Although there are no available experimental data, the over-all relative insensitivity of the calculated functions in terms of the deviation in the chosen frequency and isomerization energy values (Table VII) suggests that the error should not exceed ±2.5% in any of the computed thermodynamic properties.

## NOMENCLATURE

$a, b, c$ = constants
$C_p^\circ$ = heat capacity
$\Delta E_{iso}$ = isomerization energy
$-(F^\circ - H_0^\circ)/T$ = free energy function
$(H^\circ - H_0^\circ)/T$ = enthalpy function, where $H_0^\circ$ is $H^\circ$ at 0° K.
$I_{ABC}$ = moment of inertia product
$M$ = molecular weight
$S^\circ$ = entropy
$T$ = absolute temperature, ° K.
$\nu$ = wave number, cm.$^{-1}$
$\sigma$ = molecular shape factor
$\Lambda$ = any one of thermodynamic properties, $C_p^\circ$, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)/T$, $S^\circ$, at temperature $T$

### Superscript

° = ideal state (reference state)

### Subscript

$p$ = pressure

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# Freezing Point Depression in Fluorine Systems

W. D. ENGLISH, W. A. CANNON, and W. E. CRANE
Astropower Laboratory, McDonnell Douglas
Astronautics Co., Western Division, Newport Beach, Calif. 92660

**The eutectic composition in the system fluorine–oxygen difluoride was determined to be 0.59 ± 0.02 mole fraction fluorine; the eutectic temperature is 43° ± 0.5° K.**

IN SOME test programs using liquid fluorine and liquid hydrogen, it was desirable to lower the freezing point of fluorine without appreciably affecting its chemical reactivity. The use of a eutectic seemed the method of choice, and oxygen difluoride, $OF_2$, was selected as the other component. Oxygen was also suggested, but was not used because of reports of its quenching effect on the fluorine-hydrogen reaction (*2, 7, 8*), an effect also found in research on the ignition of $F_2(l)$–$H_2(l)$ (*3*) and reported in the $OF_2$–$H_2$ reaction (*11*).

Theoretical calculations of the freezing point depression in the $F_2$–$OF_2$ system suggested that experimental investigation was warranted.

## THEORETICAL

The equilibrium or phase diagram of a two-component solid-liquid system may assume several general forms according to the nature of the components (*4*); these forms may be classified as eutectic systems, completely miscible solid solutions, or partially miscible solid solutions. If nonpolar compounds are to form solid solutions, they must be of analogous chemical constitution, similar crystal structure, and nearly equal molecular volume. While little is known of the crystal structures of $F_2$ and $OF_2$, the first and last conditions above are not satisfied, and solid solutions probably will not form. Furthermore, there is no known tendency toward compound formation between

$OF_2$ and $F_2$. Thus either a simple eutectic or monotectic system is probable, and the latter is rarely encountered.

If the system is assumed to be a simple eutectic, with the solution of each component in the other obeying Raoult's law and the liquidus curves conforming to equations for ideal solutions, the following considerations apply.

From the Clausius-Clapeyron equation it can be shown that for equilibrium between solid and vapor, at constant pressure,

$$\frac{d\ln P_s}{dT} = \frac{L_s}{RT^2} \tag{1}$$

For an equilibrium between liquid and vapor, the corresponding equation is

$$\frac{d\ln P_L}{dT} = \frac{L_e}{RT^2} \tag{2}$$

If it is assumed that Equation 2 holds for supercooled solution in contact with solid, then

$$\frac{d\ln(P_s/P_L)}{dT} = \frac{L_s - L_e}{RT^2} = \frac{L_f}{RT^2} \tag{3}$$

At the freezing point of a solution, the vapor pressure of the solid solvent must equal the partial pressure, $P_1$, of the solvent in solution; hence

