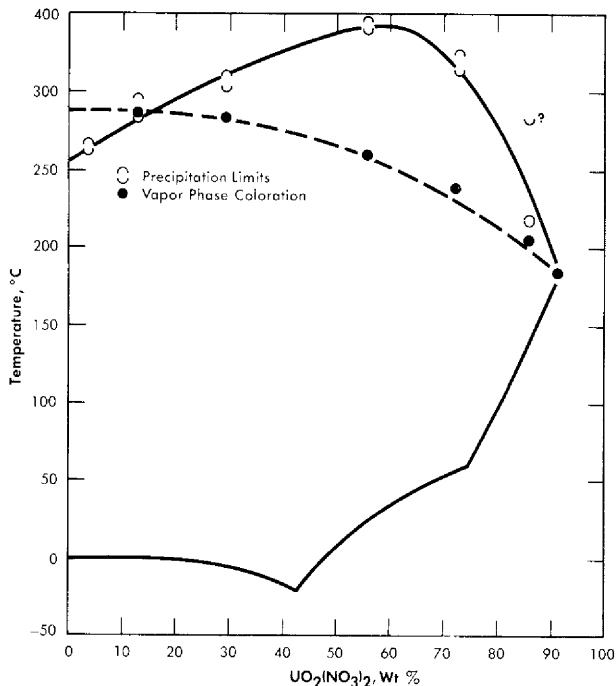
FIG. 3–10. The $UO_2(NO_3)_2$-H_2O system.
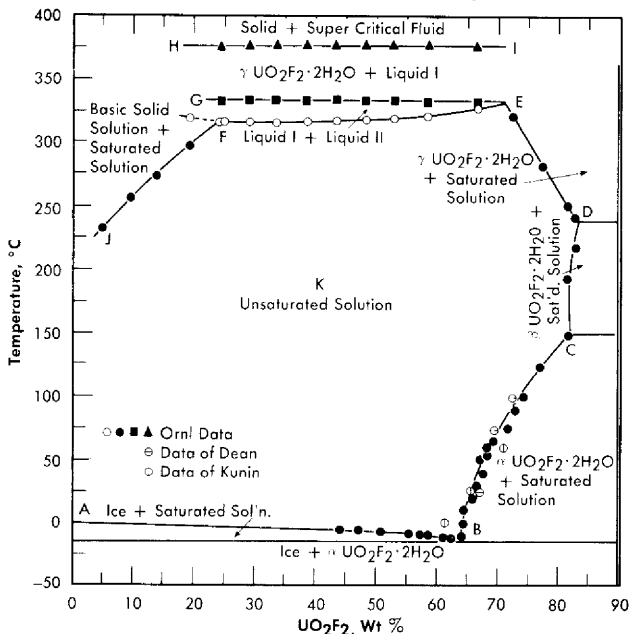

FIG. 3–11. Phase equilibria of aqueous solutions of UO_3 and HF in stoichiometric concentrations.
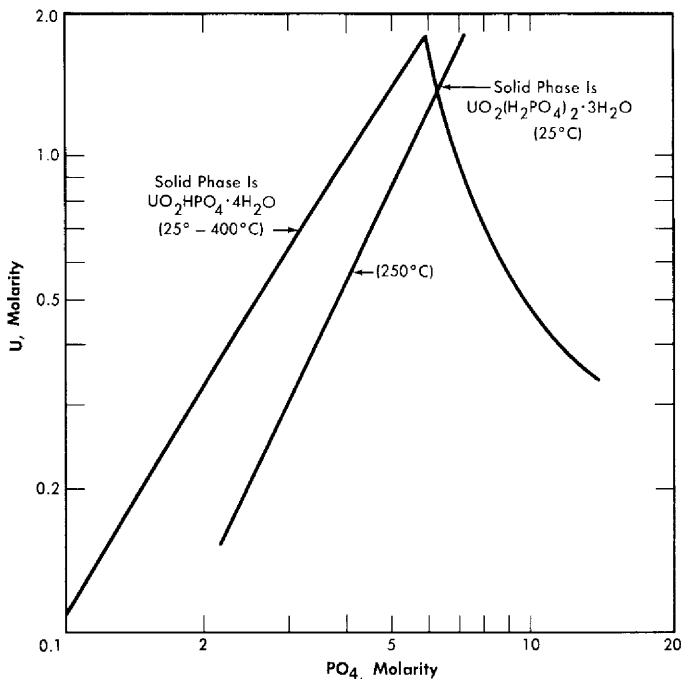
FIG. 3–12. Solubility of UO_3 in H_3PO_4 solution.

nitrate ion is, moreover, not completely stable in fissioning solutions; elemental nitrogen is one of the products of radiation decomposition. Although uranyl nitrate solutions have proved quite satisfactory in low-power water-boiler type research reactors, where makeup nitric acid can be added as needed [13], they do not appear attractive for high-temperature, high-power aqueous homogeneous reactors.

Uranyl fluoride. Uranyl fluoride is a very attractive fuel solute because of the low neutron capture cross-section of fluorine. However, at high temperatures it undergoes hydrolysis, which means that excess HF would be required to maintain homogeneity. Hydrogen fluoride is also a component of the vapor phase. Both liquid and vapor are very corrosive toward zirconium and titanium, but less corrosive toward stainless steel (see Article 5–3.3). Figure 3–11 shows the phase relationships in this system [14].

Uranium phosphate. Neither hexavalent nor tetravalent uranium phosphate is sufficiently soluble in water to be of reactor interest, but both UO_2 and UO_3 are quite soluble in moderately strong phosphoric acid. These solutions have been the subject of considerable study at the Los Alamos Scientific Laboratory [15]. The solubility of UO_3 in phosphoric acid is illustrated by Fig. 3–12 [16]. Although the solubilities of uranyl
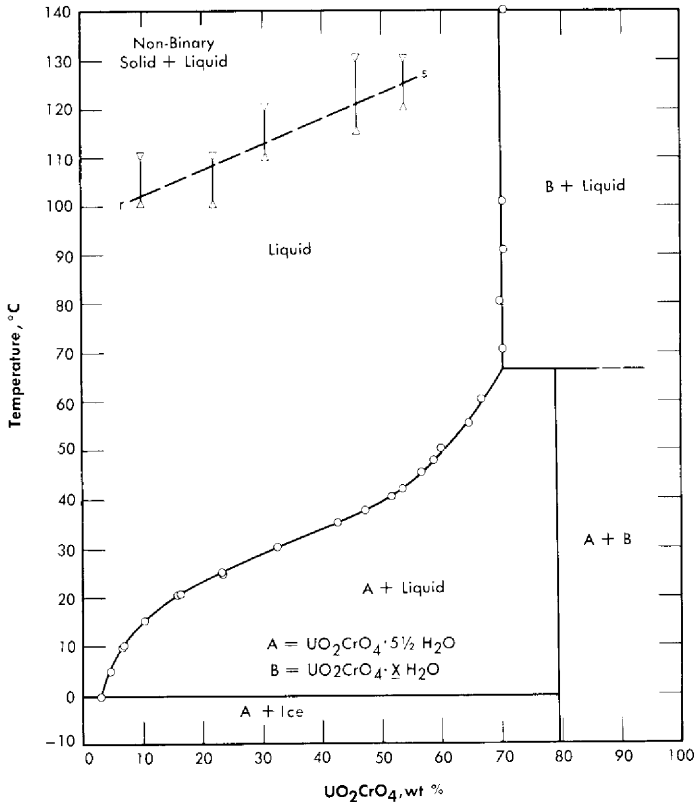
FIG. 3–13. The system UO_2CrO_4-H_2O.

phosphate and uranyl sulfate in water are quite different, their respective solubilities in concentrated phosphoric acid and concentrated sulfuric acid are analogous; in either case temperatures as high as 450°C can be obtained with no phase separation. Phosphorus has an advantage over sulfur in possessing a somewhat lower neutron absorption cross section, but both anions appear to be stable under radiation. Both the phosphate and sulfate solutions in concentrated acid at temperatures of 450°C are extremely corrosive toward most metals and alloys except the noble metals. Attempts to operate experimental high-temperature reactors using uranium phosphate-phosphoric acid fuel solutions have failed because of catastrophic corrosion rates due to imperfections in noble metal plating or cladding of the reactor core and heat-exchanger tubing [17] (see Section 7–5).

