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THERMODYNAMIC PROPERTIES OF UF_6 AT HIGH TEMPERATURES

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THERMODYNAMIC PROPERTIES OF UF_6 AT HIGH TEMPERATURES

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SUMMARY

The equilibrium composition of the mixture resulting from the decomposition of uranium hexafluoride is calculated for temperatures ranging from 600°K to 4000°K at pressures from 0.01 atmospheres to 10 atmospheres. The species considered include UF_6, UF_5, UF_4, U, F and F_2. In addition to the composition, the thermodynamic properties of the mixture are evaluated and tabulated. The model employed for calculating the properties of UF_6, UF_5 and UF_4 is that appropriate for a rigid rotor, harmonic oscillator model.

INTRODUCTION

Uranium hexafluoride is one of the more familiar uranium compounds used in the processing of nuclear fuels. As a result of work related to its use in present day nuclear technology, the thermodynamic properties and phase relations of UF_6 at temperatures below 600°K are well known[1]. The recent interest in gas-core reactors and nuclear powered lasers[2-4] brought about renewed interest in the thermodynamic properties of UF_6 at high pressures and temperatures. Currently, there is a continuing effort at the University of Florida to measure the thermodynamic properties using a device called the ballistic piston compressor. Available measurements included the ratio of the specific heats and pressure and temperature[5].

The object of this investigation is to present a method for the systematic evaluation of the thermodynamic properties of and the chemical and phase

changes in UF_6 over a wide range of pressures and temperatures. The calculations allow for the presence of UF_6, UF_5, UF_4, U, F and F_2. For the range of pressures and temperatures considered in this investigation, the partial pressures of the various vapors did not exceed their saturation pressures; thus, all the species present are in the gaseous state.

Nagarajan[6] was among the first to study the thermodynamic properties of UF_6 at high temperatures. His calculations were based on a rigid rotor, harmonic oscillator model and were carried out to 1600°K. Galkin et al.[7] studied the thermodynamic properties of the uranium pentafluoride while Tumanov[8] presented an empirical method for calculating the thermodynamic properties of UF_4. Recently, Galkin and Tumanov[9] studied the chemical and phase transformations in UF_6 up to 3400°K; the species considered where UF_6, UF_5, UF_4, F and F_2. They found UF_6 to be stable up to about 1800°K at one atmosphere with a sharp breakdown beginning at 2200°. The partial pressure of UF_5 was found to peak at 2400°K, while the tetrafluoride peaked at about 3200°K. Complete decomposition of UF_6 into UF_4 and fluorine was found to occur in the range, 3200 - 3400°K.

The work presented here extends that of Ref. 9; one more species, uranium gas, has been added to the system and the temperature range has been extended to 4000°K. In addition, the enthalpy, entropy, free energy, specific heats and the ratio of the specific heats have been calculated and tabulated.

ANALYSIS

Six species are considered in this analysis of the chemical and phase changes of UF_6 at high temperatures. These are F, F_2, U, UF_4, UF_5 and UF_6

and will be designated as species 1-6, respectively. The equilibrium constant approach[10] is used to determine the equilibrium composition of the mixture. There are six unknowns, these being the partial pressures or the number of moles of each constituent gas, so that six equations are needed to determine the system. Two equations are obtained from conservation of element considerations. Starting with one mole of UF_6, the conservation of element equations can be written as

$$1 = n_3 + n_4 + n_5 + n_6$$

and

$$6 = n_1 + 2n_2 + 4n_4 + 5n_5 + 6n_6 \tag{1}$$

where n_i is the number of moles of species i. The other four equations can be obtained from the law of mass action[10]. This law states that, for the reaction

$$\sum_{j=1}^{\nu} a_j A_j \rightleftarrows \sum_{j=1}^{\nu} b_j A_j \tag{2}$$

where A_j represents a reactant or product, a_j the number of moles of the reactants, b_j the number of moles of the products and ν the number of species present, the equilibrium constant is given by

$$K_p(T) = \prod_{j=1}^{\nu} P_j^{(b_j - a_j)}$$

where P_j is the partial pressure of species j. The law of mass action may be applied to any four reactions involving the six gases present. The four reactions considered in this analysis are

(i) $F_2 \rightleftarrows 2F$

(ii) $UF_6 \rightleftarrows UF_4 + 2F$

(iii) $UF_5 \rightleftarrows UF_4 + F$

(iv) $UF_4 \rightleftarrows U + 4F$

Applying the law of mass action to these reactions and using the relation $\frac{P_i}{P} = \frac{n_i}{n}$, one finds

$$K_{p_1}(T) = \frac{P_1^2}{P_2} = \frac{n_1^2}{n_2} \cdot \frac{P}{n} \tag{3}$$

$$K_{p_2}(T) = \frac{P_1^2 P_4}{P_6} = \frac{n_1^2 n_4}{n_6} \left(\frac{P}{n}\right)^2 \tag{4}$$

$$K_{p_3}(T) = \frac{P_1 P_4}{P_5} = \frac{n_1 n_4}{n_5} \left(\frac{P}{n}\right) \tag{5}$$

$$K_{p_4}(T) = \frac{P_1^4 P_3}{P_4} = \frac{n_1^4 n_3}{n_4} \left(\frac{P}{n}\right)^4 \tag{6}$$

where P and n are the total pressure and the total number of moles, respectively.

The equilibrium constants, K_p, are given in terms of the Gibbs free energies. For the general reaction indicated by equation (2), the equilibrium constant is

$$K_p(T) = \mathrm{Exp}\ [\ -\Delta F^\circ/RT]$$

where

$$\Delta F^\circ = \sum_{j=1}^{\nu} (b_j - a_j) F_j^\circ(T),$$

$F_j^\circ(T)$ is the standard free energy of species i and R is the universal gas constant. The equilibrium constant for reaction (i) is tabulated in Ref. 11

along with the Gibbs free energies of both monatomic and diatomic fluorine. The free energy of uranium is given in Ref. 12 while the free energies of UF_6, UF_5 and UF_4 are calculated in Appendices A, B and C respectively.

Equations (1) and equations (3) - (6) represent a system of six simultaneous equations which can be solved by iteration to determine the composition. Having determined the composition, the thermodynamic properties of the system follow from the expressions

$$h = \frac{1}{M} \sum_{i=1}^{6} [n_i\{H(T) - H(298)\}_i + n_i(\Delta H_{f298})_i] \tag{7}$$

$$s = \frac{1}{M} \{ \sum_{i=1}^{6} n_i \, S_i^\circ(T) - R \sum_{i=1}^{6} n_i \, \ell n \, (\frac{n_i P}{n})\} \tag{8}$$

$$f = h - Ts \tag{9}$$

$$c_p = \sum_{i=1}^{6} \frac{n_i \, C_{Pi}(T)}{M} \tag{10}$$

$$c_v = \sum_{i=1}^{6} \frac{n_i \, C_{v_i}(T)}{M} \tag{11}$$

$$\gamma = c_p/c_v \tag{12}$$

In the above equations H(T) is the enthalpy per mole, ΔH_{f298} is the heat of formation per mole at 298°K[11,13], $S_i^\circ(T)$ is the entropy per mole at one atmosphere, $C_p(T)$ and $C_v(T)$ are the molar specific heats, M is the total mass of the system, or 352 grams per initial mole of UF_6; h, s, f, c_p and c_v the enthalpy, entropy, Gibbs free energy and specific heats per unit mass of the mixture. The thermodynamic functions for F and F_2 are taken from Reference 11, while those for U come from Reference 12. Thermodynamic properties of UF_6, UF_5, and UF_4 are calculated according to procedures outlined in Appendices A,B, and C.