$$\frac{d\ln(P_1/P_L)}{dT} = \frac{L_f}{RT^2} \tag{4}$$

The mole fraction of solvent in solution, $X_1$, is equal to $P_1/P_L$, where $P_L$ is equal to the vapor pressure of the pure solvent. Therefore

$$\frac{d\ln X_1}{dT} = \frac{L_f}{RT^2} \tag{5}$$

If Equation 5 is integrated between $T$ and $T_o$ (where $X_1 = 1$),

$$\ln X_1 = -\frac{L_f}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \tag{6}$$

where $T$ is the freezing point of the solution at solvent concentration $X_1$. This assumes that $L_f$ is independent of temperature, which is not strictly true, but this approximation was used, since the normal variation of $L_f$ with temperature would increase the freezing point depression in contrast to the real nonideality of the solutions, which tends to decrease the depression.

Equation 6 is derived without any assumption concerning which component is the solid phase and is therefore applicable to both components of the liquid mixture. Accordingly, the freezing point, $T$, was calculated for various concentrations of $F_2$ in $OF_2$ and $OF_2$ in $F_2$. Solid fluorine is reported to undergo a transition at 45.55° K. with a heat of transition of 173.9 cal. per mole (*6*). Inasmuch as the solid fluorine can exist in two forms above the predicted eutectic temperature, the theoretical phase diagram was calculated using a value of 122 cal. per mole as the heat of fusion of fluorine (*6*) until the transition temperature was reached, after which the liquidus curve was assumed to undergo a change of slope corresponding to the heat of fusion plus the heat of transition. No value for the heat of fusion of $OF_2$ could be found in the literature, so it was estimated that the entropy of fusion was 6.5, which implies a heat of fusion of 320 cal. per mole. This value was used for the calculations involved in constructing the phase diagram. The $F_2$- and $OF_2$-rich liquidus curves meet at a theoretical minimum freezing point of 40° K. at 0.54 mole fraction $F_2$.