Uranyl chromate. Uranyl chromate solutions also suffer from hydrolysis at elevated temperatures; excess chromic acid is required for stability [18]. This system is, however, not unattractive insofar as corrosion of stainless and carbon steels is concerned. The conditions of acidity and oxidation-
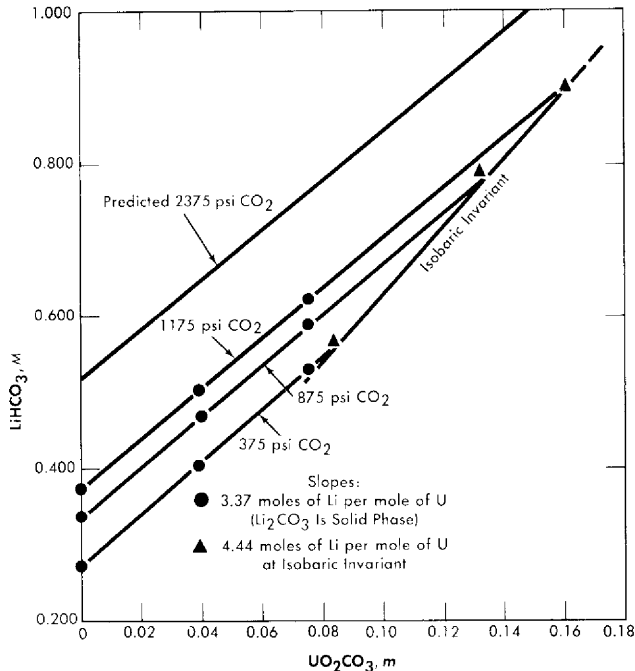
FIG. 3-14. Variation of Li_2CO_3 solubility with UO_2CO_3 concentration at constant CO_2 pressure (250°C).

reduction potential determine the valence state of the chromium, but present knowledge is not adequate to specify required conditions for reliable behavior at elevated temperatures and under reactor radiation. Figure 3-13 shows the phase diagram insofar as it has been established.

Uranyl carbonate. Uranium trioxide is quite soluble in alkali carbonate solutions. This solubility can be attributed to the complexing of UO_3 or uranyl ion by the bicarbonate ion to form uranium-containing anions. In any event, one would not expect the solubility of uranium to be retained at high temperature unless the carbonate content of the aqueous phase were kept high. This can be accomplished by retaining an adequately high partial pressure of CO_2 over the solution. The solubility of UO_3 in Li_2CO_3 solutions at 250°C has been studied [19], and the significant results are shown in Figs. 3-14 and 3-15. Referring to Fig. 3-14, we see that at a constant CO_2 pressure the concentration of uranium increases linearly with the lithium concentration until a limit is reached at the isobaric invariant. The uranium concentration cannot be increased further unless the CO_2 pressure is increased. Figure 3-15 is a projection of the compositions of solutions saturated with respect to lithium and uranium at 250°C and at a constant total pressure (CO_2 + steam) of 1500 psi. The projection
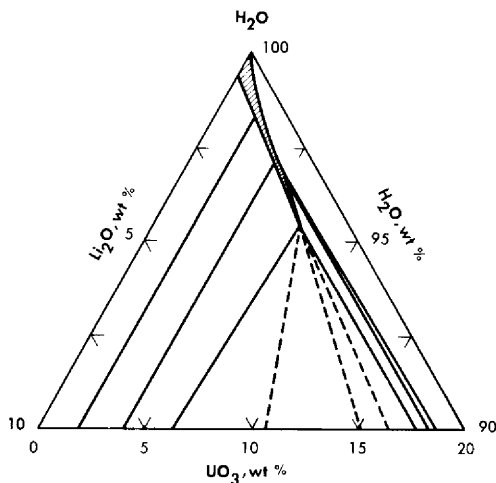
FIG. 3–15. The system $Li_2O-UO_3-CO_2-H_2O$ at 250°C and 1500 psi.

figure gives no information concerning the concentration of carbonate in the liquid phase. The region in which a single homogeneous liquid phase exists is the very narrow shaded region near the H_2O apex. Although the scope of this region is small, there should be no difficulty in maintaining a homogeneous liquid phase if an adequate pressure of CO_2 is kept on the system and an appropriate composition is selected in preparing the solution.

3–2.4 Solubilities of nonuranium compounds. *Thorium.* Thorium solutions having concentrations as high as 0.5 m would be useful for one-region breeder reactors. For the breeder blanket of a two-region reactor concentrations of about 6.0 m thorium appear to be optimal, although somewhat lower concentrations would be of interest. At the present time only thorium nitrate or phosphate solutions in the presence of excess acid have been demonstrated to have the required solubilities at elevated temperatures; both of these solutions have substantial disadvantages. Thorium chloride would be expected, by analogy, to show substantial solubility at elevated temperatures, but this system has not been investigated in detail. Complex organic salts, such as thorium acetylacetonate, have high solubilities at relatively low temperatures, but these have not been investigated for use in aqueous solutions at temperatures above 100°C.

Data from the literature on the solubility of thorium sulfate at low temperatures both alone and in the presence of other solutes [20] indicate that such solutions will probably not be satisfactory at elevated temperatures.

Thorium phosphate (or thorium oxide) is very soluble in concentrated phosphoric acid. Solutions containing up to 1100 g Th/liter with PO_4/Th
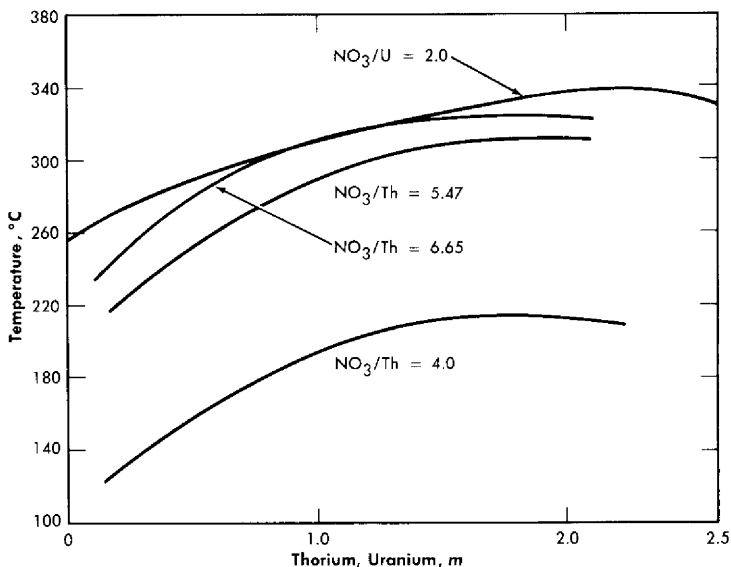
FIG. 3–16. Hydrolytic stability of thorium nitrate and uranyl nitrate solutions.

ratios of 5 and 7 could be prepared and appeared to be thermally stable but had high viscosities. Solutions containing 400 g Th/liter at PO_4/Th ratios of 10 were thermally stable at 250 to 300°C with viscosities little higher than that of concentrated phosphoric acid. Efforts to improve the properties of thorium phosphate-phosphoric acid systems by the inclusion of HF, HNO_3, $H_2SO_4^=$, $SeO_4^=$, SO_4, Li^+, or Mg^{++}, alone or in combination, have not proved encouraging [21].

The thorium nitrate-water system has been reported [22] as having considerable solubility up to about 225°C, at which point hydrolytic precipitation occurs. Further investigation [23] revealed a maximal stability for the 80 w/o material (to around 255°C). Increasing the acidity of the solutions (increasing the NO_3^-/Th ratio) suppresses hydrolysis and increases the stability of the solutions as indicated by Figure 3–16, which shows the precipitation temperatures for various solutions [24]. The intensity of vapor phase coloration at elevated temperatures (rapidly reversible) increased as the nitrate/thorium ratio was raised above 4.0.

Plutonium. A considerable investigation of the chemistry of plutonium in aqueous uranyl sulfate solutions has been directed, not toward the achievement of solubility, but toward the achievement of *in*solubility in order to provide the basis for continuous processing of a U^{238} blanket solution for plutonium production [25] (see Chapter 6).