When carrying out calculations similar to those outlined above, the possible appearance of condensed phases of one or more of the constituent species should not be overlooked. Specifically it is possible for condensed phases of UF_5, UF_4, and U to appear in the temperature and pressure range considered here: if the partial pressure of a substance exceeds its saturated vapor pressure at some temperature, a condensed phase will be present at that temperature and the calculations should be repeated to allow for the presence of such a condensed phase. Expressions for the saturated vapor pressure of UF_5, UF_4 and U are listed below. Values calculated using these expressions were compared, at each calculation step, with the partial pressures of the appropriate species to insure that the exclusion of condensed phases is a valid assumption.

$$UF_5 \text{ solid: } \log_{10} P(\text{mm}) = \frac{-8001}{T} + 13.994; \ (515 - 619°K) \tag{13a}$$

$$UF_5 \text{ liquid: } \log_{10} P(\text{mm}) = \frac{-5388}{T} + 9.819; \ (619 - 685°K) \tag{13b}$$

$$UF_4 \text{ solid: } P(\text{Atm}) = \text{Exp}\left[\frac{-(75{,}100 - 90.3T + 13.8T \log_{10}T)}{RT}\right]; (298\text{-}1300°K) \tag{14a}$$

$$UF_4 \text{ liquid: } P(\text{Atm}) = \text{Exp}\left[\frac{-(70{,}100 - 115.2T + 23.0T \log_{10}T)}{RT}\right]; (1309\text{-}1710°K) \tag{14b}$$

$$U \text{ solid: } P(\text{Atm}) = \text{Exp}\left[\frac{-(117{,}000 - 71.8T + 12.0T \log_{10}T)}{RT}\right]; (298\text{-}1405°K) \tag{15a}$$

$$U \text{ liquid: } P(\text{Atm}) = \text{Exp}\left[\frac{-(110{,}200 - 47.2T + 5.75T \log_{10}T)}{RT}\right]; (1405\text{-}4200°K) \tag{15b}$$

Equations (13) are given in Reference 14 while equations (14) and (15) are taken from Reference 15.

RESULTS AND DISCUSSION

The equilibrium composition of the mixture resulting from uranium hexafluoride decomposition and the thermodynamic properties of this mixture were calculated for pressures of 0.01, 0.1, 1, and 10 atmospheres, over a temperature range from 600 to 4000°K. The gases were assumed to be ideal and the thermodynamic functions for UF_6, UF_5, and UF_4 were obtained using harmonic oscillator, rigid-rotor models.

The composition of the mixture is shown in Figures 1-4 and is listed in Tables 1-4. Figure 1 shows plots of the partial pressures of the six species considered versus temperature at a total pressure of 0.01 atmospheres. Note that uranium hexafluoride is stable up to 1600°K even at this low pressure. After the breakdown begins at 1600°K the partial pressure of UF_6 drops off rapidly. Uranium pentafluoride partial pressure peaks at 2000°K while UF_4 reaches a maximum at slightly less than 2400°K. These compounds also exhibit a rapid drop in partial pressure after reaching their peaks. Above 2800°K the decomposition is complete and the mixture is composed of only uranium and monatomic fluorine gases, with very slight traces of the other species.

The plots of the equilibrium partial pressures for the other total pressures considered have similar general characteristics. Figure 2 shows that the initial drop in the hexafluoride partial pressure begins at 1800°K when the total pressure is 0.1 atmospheres. Total breakdown to uranium and fluorine takes place at 3200°K with the pentafluoride and the tetrafluoride peaking at 2200°K and 2550°K respectively. At one atmosphere, as shown in Figure 3, the hexafluoride is stable up to 2000°K with the decomposition being completed at approximately 3600°K. At a total pressure of 10 atmospheres Figure 4 shows

decomposition starting at 2400°K and being completed at a temperature greater than 4000°K. Basically a pressure increase only shifts the decomposition to a higher temperature and slows the rate of decrease of the partial pressures of the uranium compounds.

Figure 5 shows the ratio of specific heats for pressures of 0.01 and 10 atmospheres as a function of temperature and compares the results of the theory with the measurements of Ref. 5. The behavior below 1600°K is that typical of pure UF_6. Above 1600°K, the behavior reflects the decomposition indicated in Figures 1 and 4. It is seen that the results of the theory are in good agreement with experiment.

The thermodynamic properties of the mixture are listed in Tables 5-8. The large negative values for the enthalpy and free energy are a result of the choice of the enthalpy reference, which is chosen so that the enthalpies of the elements in their naturally occurring state are zero at 298°K. Thus the enthalpy of the mixture as calculated by Equation 7 is a large negative number since UF_6, UF_5, and UF_4 have large negative heats of formation[13]. Table 5 lists the thermodynamic properties for a pressure of 0.01 atmosphere over the temperature range from 600°K to 4000°K, while 6, 7, 8 list the thermodynamic properties for pressures of 0.1, 1, and 10 atmospheres respectively, over the same temperature range. The properties of the mixture are given per gram of mixture, except of course in the case of γ which is dimensionless.

The thermodynamic functions of UF_6, UF_5, and UF_4 are listed in Tables 9-11. This data is a result of calculations performed as outlined in Appendices A, B, and C. These properties are given on a per mole basis.

Comparison of the partial pressures listed in Tables 1-4 with saturated vapor pressures of UF_5, UF_4 and U has confirmed the validity of a totally gaseous system. The saturated vapor pressures are given in Tables 12, 13 and 14 at selected temperatures. The partial pressures of all three species are well below the saturated vapor pressures over all ranges of temperature and pressures considered.

Finally the equilibrium constants for Reactions (ii), (iii), and (iv) are included in Table 16. These values were calculated from the free energy data given in Tables 9-12 and Ref. 11. The very small values of the equilibrium constants at low temperatures are indicative of the stability of uranium hexafluoride at temperatures less than 1500°K.

CONCLUSION

The model for the decomposition of uranium hexafluoride presented here, which allows for the presence UF_6, UF_5, UF_4, F, F_2, and U as possible constituents, shows that the compound is very stable up to 1500°K for pressures greater than 0.01 atmospheres. However in the temperature range between 1500°K and 4000°K UF_6 breaks down into a mixture of uranium and monatomic fluorine gases. Both uranium pentafluoride and uranium tetrafluoride gases become important in the 2000-3500°K range. Diatomic fluorine is of negligible importance over the entire temperature range considered. An increase in pressure increases the temperature at which the decomposition begins and slows the rate of decomposition.

Certainly the thermodynamic properties of the mixture are affected by the hexafluoride breakdown. The values of the thermodynamic properties vary widely as the composition shifts. Any work involving UF_6 above 1500°K should take decomposition into consideration.

APPENDIX A: THERMODYNAMICS PROPERTIES OF UF_6

The thermodynamic properties of ideal gases can be calculated from knowledge of their partition functions [16,17]. The partition function consist of translational, rotational, vibrational, and electronic components. Expressions for these components, and the derivation of the thermodynamic properties from them, are outlined below.

The translational partition function has the same form for all molecules. Designating the partition function by Z, the translational component Z_t can be expressed as

$$Z_t = \left(\frac{2\pi m}{h^2}\right)^{3/2} N \frac{(kT)^{5/2}}{P} \tag{A1}$$

where m is the mass of the particle, h is Planck's constant, k is Boltzmann's constant, N is Avogadro's number, P is the absolute pressure and T is the temperature[16]. The mass per particle for UF_6 is 5.84×10^{-22} grams.

