# The F-Hg System (Fluorine-Mercury)

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## Equilibrium Diagram

No phase diagram for the F-Hg system is available. Only the melting points of its constituents are known. The F-Hg phase relationships are likely to be similar to those of the Cl-Hg [1994Gum] and Br-Hg [2000Gum] systems. By analogy, $HgF_2$ should melt congruently and $Hg_2F_2$ should form in a syntectic reaction. A eutectic between $HgF_2$ and $Hg_2F_2$ is expected, and a limited miscibility between liquid Hg and $Hg_2F_2$ is anticipated. A report by [1990Voy] of high solubility of Hg in the molten $HgF_2$ is questionable; rather, it is more likely that the apparent solubility represents a chemical reaction between Hg and $HgF_2$ with the formation of $Hg_2F_2$.

Elemental fluorine was not assessed within the Alloy Phase Diagram Program. An evaluation will therefore be presented here. Fluorine, as well as nitrogen, oxygen, chlorine, and bromine, exists in dimeric form in solid, liquid, and gaseous states. The dissociation enthalpy of $F_2$ is 153.4 kJ/mol, and the dissociation constant, $K_p = p_F{}^2/p_{F_2}$, increases with temperature, being only $2 \times 10^{-16}$ Pa at 25 °C, $2 \times 10^3$ Pa at 727 °C, and as much as $3 \times 10^7$ Pa at 1727 °C [1973Ber]. Solid $F_2$ exists in two allotropic modifications $\alpha$ and $\beta$. The existence of an $\alpha F_2 <-> \beta F_2$ transformation was missed in an early investigation by [1937Kan], who performed heat capacity measurements, but a later investigation, also by heat capacity measurements, by [1953Hu] found a transformation at 45.55 K. Correction to the International Temperature Scale of 1990 (ITS-90) changes this numerical value to 45.54 K.

The following values of the melting point of $F_2$ at normal pressure were reported as 55.2 [1937Kan] and 53.54 ± 0.02 K [1953Hu], both from heat capacity measurements, with 53.49 ± 0.01 K [1970Str2] from vapor pressure measurements during the freezing of liquid $F_2$. The latter value referred to the ITS-90 and is selected at normal pressure of 0.101325 MPa due to its high precision and 99.99% purity of the $F_2$. According to [1970Str2], the $F_2$ triple point is fixed as 53.477 ± 0.002 K (ITS-90) and 0.252 ± 0.005 kPa. The boiling behavior of $F_2$ as a function of pressure was investigated by [1930Cad], [1934Cla], [1937Kan], [1953Hu], [1970Pry], and [1970Str1]. These authors found the following values of the boiling point at normal pressure of 0.101325 MPa.: 84.93 ± 0.1, 85.21 ± 0.1, 85.4, 85.02 ± 0.02, 85.950 ± 0.003, and 84.950 ± 0.003 K, respectively. The latter two values originated from the same laboratory and differ only by the temperature scale that was used. Measurements of vapor pressure performed by [1970Pry] and [1970Str1] were of the highest precision accuracy, and 99.99% $F_2$ purity and are preferred with the value of [1970Pry] being 84.958 ± 0.003 K in the ITS-90 temperature scale. The critical point was estimated by [1930Cad] and [1970Pry] by fitting equations relating vapor pressure or density versus temperature. The selected values from [1970Pry], 144.32 ± 0.05 K (ITS-90) and 5.215 MPa, are more precise than the earlier estimations of the critical point by [1930Cad]: 144 K and 5.57 MPa. A unary $F_2$ phase diagram is shown in Fig. 1.

Physical properties of Hg related to its phase transitions were assessed in the Hg unary evaluation [1992Gum]. The Hg melts at −38.8290 °C and boils at 356.623 °C at 0.101325 MPa.

## Compounds

Two compounds are formed in the F-Hg binary system: $Hg_2F_2$ (mercurous fluoride) and $HgF_2$ (mercuric fluoride). Both may be formed by direct reaction between the elements but preparation by more complicated chemical reactions is more common. $Hg_2F_2$ is probably a white solid when pure [1980Mes], but it is usually contaminated with other oxides to give a yellowish substance that melts at 570 °C and decomposes below 650 °C at normal pressure [1918Ruf]. $Hg_2F_2$ when in a closed container under reduced pressure of 1300 Pa may be decomposed at about 450 °C according to the reaction $Hg_2F_2 <=> HgF_2 + Hg(G)$. [1990Emu] synthesized a new form of $Hg_2F_2$ grown from its vapor in a quartz ampoule filled with He. The resultant crystal was yellow and showed some chemical and physical features of the previously reported $Hg_2F_2$, but it showed a different Raman spectrum and crystallographic characterization. Because its Raman spectrum was *qualitatively* not changed between −238 and 227 °C, no phase transition for this new form of $Hg_2F_2$ is expected in this temperature range. No purity of this substance was specified, and, therefore, one could treat it as a metastable or impurity stabilized polymorph of $Hg_2F_2$.