The possible use of aqueous solutions of plutonium in homogeneous reactors has been reviewed by Glanville and Grant [26] in order to determine

TABLE 3–1

THE SOLUBILITY OF PLUTONIUM COMPOUNDS AT ROOM TEMPERATURE

	Pu^{III}	Pu^{IV}	Pu^{VI}
Fluoride	Soluble in presence of fluoride complexing ions; e.g., Zr	Soluble in presence of fluoride complexing ions; e.g., Zr or Al	>40 g Pu/liter in 19 M HF
Chloride	Soluble in water and dilute acids	Of the order of 50 g Pu/liter in 6 M HCl	$\sim$350 g Pu/liter
Bromide	Soluble in water	Of the order of 1 g Pu/liter in 5 M HBr	No information
Bromate	No information	>8 g Pu/liter in 1.5 M H_2SO_4, 0.15 M $KBrO_4$	No information
Iodate	1.5 mg Pu/liter in 0.0017 M KIO_3, 0.17 M H_2SO_4	Max. reported is 94.5 mg Pu/liter in 0.1 M KIO_3, 6 M HNO_3	0.6 g Pu/liter in 0.2 M KIO_3
Perchlorate	Of the order of grams of Pu/liter in dilute $HClO_4$	Of the order of grams of Pu/liter in dilute $HClO_4$	Of the order of grams of Pu/liter in dilute $HClO_4$
Nitrate	>7.7 g Pu/liter in 0.9 M HNO_3	500 g Pu/liter in 2 M HNO_3	$\simeq$500 g Pu/liter
Sulfate	125 g Pu/liter in 0.1 M H_2SO_4	>125 g Pu/liter in 0.1 M H_2SO_4	No information
Chromate	No information	Soluble in 10 M HNO_3, 0.25 g Pu/liter in 0.1 M $Na_2Cr_2O_7$, 0.1 M HNO_3	No information
Phosphate	Max. reported is 3.89 g Pu/liter in 0.8 M H_3PO_4, 0.9 M HCl	0.55 g Pu/liter in 1 M H_2SO_4	>0.7 g Pu/liter in 0.6 M H_3PO_4, 0.1 M HNO_3
Carbonate	Soluble in 45% K_2CO_3	0.1 g Pu/liter in 0.2 M Na_2CO_3, 0.2 M CH_3COONa	>8.4 g Pu/liter in 0.02 M Na_2CO_3
Oxalate	0.46 g Pu/liter in 0.5 M $H_2C_2O_4$, 3.7 M H^+	Max. reported is >0.244 g Pu/liter in 0.1 M $H_2C_2O_4$, 1 M HNO_3, 1 M HF	Of the order of grams of Pu/liter
Benzoate	Very soluble	Very soluble	No information

which compounds of plutonium appear most worthy of experimental study as fuel solutes. Table 3–1 summarizes the available low-temperature solubility information for three valence states of plutonium in the presence of different anions.

Limited experimental work has been performed in which the solubilities of plutonium carbonates, sulfates, and phosphates have been determined at temperatures up to 300°C [27]. No substantial solubilities have been established at temperatures above 200°C.

Protactinium. No efforts have been made to achieve high solubilities of protactinium in order to use it as a component of reactor fuel solutions. Rather, the chemistry of protactinium has been examined in order to devise processes for removing Pa[233] continuously from thorium breeder blanket systems. A project was undertaken by the Mound Laboratories [28] to separate gram quantities of the longer-lived Pa[231] which could be used in studies of the chemistry of protactinium.

Considerable information concerning the low-temperature chemical behavior of Pa has accumulated as a by-product of the development of chemical processes for the separation of U[233] from irradiated thorium materials [29].

Neptunium. Np[239] is in a class with Pa[233]; no efforts have been made to use it as a fuel solute, but consideration has been given to its formation in and removal from blanket solutions of U[238] [30a]. The chemistry of neptunium has been reviewed by Hindman et al. [30b], and the hydrolytic behavior has been reviewed by Kraus [30c]. Continuous separation of Np[239] would provide a Pu[239] product of high purity by radioactive decay, whereas plutonium recovered from long-term irradiation of U[238] usually contains appreciable amounts of Pu[240]. Spectrophotometric cells for use at elevated temperatures and pressures in the study of the chemistry of neptunium (and other materials) have recently been developed by Waggener [30d] and have been used to measure the absorption spectra of dilute neptunium perchlorate in its six-, five-, four-, and three-valence states, using heavy water as the solvent. Dilute solutions of neptunyl nitrate in nitric acid have been so studied at temperatures up to 250°C; the pentavalent state was found to be stable under the test conditions [30e].

3–3. Radiation Effects*

3–3.1 Introduction. Any aqueous reactor fuel solution will be subjected to intense fluxes of high-energy radiations. The action of these radiations both on the water and on the solute is of considerable importance in

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*Taken from material prepared by C. J. Hochanadel for The Reactor Handbook.

reactor design and operation. Energy will be dissipated in a fuel solution by the stopping of fast charged particles. These include mainly the fission recoil particles, the recoil particles such as protons produced by elastic neutron scattering, and the fast electrons resulting from the absorption of gamma rays and from the decay of radioactive fission products. The extent to which each contributes to the total energy absorbed in the fuel solution depends upon the design of the reactor and the composition of the solution.

Water is decomposed by all types of high-energy radiations to give hydrogen, hydrogen peroxide, and oxygen [31]. If the decomposition products are confined in solution, a radiation-induced back reaction will occur and, eventually, steady-state concentrations (pressures) of products will be attained. The rate of decomposition, the rate of the back reaction, and hence the steady-state concentrations are sensitive to the conditions of the system, such as the nature of the radiation, the type and concentration of solutes present, and the temperature. In particular, the addition of hydrogen suppresses the decomposition of pure water.

The solutes may also be acted upon by direct absorption of the energy of the radiations (or by transfer of energy from the solvent) and also by reactions with the intermediate reactive species produced by the decomposition of the water.

3–3.2 Primary and secondary reactions in pure water. The fast charged particles give up energy to the electronic systems of the molecules of the medium, thereby producing various excited and ionized states. In liquid water, the ionized and excited molecules are rapidly transformed into the free radicals H and OH. These are formed in relatively high concentrations along the tracks of the fission recoils or other charged particles. As a result, many of the radicals combine before they can diffuse apart, thereby producing the stable molecules H_2O, H_2, and H_2O_2. The primary chemical species are therefore considered to be H, OH, H_2, and H_2O_2; their yields per 100 ev of energy absorbed are expressed as $G(H)$, $G(OH)$, $G(H_2)$, and $G(H_2O_2)$. The primary chemical reaction can be written:

$$3 \, H_2O \longrightarrow H + OH + H_2 + H_2O_2. \qquad (3-1)$$
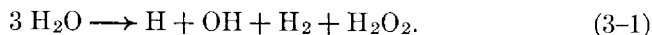
Some minor subtleties emerging from recent studies of the radiolysis of aqueous solutions are: (a) although stoichiometry demands that $G(H) + 2G(H_2) = G(OH) + 2G(H_2O_2)$, the yields of H and OH and also the yields of H_2 and H_2O_2 are not necessarily equal to each other [32]; (b) the yields of H_2 and H_2O_2 are lowered by solutes which scavenge the precursors in the particle tracks [33]; (c) HO_2 may be another "primary" chemical species produced in small yield in the particle tracks [34].
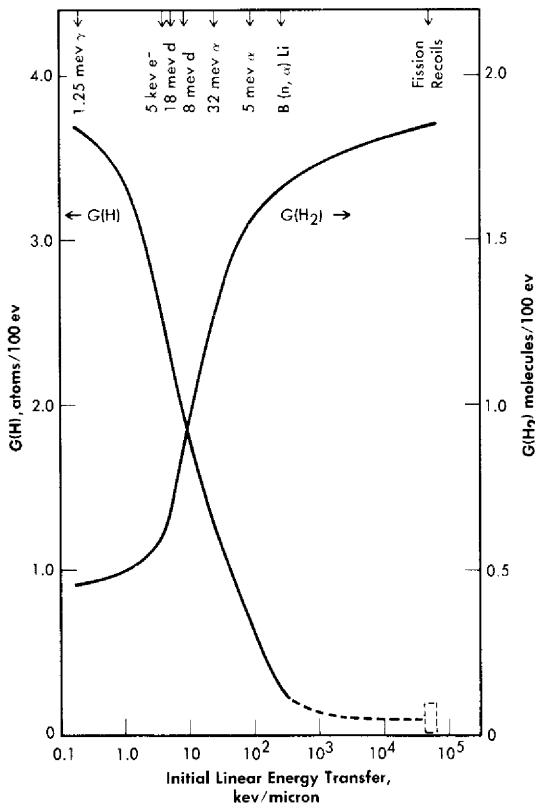
Fɪɢ. 3–17. Yields of atomic and molecular hydrogen from the decomposition of water by various ionizing radiations.