The rotational partition function is dependent on the structure of the particular molecule involved. For a polyatomic molecule the rotational partition function is given by[16]

$$Z_R = \frac{8\pi^2}{\sigma h^3} (I_x I_y I_z)^{1/2} (2\pi kT)^{3/2} \tag{A2}$$

where σ, the rotational symmetry number, is 12 for octahedral molecules such as UF_6[1]. A molecule of this type is a spherical top and all three of its principle moments of inertia are equal. The moments of inertia are

$$I_x = I_y = I_z = 4.0\ m_F r^2$$

where m_F is the mass of the fluorine atom and r is the U-F bond distance, 1.99Å.[6] The expression given above assumes the molecule to be a rigid rotor.

The vibrational partition function also depends on the molecular structure. Assuming a harmonic oscillator model, one finds

$$Z_v = \prod_{i=1}^{n} \frac{1}{1 - \exp(- hc\nu_i/kT)} \tag{A3}$$

where n is the number of principle vibration frequencies, ν_i is the frequency in cm^{-1} units, and c is the speed of light.[16,17] Uranium hexafluoride has six principle frequencies, which are: $\nu_1 = 667.0\ cm^{-1}$, $\nu_2 = 535.0\ cm^{-1}$, $\nu_3 = 623.0\ cm^{-1}$, $\nu_4 = 181\ cm^{-1}$, $\nu_5 = 202.0\ cm^{-1}$, and $\nu_6 = 140.0\ cm^{-1}$.[1] For an octehedral molecule, ν_1 is non-degenerate, ν_2 is doubly degenerate and ν_3, ν_4, ν_5, and ν_6 are triply degenerate[17]. Thus n is fifteen in this case. In general for non-linear polyatomic molecules n = 3P-6 where P is the number of atoms in the molecule.

The electronic partition function used in this analysis assumes the molecule to be in its ground state. Thus

$$Z_e = g_{e_o} \quad . \tag{A4}$$

with g_{e_o} being unity in the case of the hexafluoride.

In summary the partition function is the product of the four functions or $Z = Z_T Z_R Z_v Z_e$. Having defined the partition function we can then derive the thermodynamic functions from it. The results of this derivation are given below.

For enthalpy[16,17]

$$H = RT + RT^2 \left[\frac{\partial(\ell nZ)}{\partial T}\right]_V + H_o ,$$

and substituting for Z

$$H - H_o = 4RT + \sum_{i=1}^{n} \frac{R\,\theta_i}{\exp(\theta_i/T)-1} , \quad \theta_i = \frac{hc\nu_i}{k} \tag{A5}$$

where H_o is the enthalpy at absolute zero. In order to establish 298°K as the reference temperature one employs the relation

$$H - H_{298} = (H - H_o) - (H_{298} - H_o).$$

The entropy is given by[16,17]

$$S = R + RT\left[\frac{\partial(\ell nZ)}{\partial T}\right]_V + R\,\ell n(Z/N)$$

or

$$S = (H - H_o)/T + R\,\ell n(Z/N) . \tag{A6}$$

The expression for the Gibbs free energy is[17]

$$F = H_o - RT\,\ell n(Z/N)$$

or

$$-(F - H_o)/T = R\,\ell n(Z/N) \tag{A7}$$

The specific heats may also be determined from

$$C_p = (\partial H/\partial T)_p = 4R + \sum_{i=1}^{n} \frac{R(\theta_i/T)^2 \exp(\theta_i/T)}{[\exp(\theta_i/T) - 1]^2} \tag{A8}$$

and

$$C_v = C_p - R . \tag{A9}$$

The results of the calculation of the thermodynamic properties of uranium hexafluoride using the procedure and equations outlined above are given in Table 9. These values along with the heat of formation were used to calculate the mixture properties. The heat of formation of UF_6 is given as - 505 kcal/mole in Reference 13.

APPENDIX B: THERMODYNAMIC PROPERTIES OF UF_5

The thermodynamic properties of uranium pentafluoride can be calculated using Equations A1-A9 provided the required structural and vibrational data can be obtained. For the translational partition function only the mass, m, is required. The pentafluoride molecular weight is 333 grams so that the mass per particle is 5.54×10^{-22} grams.

Spectroscopic data required for the determination of the rotational and vibrational functions is more difficult to obtain. Until recently no thermodynamic data was available for UF_5. However in Reference 7 a semi-empirical method is developed for the calculation of the thermodynamic properties. Many pentafluorides exist in trigonal bipyramid and tetragonal pyramid forms. The effect of this difference on the thermodynamic data as calculated using the partition function method is shown to be slight[7], so that calculations may be made assuming either of the two possible structures. In this analysis the molecule is assumed to be trigonal bipyramid. The eight normal vibrational frequencies and their degeneracies for UF_5 assuming this structure are[7]

$$\nu_1 = 677 \text{ cm}^{-1} \qquad g_1 = 1$$

$$\nu_2 = 684 \qquad g_2 = 1$$

$\nu_3 = 663$ $g_3 = 1$

$\nu_4 = 521$ $g_4 = 1$

$\nu_5 = 606$ $g_5 = 2$

$\nu_6 = 372$ $g_6 = 2$

$\nu_7 = 99$ $g_7 = 2$

and $\nu_8 = 178$ $g_8 = 2$.

The product of the principle inertias is given as 728×10^{-115} gm^3 cm with the bond distance being 1.994Å.[7] The rotational symmetry number for this type molecule is 6 while the ground electronic state is doubly degenerate[7].

With the above data the thermodynamic properties of UF_5 can be calculated using Equations A1-A9. The results are listed in Table 10. This data along with the heat of formation of UF_5 at 298°K, - 440 kcal/mole, was used to calculate the mixture properties[13].

APPENDIX C: THERMODYNAMIC PROPERTIES OF UF_4

In attempting to use Equations A1-A9 to calculate the thermodynamic properties of uranium tetrafluoride many of the same problems that caused difficulty in the pentafluoride case arose again. These problems are discussed in reference 8, and procedures similar to those used in the pentafluoride calculation are employed again.

The structure of the tetrafluoride molecule is not known but it is assumed to be a regular tetrahedron. The implication here is that the thermodynamic

functions are relatively insensitive to the particular structure chosen. The vibrational frequencies and degeneracies for the assumed tetrahedral structure are[7]

$$\nu_1 = 555 \text{ cm}^{-1} \qquad g_1 = 1$$

$$\nu_2 = 147 \qquad g_2 = 2$$

$$\nu_3 = 566 \qquad g_3 = 3$$

$$\nu_4 = 177 \qquad g_4 = 3$$

The moments of inertia are equal because a tetrahedral molecule is a spherical top. From Reference 8 one finds that $I_x = I_y = I_z = 366 \times 10^{-40}$ gm cm^2. The rotational symmetry number is 12 for molecules of this type. The molecular weight is 314 grams and this results in a particle mass of 5.21×10^{-22} grams. The electronic ground state degeneracy is assumed to be unity. The heat of formation of gaseous UF_4 at 298°K is given in Reference 13 as -366 kcal/mole. The results obtained using the above data and Equations A1-A9 are listed in Table 11.

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TABLE 1: PARTIAL PRESSURES OF CONSTITUENT SPECIES, TOTAL PRESSURE = 0.01 ATM.