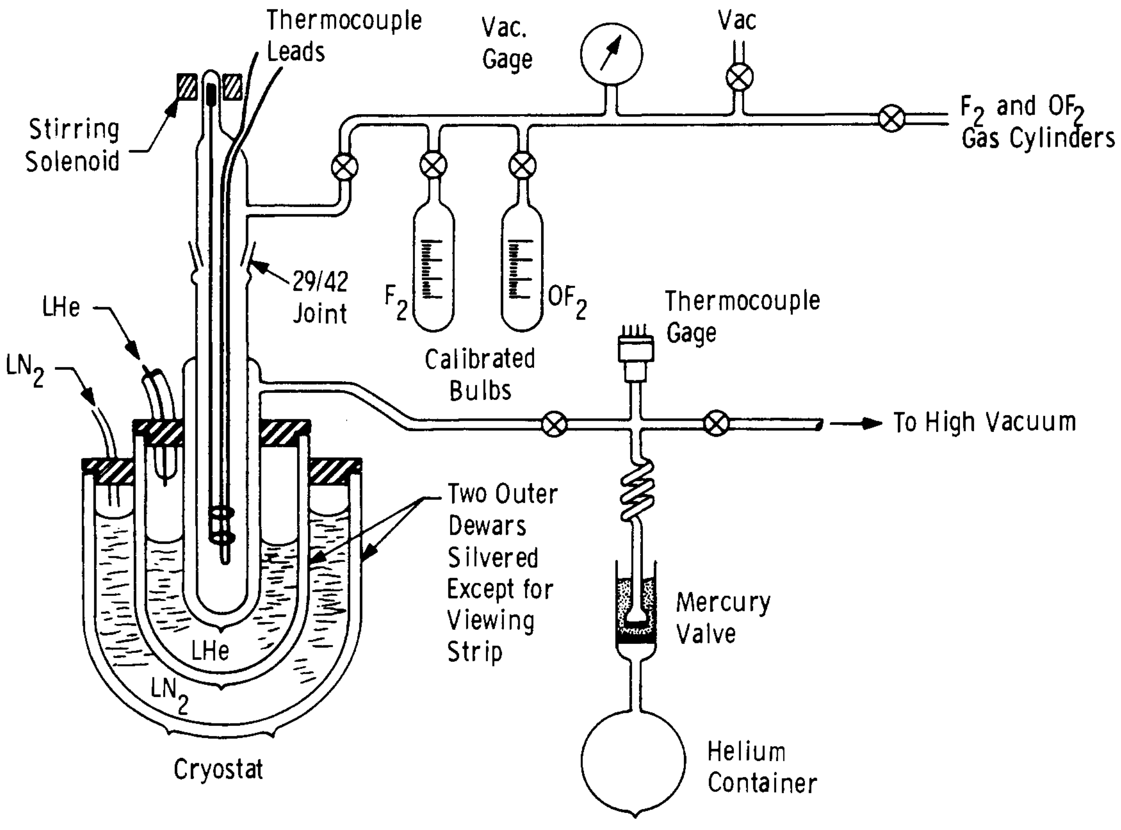

Figure 1. Freezing point apparatus

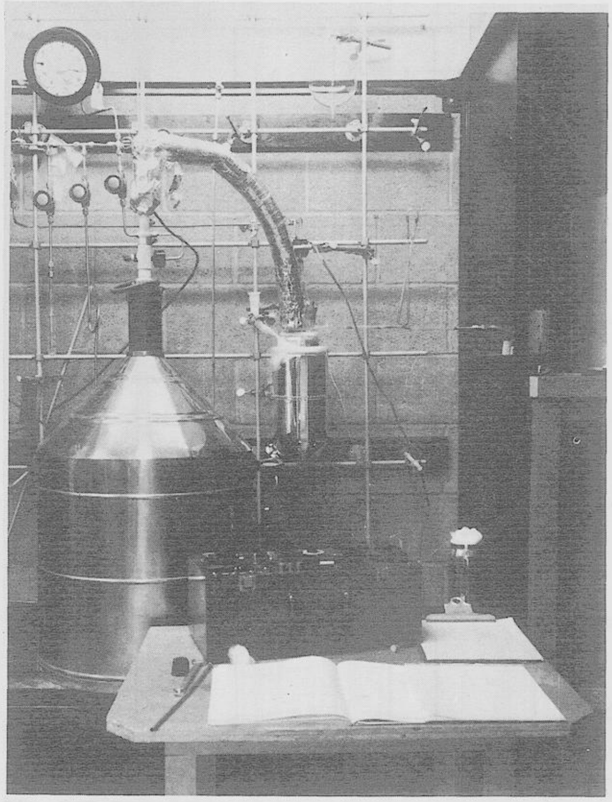

Figure 2. Freezing point apparatus

## APPARATUS

A borosilicate glass apparatus was designed and built for this experiment (Figures 1 and 2); in the annulus the pressure can be controlled to control heat transfer rates.

Liquid helium was supplied to the cooling bath from 25-liter transport Dewars connected to the apparatus by insulated lines. Liquid nitrogen was poured into the heat shield when needed.

Temperatures were measured with a copper-constantan thermocouple inserted in the thermowell with an external reference junction at liquid nitrogen temperature. Thermoelectric potentials were measured with a Grey Type E-3067 potentiometer and temperatures estimated from the tables and data of Powell, Bunch, and Corruccini (*9*). The thermocouple calibration was checked against boiling liquid nitrogen and hydrogen as fixed points. At 50° K., the thermoelectric e.m.f. for copper-constantan is about 12.1 $\mu$v. per degree. With a sensitivity of 5 $\mu$v. or better for the potentiometer, the sensitivity of the temperature reading is about 0.4°.

## MATERIALS

The oxidizers tested were obtained in the gaseous state from commercial suppliers. Fluorine supplied by Air Products and Chemicals was passed over sodium fluoride to reduce the HF content to 0.02 volume % or lower. Oxygen difluoride supplied by the Allied Chemical Division of the General Chemical Co. was also treated with sodium fluoride to remove HF.