The yields of the primary chemical species depend markedly on the type of radiation or, more specifically, on the energy transferred to the solution per unit length along the track of the charged particle. The linear energy transfer (LET) parameter varies from 5×10^4 kev per micron of path for fission recoils to 0.2 kev/micron for fast electrons. The yields $G(H_2)$ and $G(H_2O_2)$ are largest for radiations such as fission recoils with large LET, while the yields $G(H)$ and $G(OH)$ are largest for radiations such as fast electrons with small LET [31]. This is illustrated in Fig. 3–17, where the yields [35] $G(H_2)$ and $G(H)$ are plotted as a function of LET.

The free radicals which escape immediate combination and diffuse into the bulk of the solution may react with solutes present, including the H_2 and H_2O_2. In water with no added solutes, the principal back reactions of the free radicals are believed to be:

$$H + H_2O_2 \longrightarrow H_2O + OH, \qquad (3\text{--}2)$$

$$OH + H_2 \longrightarrow H_2O + H, \tag{3-3}$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2, \tag{3-4}$$

$$2HO_2 \longrightarrow H_2O_2 + O_2, \tag{3-5}$$

$$H + O_2 \longrightarrow HO_2, \tag{3-6}$$

$$HO_2 + H_2O_2 \longrightarrow H_2O + OH + O_2. \tag{3-7}$$
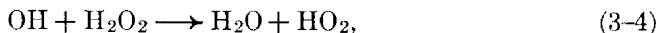
Reactions (3–2) and (3–3) provide a chain mechanism for the back reaction of H_2 and H_2O_2 to reform water [36], thereby leading to steady-state concentrations of decomposition products. The steady-state concentration will depend on the relative yields of molecular products and free radicals in reaction (3–1). For gamma rays, which produce the free radicals in high yield and the molecular decomposition products in low yield, the steady state in pure water is essentially zero. For fission recoils, which produce essentially no free radicals to promote the back reaction, the steady-state concentration (pressure) is very high (several thousand psi). Reactions (3–4) and (3–5) provide a mechanism for decomposing H_2O_2 to O_2, and reactions (3–3), (3–5), (3–6), and (3–7) provide a mechanism for combining H_2 and O_2 to form water at higher temperatures [37].

Dissolved materials may be oxidized or reduced. In general, H atoms usually reduce the solute and OH radicals reoxidize it. Assuming equal numbers of H and OH, the net result depends on the action of the H_2O_2. The peroxide may act in either way (depending on the oxidation-reduction potentials) but usually oxidation is favored. In the presence of O_2, the H-atom may be converted to HO_2, which usually acts as an oxidizing agent.

3–3.3 Decomposition of water in uranium solutions.

In Table 3–2 are listed the hydrogen yields from the decomposition of solutions of various uranyl salts [38]. The yield depends on the type of radiation and on the solute concentration, but is independent of temperature. Figure 3–18 shows how the yield of hydrogen produced by fission recoil decomposition, and by gamma-ray decomposition, decreases with increasing uranium concentration. This decrease may result from scavenging of H-atoms in the particle tracks by the uranyl ions. Decomposition by fission recoil particles produces mostly H_2 (and an equivalent amount of H_2O_2 plus O_2); the yields $G(H)$ and $G(OH)$ are very small, probably in the range 0 to 0.1 per 100 ev.

In an aqueous homogeneous reactor fuel solution, the water is decomposed by fission recoils, proton recoils, and fast electrons. The rate of hydrogen formation, in moles per liter per minute, can be expressed by the equation:
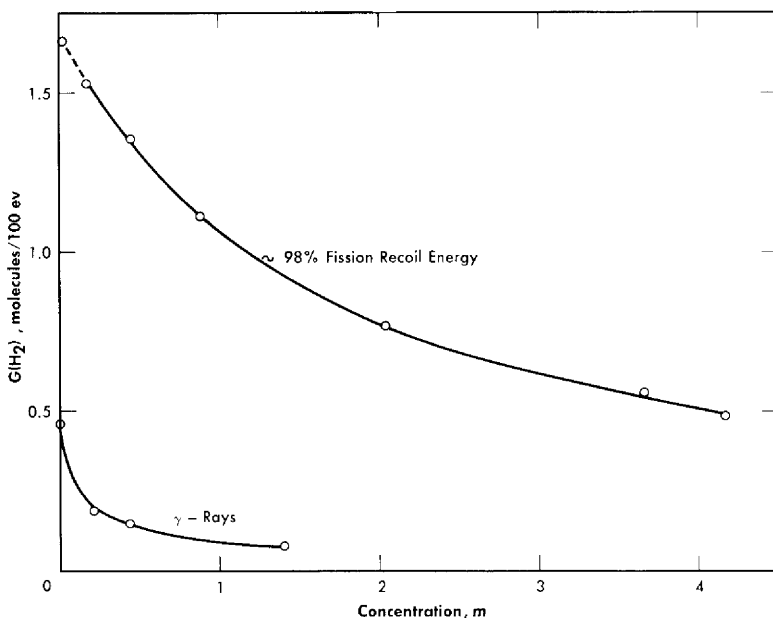
FIG. 3–18. The effects of uranium concentration and type of radiation on the initial H_2 yield from irradiated UO_2SO_4 solutions.

$$\frac{d(\mathrm{H_2})}{dt} = 0.00622[G_f \times W_f + G_p \times W_p + G_e \times W_e], \qquad (3\text{–}8)$$

where G is the hydrogen yield in molecules per 100 ev absorbed; and W is the power density in kilowatts per liter. The subscripts f, p, and e refer to the values for fission recoil particles; protons produced by neutron scattering, and electrons produced by gamma-ray absorption and by radioactive decay of fission products. For an operating homogeneous reactor, about 96% of the hydrogen gas produced in solution is due to the fission recoil particles, 2% to the neutrons, and 2% to the gamma rays. Therefore the last two terms in Eq. (3–8) are usually neglected. The fraction due to recoils is usually above 0.96, since part of the energy of the prompt neutrons, gamma rays, and radioactive decay escapes from the solution. The value of G_f for a given solute concentration can be obtained from Fig. 3–17 and the value for W_f can be calculated from the neutron flux, the concentration of fissionable atoms, the fission cross section, and the kinetic energy of the fission recoils.

Along with the hydrogen, an equivalent amount of oxidant (either peroxide or O_2) will be formed.

TABLE 3–2

INITIAL RATES OF H_2 GAS PRODUCTION FROM REACTOR-IRRADIATED
URANIUM SOLUTIONS

Solute	Concentration		Fission energy total energy	pH	$G(H_2)$
	g U/liter	g U^{235}/liter			
	0.399	0.372	0.688		1.61
	4.03	3.76	0.957	3.26	1.66
	18.6	1.63	0.906	2.90	1.48
	38.1	0.274	0.619		0.95
	40.7	37.9	0.995	2.42	1.53
	102.1	37.4	0.995	2.00	1.35
	105.2	38.9	0.995	0.10*	1.20
	108.4	40.1	0.995		1.35
	202.3	0.063	0.273		0.69
UO_2SO_4	202.5	37.6	0.995	1.61	1.11
	203.4	189.6	0.999		1.11
	227.0	1.63	0.906		0.98
	310.4	0.096	0.364		0.62
	386.0	1.63	0.906		0.80
	431.3	37.8	0.995	1.32	0.77
	436.8	3.10	0.949		0.73
	477.2	0.148	0.467		0.56
	713.5	33.5	0.995		0.56
	796.0	37.4	0.995	1.03	0.49
	4.25	3.96	0.959	4.25	1.63
	40.1	37.3	0.995	3.32	1.58
UO_2F_2	118.8	37.1	0.995	2.98	1.36
	272.0	37.2	0.995	2.64	1.11
	377.0	39.3	0.996	1.35*	0.84
	405.7	42.3	0.996	2.41	0.95
	4.24	3.95	0.960		1.63
$UO_2(NO_3)_2$	42.3	39.4	0.995	2.05	1.5
	318.0	2.29	0.932	1.03	0.6
	420.1	36.9	0.994	0.60	0.55
	42.2	39.3	0.995	1.95	1.45
$U(SO_4)_2$	92.5	35.1	0.996	0.1	1.25
	350.0	32.0	0.995	0.1	0.75

*pH adjusted by adding acid.