Temp °K	P_6 Atm	P_5 Atm	P_4 Atm	P_2 Atm	P_1 Atm	P_3 Atm
800	1.00×10^{-2}	—	—	—	—	—
1200	9.98×10^{-3}	8.30×10^{-6}	2.31×10^{-10}	$2.42 \times .0^{-10}$	8.30×10^{-6}	—
1600	8.79×10^{-3}	$5.94 \times .0^{-4}$	3.90×10^{-6}	2.01×10^{-8}	6.01×10^{-4}	—
2000	1.78×10^{-3}	2.84×10^{-3}	8.44×10^{-4}	9.25×10^{-8}	4.53×10^{-3}	—
2400	9.17×10^{-6}	3.16×10^{-4}	3.11×10^{-3}	3.59×10^{-8}	6.55×10^{-3}	5.02×10^{-8}
2800	9.00×10^{-9}	2.80×10^{-6}	3.40×10^{-4}	1.75×10^{-8}	8.37×10^{-3}	1.28×10^{-3}
3200	1.04×10^{-14}	1.96×10^{-11}	1.82×10^{-8}	7.3×10^{-9}	8.57×10^{-3}	1.43×10^{-3}
3600	—	—	7.3×10^{-12}	3.6×10^{-9}	8.57×10^{-3}	1.43×10^{-3}
4000	—	—	—	—	8.57×10^{-3}	1.43×10^{-3}

TABLE 2: PARTIAL PRESSURES OF CONSTITUENT SPECIES, TOTAL PRESSURE = 0.1 ATM.

Temp °K	P_6 Atm	P_5 Atm	P_4 Atm	P_2 Atm	P_1 Atm	P_3 Atm
800	1.00×10^{-1}	—	—	—	—	—
1200	9.99×10^{-2}	2.65×10^{-5}	2.36×10^{-10}	2.37×10^{-9}	2.60×10^{-5}	—
1600	9.60×10^{-2}	1.97×10^{-3}	3.94×10^{-6}	2.18×10^{-7}	1.98×10^{-3}	—
2000	5.71×10^{-2}	1.93×10^{-2}	1.19×10^{-3}	2.12×10^{-6}	2.17×10^{-2}	—
2400	4.54×10^{-3}	1.78×10^{-2}	1.99×10^{-2}	2.78×10^{-6}	5.77×10^{-2}	5.35×10^{-11}
2800	5.24×10^{-5}	2.07×10^{-3}	3.19×10^{-2}	1.08×10^{-6}	6.60×10^{-2}	3.12×10^{-5}
3200	9.25×10^{-8}	1.77×10^{-5}	1.66×10^{-3}	7.15×10^{-7}	8.47×10^{-2}	1.36×10^{-2}
3600	2.06×10^{-12}	1.60×10^{-9}	7.3×10^{-7}	3.60×10^{-7}	8.57×10^{-2}	1.43×10^{-2}
4000	—	—	1.37×10^{-9}	2.02×10^{-7}	8.57×10^{-2}	1.43×10^{-2}

TABLE 3: PARTIAL PRESSURES OF CONSTITUENT SPECIES, TOTAL PRESSURE = 1.0 ATM.

Temp °K	P_6 Atm	P_5 Atm	P_4 Atm	P_2 Atm	P_1 Atm	P_3 Atm
800	1.0	—	—	—	—	—
1200	9.99×10^{-1}	8.61×10^{-5}	2.49×10^{-10}	2.25×10^{-8}	8.0×10^{-5}	—
1600	9.87×10^{-1}	6.33×10^{-3}	3.95×10^{-6}	2.24×10^{-6}	6.34×10^{-3}	—
2000	8.42×10^{-1}	7.69×10^{-2}	1.30×10^{-3}	2.85×10^{-5}	7.94×10^{-2}	—
2400	3.68×10^{-1}	0.246	4.68×10^{-2}	9.60×10^{-5}	3.40×10^{-1}	—
2800	3.14×10^{-2}	1.37×10^{-1}	2.32×10^{-1}	8.95×10^{-5}	5.99×10^{-1}	3.32×10^{-8}
3200	1.06×10^{-3}	2.60×10^{-2}	0.314	4.30×10^{-5}	0.658	7.07×10^{-4}
3600	1.39×10^{-5}	1.12×10^{-3}	5.29×10^{-2}	3.34×10^{-5}	0.826	0.120
4000	3.53×10^{-9}	8.42×10^{-7}	1.37×10^{-4}	2.02×10^{-5}	0.857	0.1428

TABLE 4: PARTIAL PRESSURES OF CONSTITUENT SPECIES, TOTAL PRESSURE = 10 ATM.

Temp °K	P_6 Atm	P_5 Atm	P_4 Atm	P_2 Atm	P_1 Atm	P_3 Atm
800	1.0×10^{1}	—	—	—	—	—
1200	9.999	—	—	—	—	—
1600	9.96	$2.02\times.0^{-2}$	3.98×10^{-6}	2.24×10^{-5}	2.01×10^{-2}	—
2000	9.47	0.261	1.33×10^{-3}	3.12×10^{-4}	0.263	—
2400	7.36	1.23	5.90×10^{-2}	1.52×10^{-3}	1.35	—
2800	3.32	2.36	0.655	3.34×10^{-3}	3.66	6.75×10^{-11}
3200	0.551	1.54	2.12	3.32×10^{-3}	5.78	8.03×10^{-7}
3600	4.80×10^{-2}	0.493	2.98	2.05×10^{-3}	6.47	1.80×10^{-3}
4000	4.03×10^{-3}	0.114	2.20	1.44×10^{-3}	7.23	0.453

TABLE 5: THERMODYNAMIC PROPERTIES OF MIXTURE, PRESSURE = 0.01 ATM.

Temp °K	Enthalpy h kcal/gm	Entropy s cal/gm/deg	Free Energy f kcal/gm	c_p cal/gm/°K	c_v cal/gm/°K	γ
600	- 1.410	0.349	- 1.620	0.1012	0.0955	1.059
800	- 1.385	0.379	- 1.688	0.1037	0.0981	1.057
1000	- 1.364	0.402	- 1.766	0.1050	0.0993	1.057
1200	- 1.343	0.421	- 1.849	0.1056	0.1000	1.056
1400	- 1.320	0.439	- 1.935	0.1060	0.1003	1.057
1600	- 1.286	0.462	- 2.025	0.1062	0.1002	1.060
1800	- 1.215	0.503	- 2.120	0.1058	0.0986	1.073
2000	- 1.060	0.584	- 2.228	0.1044	0.0941	1.110
2200	- 0.852	0.683	- 2.356	0.1026	0.0880	1.165
2400	- 0.747	0.730	- 2.498	0.1018	0.0854	1.192
2600	- 0.684	0.755	- 2.646	0.1017	0.0845	1.204
2800	0.319	1.123	- 2.825	0.1072	0.0725	1.479
3000	0.607	1.224	- 3.065	0.1090	0.0695	1.568
3200	0.630	1.232	- 3.310	0.1093	0.0697	1.567
3400	0.652	1.238	- 3.557	0.1096	0.0700	1.564
3600	0.674	1.244	- 3.806	0.1100	0.0704	1.561
3800	0.696	1.250	- 4.055	0.1104	0.0709	1.557
4000	0.718	1.256	- 4.306	0.1109	0.0714	1.553

TABLE 6: THERMODYNAMIC PROPERTIES OF MIXTURE, PRESSURE = 0.1 ATM.