## PROCEDURE

The quantities of fluorine and oxygen difluoride were measured by volume in the liquid state; weights were cal-

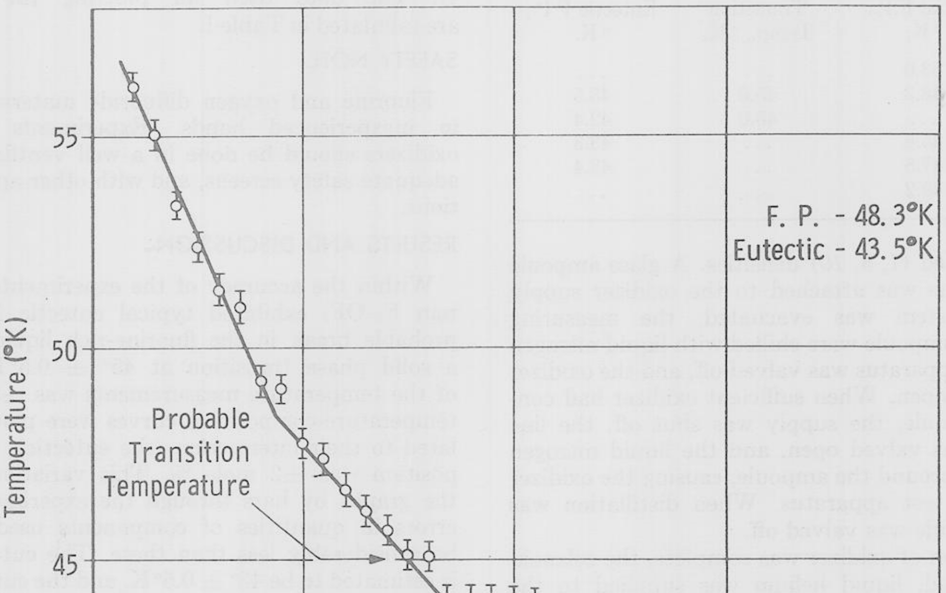

Figure 3. Cooling curve, 80 mole % $F_2$, 20 mole % $OF_2$

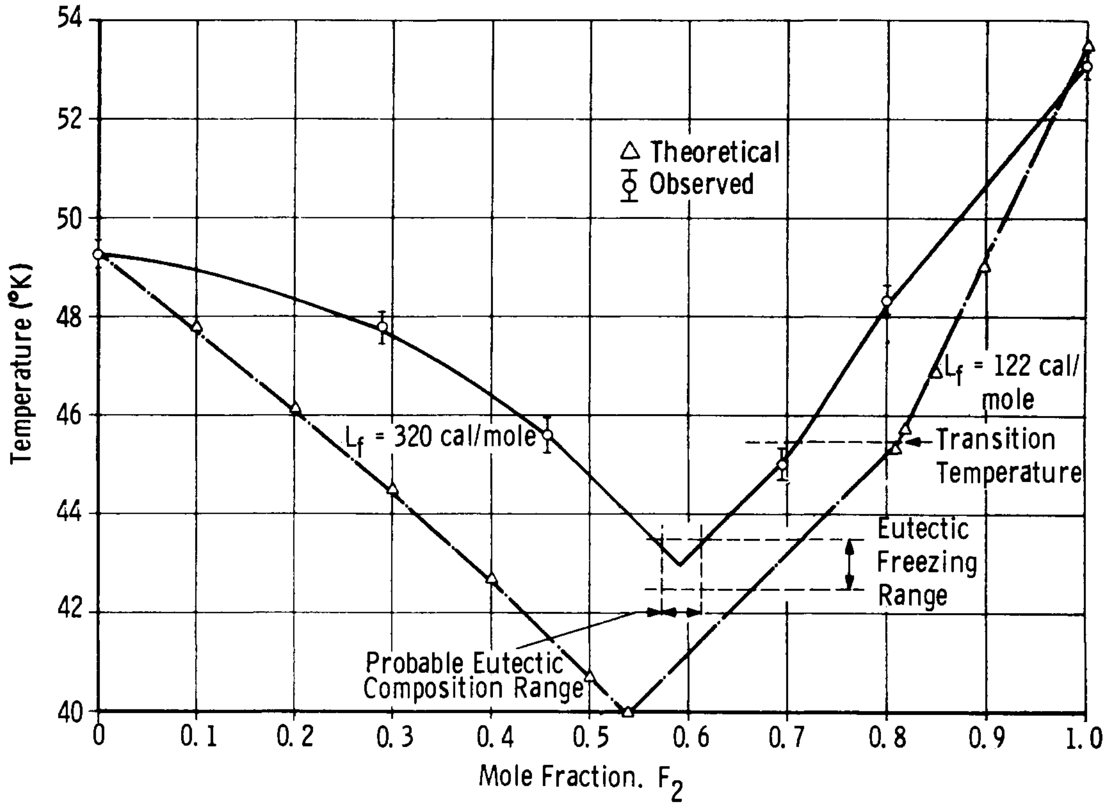

Figure 4. Phase diagram, $OF_2$–$F_2$

Table I. Observed Freezing Points of $OF_2$–$F_2$ Mixtures

| $F_2$, Mole % | Initial F.P., °K. | Transition Temp., °K. | Eutectic F.P., °K. |
|---|---|---|---|
| 100.0 | 53.0 | . . . | . . . |
| 80.0 | 48.3 | 45.0 | 43.5 |
| 69.5 | . . . | 45.0 | 42.4 |
| 46.0 | 45.6 | . . . | 43.3 |
| 28.0 | 47.8 | . . . | 43.4 |
| 0.0 | 49.2 | . . . | . . . |

culated from reported (*1, 5, 10*) densities. A glass ampoule of calibrated volume was attached to the oxidizer supply manifold. The system was evacuated, the measuring apparatus and the ampoule were chilled with liquid nitrogen to 77° K., the test apparatus was valved off, and the oxidizer supply was valved open. When sufficient oxidizer had condensed in the ampoule, the supply was shut off, the line to the test unit was valved open, and the liquid nitrogen was removed from around the ampoule, causing the oxidizer to distill into the test apparatus. When distillation was complete, the ampoule was valved off.

After condensation of oxidizer was complete, the solenoid stirrer was activated, liquid helium was supplied to the cooling bath, and the pressure in the heat-transfer annulus adjusted to attain a cooling rate of about 1° K. per minute. The e.m.f. of the thermocouple was continuously monitored and the value recorded at 30-second intervals. The appearance of the oxidizer was observed visually during the experiment.