3–3.4 Recombination in uranium solutions. For fission recoil particles the radiation-induced back reaction of H_2, O_2, and H_2O_2 is relatively slow. Also, the thermal recombination rate in the absence of added catalyst is relatively slow and, as a result, the steady-state pressure of gases is very high; e.g. at 250°C the pressure is of the order of thousands of psi.

Certain solutes, notably copper salts, have been shown to act as homogeneous catalysts [39] in the thermal combination of hydrogen and oxygen in aqueous uranium solutions. This provides a convenient method for recombining the radiolytic hydrogen and oxygen gases.

The reaction rate is first order in hydrogen and in copper concentration, and independent of the oxygen concentration. The rate-determining step is the reaction of hydrogen with the catalyst, and the activation energy is about 24 kcal/mole. For a particular uranium solution, the rate of hydrogen removal, in moles/liter/min, can be expressed by

$$\frac{-d(H_2)}{dt} = k_{Cu}(Cu)(H_2), \qquad (3\text{–}9)$$

where k_{Cu} is the catalytic constant in liters/mole/min, and concentrations are given as moles/liter. Some selected values of k_{Cu} are listed in Table 3–3. Increasing the concentration of uranyl sulfate or of sulfuric acid decreases the catalytic activity of the copper somewhat, possibly as a result of complexing. Also, the rate of reaction with D_2 is about 0.6 that with H_2.

TABLE 3–3

SELECTED VALUES OF k_{Cu} AT SEVERAL TEMPERATURES AND
URANIUM CONCENTRATIONS $(Cu = 10^{-3}\, M)$

Uranium concentration, M	Temperature, °C	k_{Cu}, liters/mole/min	$10^3\, k_{Cu}/S$, psi^{-1}/min
0.17	190	4.3	0.28
0.17	220	26.6	2.3
0.17	250	90.0	12.
0.00	250	83.0*	11.
0.01 to 0.1	250	133	18.
0.01 to 0.1	275	380	61
0.01 to 0.1	295	850	149

*With $10^{-3}\, M$ $Cu(ClO_4)_2$ plus $HClO_4$ in concentrations ranging from 0.005 M to 0.05 M.

The concentration (solubility) [40] of H_2 is related to the partial pressure of hydrogen by the proportionality factor

$$S = \frac{P_{H_2}}{(H_2)},$$
(3-10)

where P_{H_2} is given in psi, (H_2) in moles/liter, and S in psi/liter/mole. Equation (3-9) can then be written

$$\frac{-d(H_2)}{dt} = k_{Cu}(Cu)\frac{P_{H_2}}{S}$$
(3-11)

At the steady state, the rates of formation and removal of hydrogen are equal, and from Eqs. (3-8) and (3-11), the steady-state pressure is given by

$$P_{(H_2)ss} = \frac{0.0062 \times G_f \times W_f \times S}{(Cu)k_{Cu}}.$$
(3-12)

Application of copper sulfate catalyst to the suppression of gas evolution during the operation of the Homogeneous Reactor Experiment was discussed by Visner and Haubenreich [41]. Design calculations for use of copper catalysts in the HRE-2 and in other reactors have been reported [42]. The use of internal recombination catalysts in homogeneous reactors is also discussed in Article 7-3.7.

3-3.5 Peroxide decomposition in uranium solutions. The hydrogen peroxide produced by decomposition of the water can undergo several secondary reactions: (a) It can react with uranyl ion to form the slightly soluble peroxide UO_4 according to the reaction

$$UO_2^{++} + H_2O_2 \rightleftharpoons UO_4 + 2H^+.$$
(3-13)
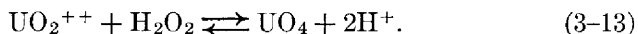
The UO_4 will precipitate if its solubility ($\sim 10^{-3} M$) is exceeded. (b) It (or the UO_4) can decompose by a radiation-induced reaction via the free radicals H and OH produced by decomposition of the water. (c) In a reactor operating at high temperatures the H_2O_2 will decompose thermally at an appreciable rate according to the over-all reaction:

$$H_2O_2 \longrightarrow H_2O + 1/2\,O_2$$
(3-14)
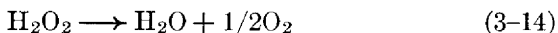
and the UO_4 will decompose thermally according to the reactions

$$UO_4 \longrightarrow UO_3 + 1/2\,O_2,$$
(3-15)

$$UO_3 + 2H^+ \longrightarrow UO_2^{++} + H_2O.$$
(3-16)
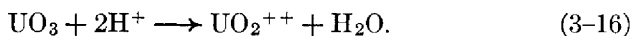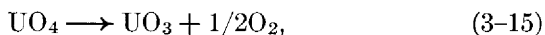
Studies of the kinetics of the thermal decomposition of peroxide in uranyl sulfate solutions [43] have shown the rate to be first order with respect to peroxide concentration in the range from 0.4 to $5 \times 10^{-3} M$, independent of uranium concentration in the range from 4.5×10^{-3} to 0.65 M, and independent of the acidity from pH 1.6 to 3.3. Traces of certain ions showed pronounced catalytic effects. The rate of decomposition could be expressed by

$$\frac{-d(\mathrm{H_2O_2})}{dt} = k(\mathrm{H_2O_2}) + k_{\mathrm{cat}}(\mathrm{Cat})(\mathrm{H_2O_2}), \qquad (3\text{–}17)$$

where $(\mathrm{H_2O_2})$ represents total peroxide concentration $(\mathrm{UO_4} + \mathrm{H_2O_2})$ in moles per liter at time t, k is the molar rate constant in the absence of catalyst, k_{cat} is the catalytic constant, and (Cat) is the concentration of catalyst in moles per liter.

Values of k for uranyl sulfate solutions $(4.5 \times 10^{-3} M$ to 0.65 $M)$ with no added catalyst depended upon the adventitious impurities present, and were in the ranges as listed in Table 3–4. The indicated activation energy is 25.5 kcal/mole. For pure water, the rate constant at 78°C was 4.5×10^{-4} per minute.

Catalytic constants, k_{cat}, for various ions added are listed in Table 3–5.

The net rate of peroxide formation is the difference between the rate of production and the rate of decomposition. At the steady state the two rates are equal. The rate of formation of peroxide in an operating reactor in terms of moles per liter per minute can be expressed in terms of the yield, G, in molecules per 100 ev of fission recoil energy, and the average fission recoil power density of the reactor, W, in kilowatts per liter, by the equation:

$$\frac{d(\mathrm{H_2O_2})}{dt} = 0.0062 \times G \times W \times 0.96. \qquad (3\text{–}18)$$

The maximum value of G for the particular solution used is that given for the $\mathrm{H_2}$ yield in Fig. 3–18. During reactor operation the radiation-induced decomposition of peroxide is negligible, and the rate of decomposition is essentially the thermal rate given by Eq. (3–17). At the steady state the peroxide concentration is given by

$$(\mathrm{H_2O_2})_{\mathrm{ss}} = \frac{0.0062 \times G \times W \times 0.96}{k + k_{\mathrm{cat}}(\mathrm{Cat})}. \qquad (3\text{–}19)$$

TABLE 3–4

MOLAR RATE CONSTANTS FOR PEROXIDE
DECOMPOSITION IN UO_2SO_4 SOLUTIONS

Temperature, °C	k, min^{-1}
53	1.2×10^{-3} to 12×10^{-3}
78	1.8×10^{-2} to 14×10^{-2}
100	1.8×10^{-1} to 12×10^{-1}

TABLE 3–5

CATALYTIC CONSTANTS AT 100° C FOR PEROXIDE
DECOMPOSITION BY VARIOUS IONS ADDED TO
UO_2SO_4 SOLUTION

Catalyst	k_{cat} (liters/mole/min)
Fe^{+2}	135,000
Ru^{+4}	121,000
Ag^{+1}	4,500
Ni^{+2}	2,600
Cu^{+2}	1,200
Fe^{+2} (promoted by 793 ppm Cu^{+2})	502,000

The maximum allowable power density, W_{max}, before precipitation of uranium peroxide occurs is given by

$$W_{max} = \frac{(H_2O_2)sol[k + k_{cat}(Cat)]}{0.0062 \times G \times 0.96}.$$
\hfill (3–20)

For example, in 0.17 M UO_2SO_2 solution at 100°C with no added catalyst, the peroxide solubility is $\approx 4 \times 10^{-3}$ M, $k \approx 1$ min^{-1}, and $G \approx 1.5$, then $W_{max} \approx 0.4$ kw/liter.