Temp °K	Enthalpy h kcal/gm	Entropy s cal/gm/deg	Free Energy f kcal/gm	c_p cal/gm/°K	c_v cal/gm/°K	γ
600	- 1.406	0.3361	- 1.607	0.1012	0.0955	1.059
800	- 1.385	0.3656	- 1.678	0.1037	0.0981	1.058
1000	- 1.364	0.3889	- 1.753	0.1050	0.0993	1.057
1200	- 1.343	0.4082	- 1.833	0.1056	0.0999	1.057
1400	- 1.321	0.4250	- 1.916	0.1061	0.1004	1.056
1600	- 1.296	0.4418	- 2.003	0.1063	0.1005	1.057
1800	- 1.259	0.4633	- 2.093	0.1063	0.1002	1.061
2000	- 1.193	0.4981	- 2.189	0.1059	0.0987	1.073
2200	- 1.067	0.5580	- 2.294	0.1048	0.0951	1.102
2400	- 0.885	0.6372	- 2.414	0.1032	0.0898	1.149
2600	- 0.755	0.6893	- 2.547	0.1021	0.0863	1.183
2800	- 0.696	0.7112	- 2.687	0.1017	0.0851	1.195
3000	- 0.503	0.7768	- 2.833	0.1026	0.0828	1.238
3200	0.490	1.098	- 3.021	0.1084	0.0714	1.519
3400	0.650	1.146	- 3.248	0.1095	0.0701	1.563
3600	0.674	1.153	- 3.478	0.1100	0.0704	1.561
3800	0.696	1.159	- 3.709	0.1104	0.0709	1.558
4000	0.718	1.165	- 3.942	0.1109	0.0714	1.553

TABLE 7: THERMODYNAMIC PROPERTIES OF MIXTURE, PRESSURE = 1.0 ATM.

Temp °K	Enthalpy h kcal/gm	Entropy s cal/gm/°K	Free Energy f kcal/gm	c_p cal/gm/°K	c_v cal/gm/°K	γ
600	- 1.406	0.3231	- 1.599	0.1012	0.0955	1.059
800	- 1.385	0.3526	- 1.667	0.1037	0.0981	1.058
1000	- 1.364	0.3759	- 1.740	0.1050	0.0993	1.057
1200	- 1.343	0.3951	- 1.817	0.1056	0.1000	1.057
1400	- 1.322	0.4116	- 1.898	0.1061	0.1004	1.056
1600	- 1.299	0.4266	- 1.982	0.1063	0.1006	1.057
1800	- 1.273	0.4420	- 2.069	0.1065	0.1007	1.058
2000	- 1.238	0.4605	- 2.159	0.1064	0.1003	1.061
2200	- 1.184	0.4862	- 2.253	0.1061	0.0992	1.070
2400	- 1.094	0.5251	- 2.354	0.1054	0.0969	1.088
2600	- 0.956	0.5801	- 2.465	0.1042	0.0929	1.121
2800	- 0.809	0.6349	- 2.586	0.1029	0.0887	1.159
3000	- 0.713	0.6681	- 2.717	0.1021	0.0863	1.183
3200	- 0.659	0.6856	- 2.853	0.1018	0.0853	1.194
3400	- 0.507	0.7309	- 2.993	0.1024	0.0835	1.226
3600	0.277	0.9542	- 3.159	0.1074	0.0749	1.433
3800	0.672	1.062	- 3.364	0.1102	0.0711	1.550
4000	0.717	1.074	- 3.578	0.1109	0.0714	1.553

TABLE 8: THERMODYNAMIC PROPERTIES OF MIXTURE, PRESSURE = 10.0 ATM.

Temp °K	Enthalpy h kcal/gm	Entropy s cal/gm/°K	Free Energy f kcal/gm	c_p cal/gm/°K	c_v cal/gm/°K	γ
600	- 1.406	0.3101	- 1.592	0.1012	0.0955	1.059
800	- 1.385	0.3396	- 1.657	0.1037	0.0981	1.058
1000	- 1.364	0.3629	- 1.727	0.1050	0.0993	1.057
1200	- 1.343	0.3821	- 1.802	0.1057	0.1000	1.057
1400	- 1.322	0.3985	- 1.880	0.1061	0.1004	1.056
1600	- 1.300	0.4130	- 1.961	0.1063	0.1007	1.056
1800	- 1.278	0.4264	- 2.045	0.1065	0.1008	1.057
2000	- 1.252	0.4399	- 2.132	0.1066	0.1008	1.058
2200	- 1.221	0.4548	- 2.221	0.1066	0.1005	1.060
2400	- 1.179	0.4728	- 2.314	0.1064	0.0999	1.065
2600	- 1.120	0.4962	- 2.411	0.1060	0.0986	1.075
2800	- 1.036	0.5257	- 2.513	0.1054	0.0964	1.092
3000	- 0.921	0.5669	- 2.622	0.1043	0.0933	1.119
3200	- 0.799	0.6063	- 2.739	0.1033	0.0899	1.149
3400	- 0.704	0.6353	- 2.864	0.1025	0.0874	1.173
3600	- 0.642	0.6531	- 2.992	0.1020	0.0860	1.186
3800	- 0.584	0.6686	- 3.125	0.1019	0.0852	1.200
4000	- 0.361	0.7254	- 3.263	0.1032	0.0829	1.246

TABLE 9: THERMODYNAMIC PROPERTIES OF URANIUM HEXAFLUORIDE

Temp °K	$H-H_{298}$ kcal/mole	$\frac{-(F-H_{298})}{T}$ cal/mole/°K	S cal/mole/°K	C_p cal/mole/°K	C_v cal/mole/°K
600	10.24	86.05	113.75	35.62	33.63
800	17.46	94.33	124.10	36.51	34.52
1000	24.81	101.14	132.32	36.94	34.95
1200	32.22	106.91	139.10	37.18	35.19
1400	39.67	111.93	144.81	37.33	35.35
1600	47.14	116.40	149.80	37.43	35.44
1800	54.63	120.33	154.22	37.50	35.51
2000	62.14	123.92	158.20	37.55	35.54
2200	69.65	127.20	161.76	37.58	35.60
2400	77.16	130.22	165.03	37.61	35.62
2600	84.69	133.02	168.04	37.63	35.64
2800	92.21	135.62	170.83	37.65	35.66
3000	99.74	138.06	173.43	37.66	35.67
3200	107.27	140.34	175.86	37.67	35.68
3400	114.81	142.50	178.14	37.68	35.69
3600	122.34	144.54	180.30	37.69	35.70
3800	129.88	146.48	182.34	37.70	35.71
4000	137.41	148.32	184.27	37.70	35.72

TABLE 10: THERMODYNAMIC PROPERTIES OF URANIUM PENTAFLUORIDE

Temp °K	$H-H_{298}$ kcal/mole	$\frac{-(F-H_{298})}{T}$ cal/mole/°K	S cal/mole/°K	C_p cal/mole/°K	C_v cal/mole/°K
600	8.33	82.32	104.57	29.45	27.46
800	14.33	89.00	113.20	30.41	28.43
1000	20.47	94.55	120.04	30.89	28.91
1200	26.67	99.29	125.70	31.16	29.17
1400	32.92	103.41	130.51	31.33	29.34
1600	39.19	107.07	134.70	31.43	29.45
1800	45.50	110.35	138.41	31.51	29.52
2000	51.79	113.33	141.73	31.56	29.58
2200	58.11	116.05	144.74	31.60	29.62
2400	64.43	118.56	147.50	31.63	29.65
2600	70.76	120.88	150.05	31.66	29.67
2800	77.09	123.05	152.37	31.68	29.69
3000	83.42	125.08	154.57	31.69	29.70
3200	89.76	126.98	156.60	31.70	29.72
3400	96.10	128.78	158.53	31.71	29.73
3600	102.44	130.49	160.34	31.72	29.74
3800	108.79	132.11	162.05	31.73	29.74
4000	115.13	133.64	163.68	31.74	29.75