The experiments were conducted with $F_2$, $OF_2$, and several mixtures of $F_2$ and $OF_2$. The recorded thermocouple potentials were converted to temperatures from which cooling curve graphs (temperature *vs.* time) were plotted for each solution concentration. Figure 3 is a typical example. Temperatures at which breaks in the curves occurred were identified, and plotted on a temperature *vs.* concentration graph to provide a typical phase diagram (Figure 4). The data used for plotting the phase diagram are tabulated in Table I.

## SAFETY NOTE

Fluorine and oxygen difluoride materials are dangerous in inexperienced hands. Experiments involving these oxidizers should be done in a well ventilated area, behind adequate safety screens, and with other appropriate precautions.

## RESULTS AND DISCUSSION

Within the accuracy of the experiments, the binary system $F_2$–$OF_2$ exhibited typical eutectic formation with a probable break in the fluorine-rich liquidus curve due to a solid phase transition at 45° ± 0.5° K. The accuracy of the temperature measurements was ±0.5° K. When the temperature-composition curves were plotted and extrapolated to their intersection (the eutectic), the error in composition was ±2 mole %. This variation is indicated on the graphs by bars through the experimental points. The errors in quantities of components used are believed to be considerably less than these. The eutectic temperature is estimated to be 43° ± 0.5° K. and the eutectic composition 0.59 ± 0.02 mole fraction fluorine.