Following reactor shutdown, peroxide formation and decomposition will result from the delayed neutrons and from the β^- and γ radiation of the fission products. The yield for peroxide formation will be essentially that for γ-rays, $G = 0.46$. The yield for radiation-induced decomposition [37] may be as high as 4.5, but will depend in a complicated way on the amount of oxygen, hydrogen, and other solutes such as fission products, corrosion products, etc., present.

3–3.6 Decomposition of water in thorium solutions. Under radiation thorium nitrate solutions decompose [44] to give H_2, H_2O_2, and O_2 from decomposition of the water, and O_2, N_2, and oxides of nitrogen from decomposition of the nitrate. Yields of H_2 and N_2 for several types of radiation, and for several concentrations of thorium nitrate, are given in Table 3–6. The hydrogen yield decreases with increasing solute concentration, the same as for uranium solutions. The nitrogen yield increases with increasing nitrate concentration. The N_2 is presumably formed by direct action of radiation on the nitrate. The N_2 yield is greater for radiations of greater LET. The N_2 yield is independent of temperature, and little or no radiation-induced back reaction takes place.

Uranyl nitrate solution also decomposes to give N_2 in yield comparable to that for thorium nitrate solution.

TABLE 3–6

THE EFFECTS OF CONCENTRATION AND TYPE OF RADIATION ON
THE YIELDS OF N_2 AND H_2 IN THE DECOMPOSITION OF THORIUM
NITRATE SOLUTIONS

$Th(NO_3)_4$, molality	$G(H_2)$ Fission recoils*	$G(N_2)$		
		Fission recoils*	ORNL graphite pile radiation	Gamma rays
0.26	1.11	0.002	0.003	0.04×10^{-3}
0.55	0.93	0.016	0.003	$0.5 \ \times 10^{-3}$
1.5	0.51	0.047	0.005	$1.5 \ \times 10^{-3}$
2.7	0.33	0.063	0.006	$1.1 \ \times 10^{-3}$
7.2	~ 0.08†	0.16		

*0.14 molal enriched UO_2SO_4 added to make the energy contributed by fission recoils $> 95\%$ of the total energy absorbed.
†Estimated by extrapolation.

3-4. PHYSICAL PROPERTIES

3–4.1 Introduction. Knowledge of the physical properties of aqueous solutions of reactor fuel materials is required for nuclear physics calculations and analysis of reactor performance, for engineering design, and, ultimately, for effective reactor operation. The scarcity of information available in 1951 concerning the properties of uranium salt solutions prompted the Homogeneous Reactor Program at ORNL to sponsor a physical properties research program at Mound Laboratory beginning in

July 1951 and carrying through December 1954. The progress of this effort is discussed in regular reports [45] and in a number of topical reports dealing with techniques, apparatus, and summarized data [46–56].

A number of compilations of physical properties data for aqueous reactor solutions have appeared, among which are included those of Van Winkle [57], Tobias [58], and sections by Briggs, Day, Secoy, and Marshall in The Reactor Handbook [59].

The properties of light and heavy water are discussed by Lottes [60] as they relate to reactor heat-transfer problems. Other properties of water are found in standard reference works [61–62].

The remainder of this section is devoted to particular properties of reactor solutions which are of interest and to some properties of the vapor phase above reactor solutions which are important for aqueous homogeneous reactors.

TABLE 3–7

LIQUID AND VAPOR DENSITIES OF D_2O

T, °C	Density, g/cc	
	Vapor	Liquid
175	0.004	0.989
180	0.005	0.983
190	0.006	0.970
200	0.007	0.957
210	0.009	0.943
220	0.010	0.929
230	0.013	0.913
240	0.016	0.898
250	0.020	0.881
260	0.024	0.864
270	0.029	0.847
280	0.034	0.829
290	0.040	0.809
300	0.048	0.787
310	0.058	0.763
320	0.070	0.735
330	0.087	0.705
340	0.105	0.668
350	0.129	0.626
360	0.163	0.573
370	0.248	0.462
371.5	0.363	0.363*

*Critical point.

3–4.2 Density of heavy water and uranyl sulfate solutions. The density of heavy water has been measured up to 250°C at Mound Laboratory by a direct method making use of a Jolly balance [51,54]. An indirect method for determining the density of heavy-water liquid and vapor has been used to extend the data up to the critical temperature [63]. Table 3–7 gives density values at convenient temperature intervals. The densities of uranyl sulfate solutions from 20 to 90°C and at concentrations up to 4.0 molal were measured by Jegart, Heiks, and Orban at Mound Laboratory [47,56]. The densities of uranyl sulfate solutions were measured by Barnett et al., of Mound Laboratory [55] at temperatures up to 250°C for concentrations (at room temperature) of 60.6 and 101.0 g U/liter of solution in light water and for uranium concentrations (room temperature) of 20.3, 40.4, and 61.2 g/liter in heavy water. Their data are presented in Table 3–8.

TABLE 3–8

DENSITIES OF LIGHT- AND HEAVY-WATER SOLUTIONS OF
URANYL SULFATE

T, °C	Density, g/ml						
	UO_2SO_4 in H_2O, g U/liter		UO_2SO_4 in D_2O, g U/liter				
	60.6	101.0	20.3	O_2, psi*	40.4	O_2, psi*	61.2
30		1.1340	1.300		1.1567		1.1842
			1.318	300	1.1598	280	
45	1.0715	1.1275	1.1245		1.1509		1.1781
			1.1263	305	1.1540	280	
60	1.0649	1.1199	1.1170		1.1433		1.1704
			1.1198	325	1.1472	300	
75	1.0562	1.1111	1.1120	340	1.1388	325	1.1628
90	1.0468	1.1008	1.1026	360	1.1297	350	1.1545
100	1.0395	1.0952	1.0954	380	1.1228	365	1.1476
125	1.0203	1.0742	1.0751	415	1.1037	410	1.1278
150	0.9984	1.0528	1.0505	480	1.0822	480	1.1053
175	0.9735	1.0293	1.0221	560	1.0572	530	1.0805
200	0.9460	1.0030	0.9920	680	1.0280	670	1.0540
225	0.9156	0.9745	0.9578	830	0.9973	840	
250		0.9440	0.9224	1090	0.9610	1080	

*Overpressure of oxygen gas as indicated. Otherwise solutions were in contact with their own vapor.

The densities of light-water solutions of uranyl sulfate were found by Marshall [64] to fit the relationship

$$d_s = \frac{1}{(78.65/U) - 1.046} + d_{H_2O},$$

where d_s is the density of the solution in g/cc, U is the weight percent uranium, and d_{H_2O} is the density of water at the same temperature and pressure as the solution. The accuracy of this formula is believed to be:

$$\pm\, 0.5\% \text{ from } 25 \text{ to } 300°C \text{ for } 0\text{–}10\% \text{ U,}$$
$$\pm\, 1.0\% \text{ from } 120 \text{ to } 250°C \text{ for } 10\text{–}50\% \text{ U,}$$
$$\pm\, 2.0\% \text{ from } 25 \text{ to } 125°C \text{ for } 10\text{–}50\% \text{ U,}$$
$$\pm\, 2.0\% \text{ from } 250 \text{ to } 280°C \text{ for } 10\text{–}50\% \text{ U.}$$

The density of heavy-water solutions of uranyl sulfate may be estimated from an analogous formula:

$$d_s = \frac{1}{(71.0/U) - 0.944} + d_{D_2O}.$$

The densities of heavy-water solutions of uranyl sulfate reported in Table 3–8 were found to be within 3% of values calculated by this formula.

Similar formulas were devised by Tobias [58] for application to the determination of the densities of solutions of mixed solutes such as uranyl sulfate-beryllium sulfate and uranyl sulfate-lithium sulfate.

Density information for other uranium salts and for thorium nitrate solutions was compiled by Day, Secoy, and Marshall [59].

3–4.3 Viscosity of D_2O and uranium solutions. The viscosity of heavy water was measured from 30 to 250°C by Heiks et al. [54]. Good agreement with four values reported by Hardy and Cottington [65] was found. The apparatus used has been described by Heiks et al. [51] and the electronic instrumentation for measuring the time of fall of a plummet containing a radioactive pellet has been described by Rogers et al. [52].