TABLE 11: THERMODYNAMIC PROPERTIES OF URANIUM TETRAFLUORIDE

Temp °K	$H-H_{298}$ kcal/mole	$\frac{-(F-H_{298})}{T}$ cal/mole/°K	S cal/mole/°K	C_p cal/mole/°K	C_v cal/mole/°K
600	7.12	76.76	96.56	24.60	22.61
800	12.09	82.65	103.72	25.11	23.13
1000	17.14	87.45	109.35	25.37	23.38
1200	22.23	91.50	113.99	25.51	23.52
1400	27.34	95.00	117.93	25.59	23.60
1600	32.46	98.08	121.35	25.65	23.66
1800	37.59	100.84	124.37	25.69	23.70
2000	42.73	103.33	127.08	25.71	23.73
2200	47.88	105.60	129.53	25.73	23.75
2400	53.02	107.69	131.77	25.75	23.76
2600	58.17	109.63	133.83	25.76	23.78
2800	63.33	111.42	135.74	25.77	23.79
3000	68.48	113.11	137.52	25.78	23.79
3200	73.63	114.68	139.18	25.79	23.80
3400	78.79	116.17	140.75	25.79	23.80
3600	83.95	117.58	142.22	25.80	23.81
3800	89.11	118.91	143.62	25.80	23.81
4000	94.27	120.18	144.94	25.80	23.82

TABLE 12: SATURATED VAPOR PRESSURE OF URANIUM PENTAFLUORIDE

Temperature °K	Vapor Pressure Atm.
600	0.006
700	0.174*

*Extrapolation

TABLE 13: SATURATED VAPOR PRESSURE OF URANIUM TETRAFLUORIDE

Temperature °K	Vapor Pressure Atm.
600	1.0×10^{-16}
800	2.9×10^{-10}
1000	1.88×10^{-6}
1200	5.90×10^{-4}
1400	2.63×10^{-2}
1600	3.13×10^{-1}

TABLE 14: SATURATED VAPOR PRESSURE OF URANIUM

Temperature °K	Vapor Pressure Atm.
600	6.15×10^{-35}
800	1.30×10^{-24}
1000	1.79×10^{-18}
1200	2.03×10^{-14}
1400	1.50×10^{-11}
1600	1.72×10^{-9}
1800	6.99×10^{-8}
2000	1.33×10^{-6}
2200	1.47×10^{-5}
2400	1.07×10^{-4}
2600	5.77×10^{-4}
2800	2.41×10^{-3}
3000	8.27×10^{-3}
3200	2.42×10^{-2}
3400	6.22×10^{-2}
3600	1.43×10^{-1}
3800	3.01×10^{-1}
4000	5.86×10^{-1}

TABLE 15: EQUILIBRIUM CONSTANTS

Temperature °K	$\text{Log}_{10} K_{P_2}$ (T)	$\text{Log}_{10} K_{P_3}$ (T)	$\text{Log}_{10} K_{P_4}$ (T)
800	- 33.86	- 18.12	——
1200	- 17.80	- 9.64	- 53.93
1600	- 9.79	- 5.40	- 33.75
2000	- 5.01	- 2.87	- 21.63
2400	- 1.84	- 1.19	- 13.53
2800	0.423	0.007	- 7.73
3200	2.11	0.900	- 3.37
3600	3.42	1.593	0.023
4000	4.45	2.14	2.75

K_{P_2} (T) is for the reaction

$$UF_6 \rightleftarrows UF_4 + 2F,$$

K_{P_3} (T) is for the reaction

$$UF_5 \rightleftarrows UF_4 + F,$$

and K_{P_4} (T) is for the reaction

$$UF_4 \rightleftarrows U + 4F.$$

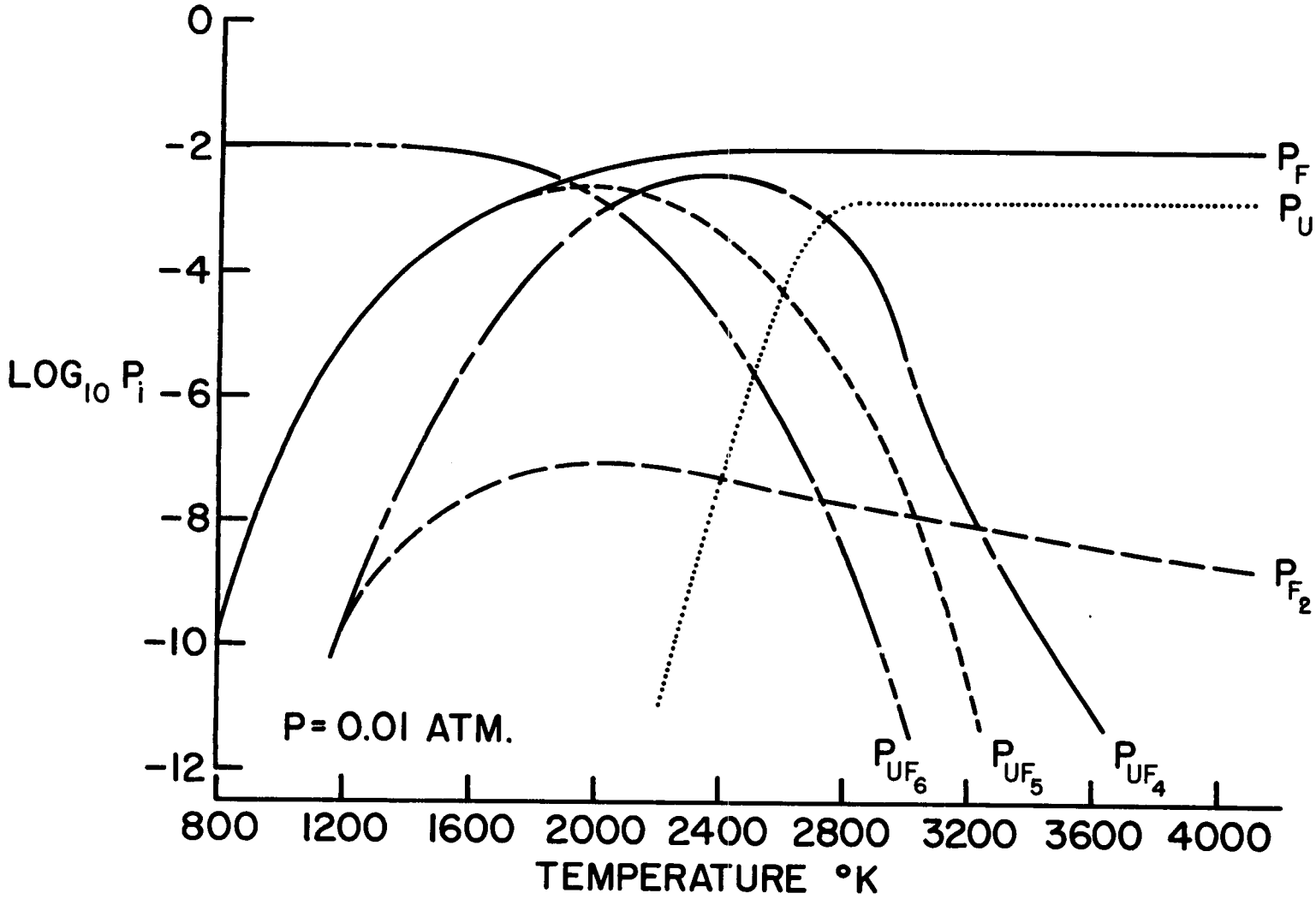

Figure 1. Partial pressures of constituent species versus temperature at 0.01 Atm.