## NOMENCLATURE

$P$ = vapor pressure, atmosphere
$L$ = latent heat, calories per mole
$R$ = gas constant, liter atmosphere per degree mole
$T$ = temperature, ° K.
$X$ = mole fraction

**Subscripts**

$s$ = solid state or solid-gas transition

$L$ = liquid state
$e$ = evaporation
$f$ = fusion
1 = solution
$o$ = freezing point of pure solvent

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# Reaction Rate of Hydrogen with Diamond Powder

WAYNE S. STANKO and JOHN C. ANGUS
Chemical Engineering Science Division, Case Western
Reserve University, Cleveland, Ohio 44106

**The rate of reaction of hydrogen with 0- to 1-micron nominal size natural diamond powder was studied over the temperature range 1272° to 1372° K., and the pressure range 51 to 68 atm. The data were fitted to an Arrhenius equation to give $r = 2.01 \times 10^7 \exp[-115{,}800/RT]P^{2.343}$ grams per square meter-second. The high activation energy indicates that the reaction is not diffusion-controlled.**

NATURAL diamond powder with 0- to 1-micron nominal size range as specified by the supplier was used in a study of the rate of reaction with hydrogen. The surface area determined by the standard BET method, using nitrogen as adsorbate, was 12.58 sq. meters per gram. Before any runs were made, the diamond was cleaned in hydrochloric acid to remove iron impurities, then subjected to a hydrogen precleaning at 1273° K. and 51 atm. to remove any oxides or graphite.

The hydrogen had a minimum purity of 99.95% as specified by the manufacturer. The oxygen content was less than 20 p.p.m.

## APPARATUS

The most essential part of the reaction system is a high pressure, high temperature reactor through which hydrogen was continually passed over the diamond crystals. The reactor is a 36- × 2-inch, 0.5-inch i.d. Hastelloy X tube, placed within a tubular electrical resistance furnace. The reactor may be operated as high as 1373° K. and 247 atm. Because of the dangers inherent in operating with hydrogen at these conditions, the entire system was enclosed within a cement block wall. The diamond sample was placed in a quartz sample holder which, in turn, was placed within the Hastelloy X tube (Figure 1).

The remainder of the system permits accurate control and measurement of the very low hydrogen flow rates (0.5 cc. per minute at reactor conditions) through the reactor, required because of the danger of entraining the diamond particles. The flow was measured by a Hastings-Raydist mass flowmeter.

A Chromel-Alumel thermocouple was used to measure the temperature. The temperature was controlled by a Wheelco on-off controller with time proportioning. The pressure was measured by a mechanical gage.

## PROCEDURE

At the start of a run, the sealed reactor was evacuated to a pressure of 10 microns of mercury and then brought to operating temperature and pressure over 2.5 hours. Once the operating temperature was reached, the flow rate was adjusted and the system held at the operating conditions. At the end of the reaction period, the furnace was turned off and the system vented to atmospheric pressure.

The reaction rates were determined by measuring the mass change of the sample. The sample holder containing the diamonds was placed within a quartz tube which was evacuated and then filled with dry air. The diamonds, sample holder, and quartz tube were then weighed. This procedure eliminated errors caused by adsorption of water vapor on the crystals. Precision was ±0.1 mg.

## RESULTS

The reaction was studied over a temperature range of 1272° to 1372° K. and a pressure range of 51 to 68 atm. (Table I). Most of the uncertainty arises from the limits to which the sample can be weighed. Some uncertainty enters during the startup and shutdown periods; but since the dependency of reaction rate on pressure and temperature is so great, this inaccuracy is believed to be negligible.

This belief was substantiated by observing the rate of