Van Winkle [57] discussed the viscosity of light and heavy water and the early data for solutions of uranyl sulfate in heavy water.

Heiks and Jegart of Mound Laboratory [50,56] measured the viscosity of uranyl sulfate solutions in light water over a concentration range of 0.176 to 2.865 molal and over a temperature range of 20 to 90°C by the use of Ostwald capillary viscometers. Using the falling-body viscometer referred to above, Barnett et al. of Mound Laboratory have measured the viscosities of light- and heavy-water solutions of uranyl sulfate at temperatures up to 250°C [55]. Table 3–9 presents a comparison of viscosities

TABLE 3–9

VISCOSITIES OF LIGHT- AND HEAVY-WATER SOLUTIONS OF
URANYL SULFATE

| T, °C | Viscosity, cp | | | | | | | | | |
| | UO$_2$SO$_4$ in H$_2$O, g U/liter | | | | | | UO$_2$SO$_4$ in D$_2$O, g U/liter | | | |
	20.2	59.7	100.4	201.4	301.1	400.7	0	20.3	40.4	61.2
30	0.857	0.946	1.04	1.40	1.97	3.04	0.969	—	—	—
45	0.629	0.701	0.773	1.05	1.39	1.98	0.713	0.773	0.789	0.827
60	0.492	0.536	0.605	0.820	1.06	1.41	0.552	0.586	0.608	0.638
75	0.403	0.436	0.483	0.638	0.821	1.10	0.445	0.467	0.487	0.513
90	0.329	0.365	0.399	0.517	0.675	0.884	0.365	0.384	0.397	0.415
100	0.292	0.327	0.351	0.454	0.589	0.767	0.323	0.342	0.350	0.365
125	0.238	0.264	0.273	0.347	0.442	0.543	0.252	0.263	0.269	0.287
150	0.194	0.213	0.223	0.275	0.335	0.437	0.208	0.216	0.222	0.233
175	0.164	0.178	0.188	0.226	0.269	0.360	0.175	0.182	0.187	0.196
200	0.142	0.153	0.158	0.192	0.230	0.298	0.151	0.154	0.160	0.169
225		0.136	0.141		0.209	0.264	0.135	0.138	0.144	0.151
250		0.125	0.130		0.190	0.238	0.124	0.125	0.133	0.137

of light- and heavy-water solutions for selected temperatures and uranium concentrations.

The viscosity of uranyl nitrate solutions is discussed by Day and Secoy [59].

3–4.4 Heat capacity of uranyl sulfate solutions. Van Winkle [57] estimated the heat capacity of dehydrated uranyl sulfate by comparison with uranyl nitrate and with salts of other metals and has estimated the heat capacity of solutions of uranyl sulfate in heavy water and in light water. The effect of temperature on the heat capacity of solutions was assumed to be the same, percentagewise, as the effect on the heat capacity of the pure solvent. Table 3–10 shows the influence of uranyl sulfate concentration upon the heat capacity of solutions at 25 and 250°C. No experimental measurements have been reported for temperatures above 103°C; values below this temperature differ from the estimates by as much as 10% [57].

3–4.5 Vapor pressure of uranyl sulfate solutions. The vapor pressures of uranyl sulfate solutions have been measured over the temperature range 24 to 100°C and at uranium concentrations up to 4.8 molal by Day [66]. The ratio of the vapor pressure of the solution to that of pure water at the

TABLE 3–10

ESTIMATED HEAT CAPACITIES OF URANYL SULFATE SOLUTIONS

Estimated Heat Capacity, cal/g $\cdot$°C

UO_2SO_4, w/o	H₂O solutions		D₂O solutions
	25°C	250°C	25°C
0	0.998	1.166	1.005
10	0.905	1.070	0.916
20	0.809	0.975	0.830
30	0.714	0.875	0.745
40	0.619	0.770	0.658
50	0.523	0.665	0.568
60	0.428	0.550	0.474
70	0.333	0.425	0.370
80	0.238	0.290	0.252
85.9 ($UO_2SO_4 \cdot 3D_2O$)	—	—	0.174
87.2 ($UO_2SO_4 \cdot 3H_2O$)	0.170	—	—

same temperature is almost independent of temperature but markedly dependent upon the solute concentration over this range. Table 3–11 shows the effect of uranium concentration upon the ratios at temperatures up to 100°C. Vapor pressure measurements have been made for light-water solutions of uranyl sulfate at temperatures up to approximately 200°C and uranium concentrations (room temperature) of 400 and 500 g/liter. Data have, however, not yet been published [45]. Other vapor pressure measurements are being made at the Oak Ridge National Laboratory. The vapor pressure lowering in uranyl sulfate solutions containing added lithium or beryllium sulfate was stated to be approximately in accord with Raoult's law [8b].

The vapor pressures of three solutions of UO_3 in phosphoric acid are shown in Table 3–12 [17], based on values read from the published curve.

3–4.6 Surface tension of uranyl sulfate solutions. The capillary rise method was adapted to conditions prevailing at elevated temperatures and pressures for measurements made at Mound Laboratory by Heiks et al. [51,54]. Briggs [59] has compiled information on the surface tension of aqueous solutions of uranyl sulfate, including the relationships established by Van Winkle.

TABLE 3–11

RATIOS OF VAPOR PRESSURES OF URANYL SULFATE
SOLUTIONS TO THAT OF PURE H_2O

UO_2SO_4, M	p/p_0 (at given temperature)			
	25°C	50°C	80°C	100°C
0.59166	0.990	0.990	0.991	0.993
1.14545	.979	.981	.984	
3.17433	.911	.920	.935	
4.1821	.863	.881	.900	

TABLE 3–12

VAPOR PRESSURES OF UO_3 SOLUTIONS IN H_3PO_4*

Temperature, °C	Vapor pressure, lb/in²		
	0.76 M UO_3 in 0.56 M H_3PO_4	0.309 M UO_3 in 2.90 M H_3PO_4	0.75 M UO_3 in 7.5 M H_3PO_4
110	23	21	21
150	66	64	64
200	200	200	200
250	460	500	500
300	1000	1150	1150
350	1700	2100	2100
400	2900	3600	3700
450	4600	5600	6600
500	6600	8000	—

*Plotted and extrapolated from Los Alamos data.

Barnett and Jegart of Mound Laboratory [53] reported the surface tension of uranyl sulfate solutions in light water at temperatures up to 75°C and concentrations up to 2.34 molal.

Barnett et al. [55], using the apparatus described by Heiks et al. [51] for capillary rise technique at elevated temperatures and pressures, measured the surface tension of light- and heavy-water solutions of uranyl sulfate at temperatures up to 250°C.

TABLE 3–13

THE pH OF UO_3–H_2SO_4–H_2O SOLUTIONS AT 25.00°C*

Molarity H_2SO_4	Molar ratio, UO_3/SO_4					
	0.7006	0.8017	0.9024	1.0029	1.1042	1.202
0.02432	1.995	2.151	2.425	3.043	3.612	3.823
0.01214	2.259	2.422	2.692	3.267	3.731	3.922
0.004866	2.619	2.784	3.046	3.526	3.874	4.038
0.003656	2.730	2.900	3.155	3.604	3.913	4.074
0.002437	2.905	3.065	3.321	3.708	3.977	4.124
0.001216	3.174	3.348	3.592	3.906	4.093	4.214
0.0004850	3.587	3.715	3.903	4.130	4.250	4.354
0.0003646	3.671	3.822	3.996	4.201	4.304	4.395
0.0002424	3.851	4.004	4.127	4.326	4.411	4.500

*These values are based on a determined pH of 2.075 for 0.01000 molar HCl, 0.900 molar KCl. For pH's relative to the analytical concentration of HCl subtract 0.075 pH unit from each of the above values.

TABLE 3–14

THE pH VALUES OF HCl, H_2SO_4, AND UO_2SO_4 SOLUTION
AS A FUNCTION OF TEMPERATURE

	M	t°C	pH	t°C	pH
HCl	0.0100	30	2.13	130	2.17
H_2SO_4	0.00490	30	1.76	180	1.93
"	0.04615	30	1.28	180	1.62
"	0.09740	30	0.96	180	1.21
UO_2SO_4†	0.04	30	2.80	150	2.58
"	0.17	30	2.20	180	2.20
"	1.1	30	1.76	180	1.81
UO_2SO_4* + H_2SO_4		30	1.22	180	1.83

*UO_2SO_4 solution which read pH 2.68 at 30°C, to which was added sufficient H_2SO_4 to bring the pH reading down to 1.22 at 30°C.