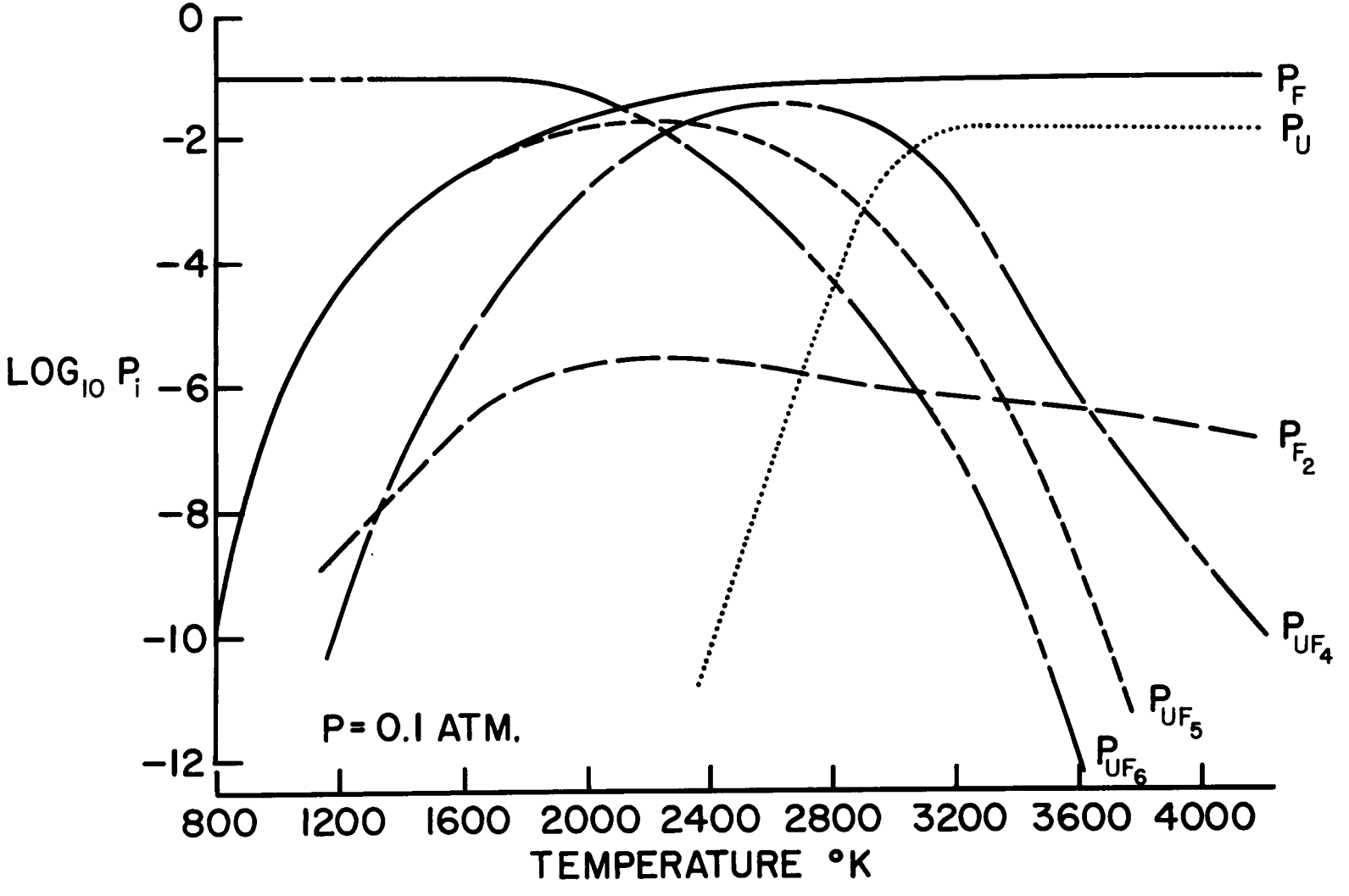

Figure 2. Partial pressures of constituent species versus temperature at 0.1 Atm.

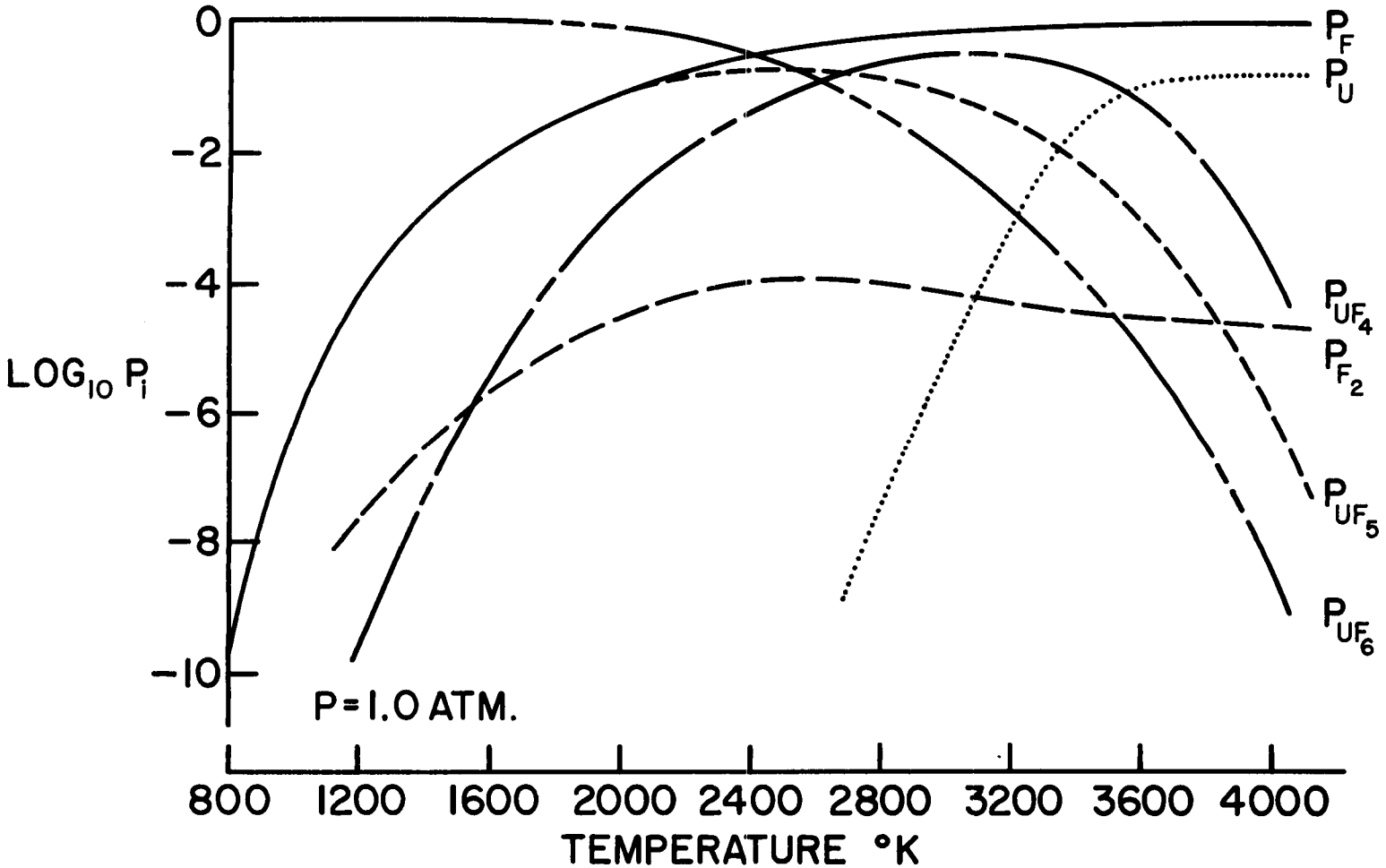

Figure 3. Partial pressures of constituent species versus temperature at 1.0 Atm.

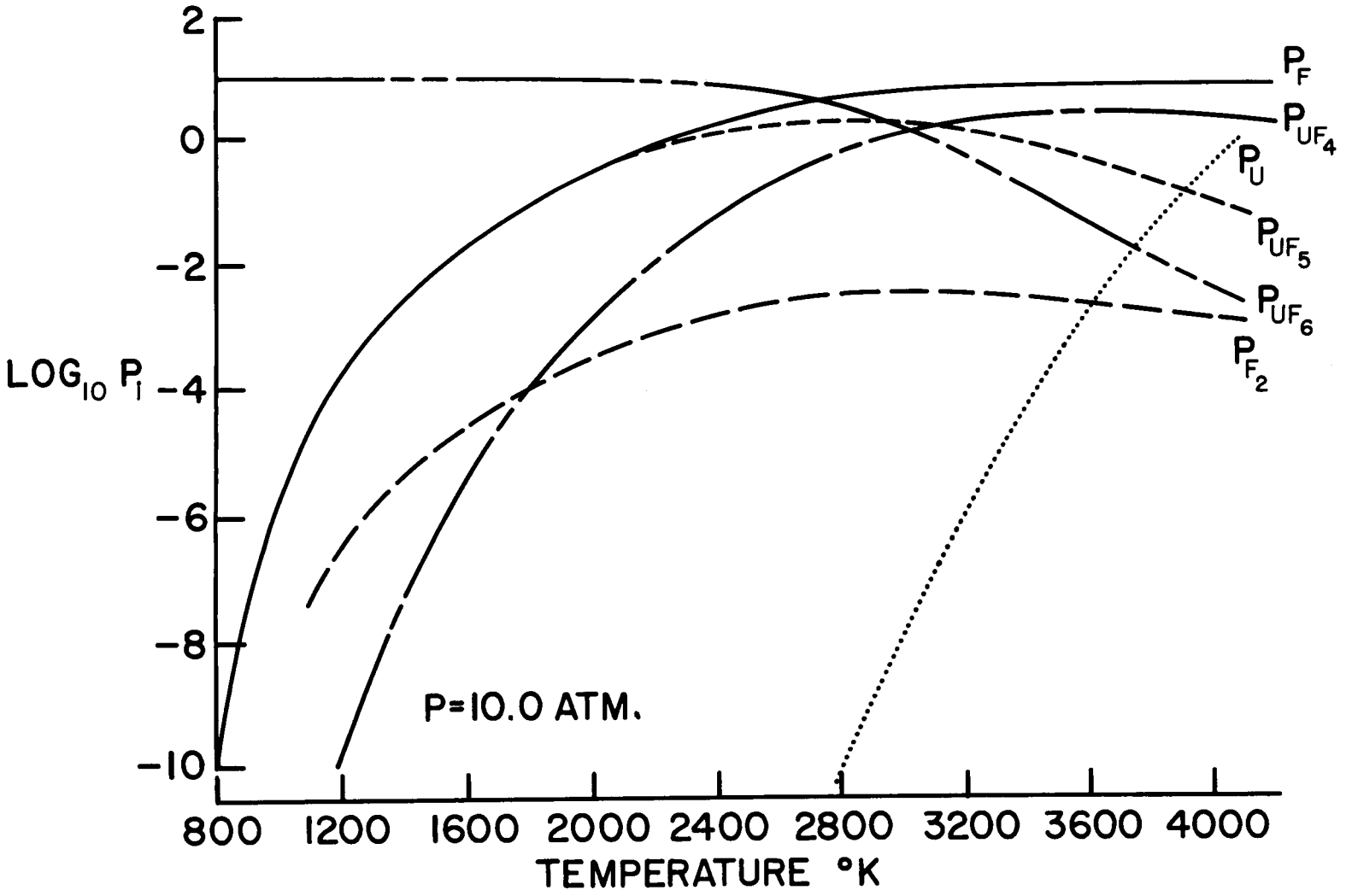

Figure 4. Partial pressures of constituent species versus temperature at 10.0 Atm.

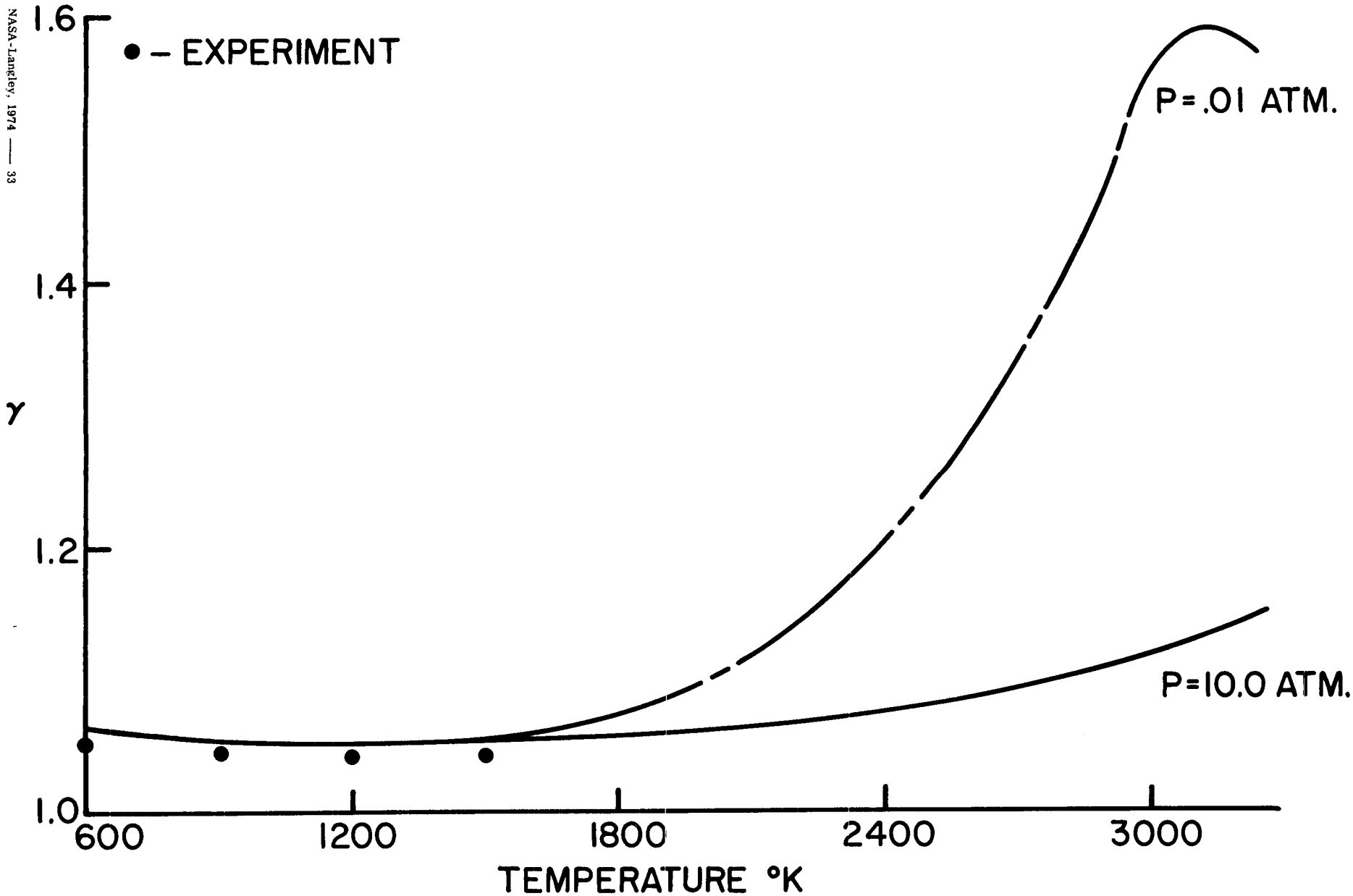

Figure 5. Ratio of specific heats as a function of pressure and temperature

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