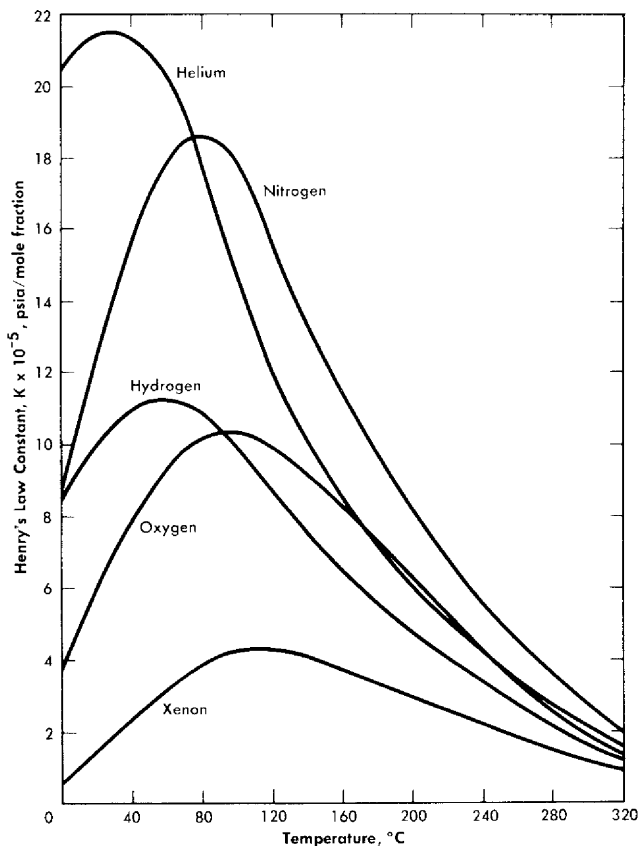†Reported values modified and extended by personal communication with M. H. Lietzke, April 1958.

FIG. 3–19. Solubility of gases in water.

3–4.7 Hydrogen ion concentration (pH). Orban of Mound Laboratory [48,56] studied the acidity of uranyl sulfate solutions from 25 to 60°C. Orban has also reported the pH values for uranyl sulfate solutions containing excess UO_3 at temperatures up to 60°C [49,56]. Secoy has compiled information concerning the effects of uranium sulfate concentration upon pH as reported by a number of investigators [59]. Marshall has utilized the relationship between pH and concentration to determine the solubility of UO_3 in sulfuric acid at elevated temperatures [7]. Table 3–13 shows the effect of sulfate concentration on pH at 25.00°C for various ratios of UO_3 to sulfate as found by Marshall.

The direct measurement of pH at elevated temperatures and pressures has been made possible through the development by Ingruber of high-temperature electrode systems for use in the sulphite pulping process of the paper industry [68]. Lietzke and Tarrant have demonstrated the applicability of Ingruber's electrode system to the measurement of the pH of
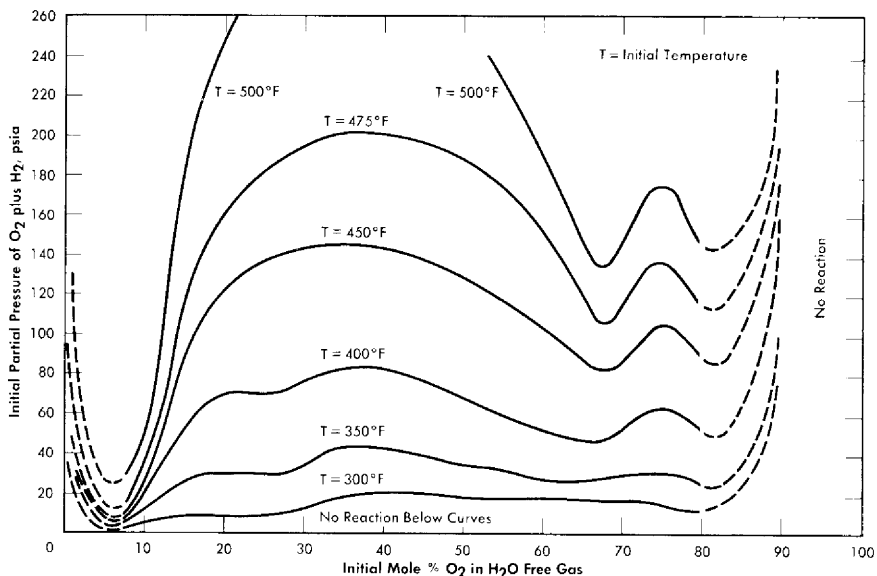
FIG. 3–20. Approximate explosion limits of spark-ignited gaseous mixtures of O_2 and H_2 saturated with H_2O vapor in $1\frac{1}{2}$-in. bomb.

solutions of HCl, UO_2SO_4, and H_2SO_4 at temperatures as high as 180°C [69]. Table 3–14 lists the values reported. Lietzke has reported the properties of the hydrogen electrode-silver chloride electrode system at high temperatures and pressures [70].

3–4.8 Solubility of gases. The solubilities of various gases in water and in reactor solutions are indicated by Fig. 3–19 [71,72].

Composition and PVT data [73,74]. Dalton's Law of additive partial pressures has been determined to correlate the *P–PVT* relationships of steam-oxygen and steam-helium mixtures in the pressure range of interest (up to 2500 psi) to within 1%.

For approximate calculations the perfect gas laws can be applied when dealing with the permanent gases under reactor conditions, but values for the properties of water vapor and D_2O vapor should be obtained from experimental data or standard tables [62].

The compositions of saturated steam-gas mixtures are predictable in a similar manner, in that the partial density of each constituent is equal to that of the pure constituent at its partial pressure.

3–4.9 Reaction limits and pressures. Stephen et al. [75] measured the effect of temperature and H_2/O_2 ratio on the lower reaction limits of the H_2–O_2-steam system in a small 1.5-in.-diameter autoclave. Their investi-
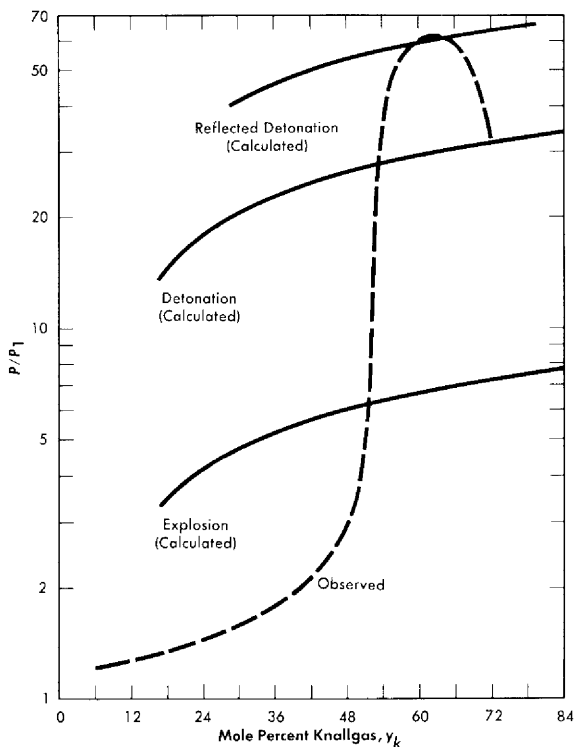
Fig. 3–21. Ratio of peak reaction pressure to initial mixture pressure vs. composition of Knallgas saturated with water vapor at 100°C. Tube diameter = 0.957 in., spark ignition energy = 180 millijoules.

gation indicated that the composition (mol basis) of the mixture at the lower limit was not temperature dependent at constant H_2/O_2. Figure 3–20 is a plot of Stephan's data showing variation in H_2/O_2 [76].

Syracuse University is investigating [77] further the effects of geometry, temperature, and method of ignition on the reaction and detonation limits of $H_2O–(2H_2 + O_2)$. Reaction pressures are also measured. Figure 3–21 shows their reported results in a long 0.957-in.-diameter tube at 100°C; these are typical of results obtained at 300°C. It is interesting to note that their lower reaction limit is 6% Knallgas,* as compared with 20% Knallgas observed by Stephan.

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*Knallgas is the term describing the 2:1 mixture of hydrogen and oxygen obtained electrolytically and considered as a single gas.

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