$HgF_2$ is colorless according to [1918Ruf] and orange according to [1963Swa]. The coloration seems to be caused by its contact with moisture, air, and light [1980Mes]. $HgF_2$ melts at 645 °C and boils with decomposition at 650 °C. The decomposition products are unspecified. Both substances, $Hg_2F_2$ and $HgF_2$, used by [1918Ruf] were only 99+% pure so the temperatures of the phase transitions are uncertain arbitrarily estimated as ±10 °C.

## Crystal Structures and Lattice Parameters

Crystal structure and lattice parameter data are collected in Tables 1 and 2, respectively. Due to technical difficulties (high reactivity and tendency to explosive reactivity of F), the $\alpha F_2$ and $\beta F_2$ structures have not been investigated intensively. [1968Mey] obtained an x-ray powder pattern of 99.99% pure $\alpha F_2$ at 23 and 39 K. The $C2/m$ space group was ascribed by the authors to $\alpha F_2$, but $C2/c$ could not be ruled out completely. The difference between $C2/m$ and $C2/c$ is the direction of tilt of the $F_2$ molecules in each lattice layer. [1970Pau] performed theoretical analysis of the [1968Mey] experimental data and

**Table 1 F-Hg crystal structures**

| Phase | Composition at.% Hg | Pearson symbol | Space group | Strukturbericht designation | Prototype | Temperature (°C) |
|---|---|---|---|---|---|---|
| $\alpha F_2$ | 0 | $mC8$ | $C2/m$(a)<br>$C2/c$(b) | … | $\alpha F_2$ | $< -227.61$ |
| $\beta F_2$ | 0 | $cP16$ | $Pm\bar{3}n$ | … | $\gamma O_2$ | $< -219.66$ |
| $HgF_2$ | 33.3 | $cF12$ | $Fm3n$ | $C1$ | $CaF_2$ | RT |
| $Hg_2F_2$ | 50 | $tI8$ | $I4/mmm$ | $D3_1$ | $Hg_2Cl_2$ | RT |
| | 50(c) | $mP8$ | $P\bar{2}_1/m$ | … | … | RT |
| $\alpha$Hg | 100 | $hR1$ | $R\bar{3}m$ | $A10$ | $\alpha$Hg | $< -38.8290$ |
| $\beta$Hg | 100 | $tI2$ | $I4/mmm$ | … | $\beta$Hg | $< -194.$ HP |

(a) According to [1968Mey, 1980Kob, 1987Nau]
(b) According to [1970Pau, 1974Eng. 1986Kir, 1987Sch, 1989Kir]
(c) Obtained by [1990Emu], a form probably metastable or stabilized by impurities

**Table 2 F-Hg lattice parameter data**

| Phase | Composition at.% Hg | Lattice parameters | | | angle° | Temperature (°C) | Reference |
|---|---|---|---|---|---|---|---|
| | | ***a*, nm** | ***b*, nm** | ***c*, nm** | | | |
| $\alpha F_2$ | 0 | 0.550 (1) | 0.328 (1) | 1.001 (1) | $\beta = 134.66$ | −250 | [1968Mey] |
| | | 0.556 (1) | 0.328 (1) | 1.013 (1) | $\beta = 135.17$ | −234 | [1968Mey] |
| | | 0.550 | 0.338 | 0.728 | $\beta = 102.17$ | −250 | [1970Pau] |
| $\beta F_2$ | 0 | 0.667 | … | … | … | $-228 < t < -220$ | [1964Jor] |
| $HgF_2$ | 33.3 | 0.555 | … | … | … | RT | [1933Ebe] |
| | | 0.55373 | … | … | … | 25 | [1963Swa] |
| $Hg_2F_2$ | 50 | 0.367 | … | 1.090 | … | RT | [1933Ebe] |
| | | 0.366 | … | 1.090 | … | RT | [1956Grd] |
| | | 0.3673 | … | 1.0882 | … | 25 | [1968Gab] |
| | | 0.3673 (1) | … | 1.0884 (2) | … | RT | [1971Dor] |
| | | 0.36700 (4) | … | 1.0901 (2) | … | RT | [1992Sch] |
| | 50(a) | 0.547 | 0.664 | 1.141 | $\alpha = 98.85$ | RT | [1990Emu] |
| $\alpha$Hg | 100 | 0.3005 | … | … | $\alpha = 70.53$ | −48 | [1992Gum] |
| $\beta$Hg | 100 | 0.3995 | … | 0.2825 | … | −194 | [1992Gum] |

(a) A form probably metastable or stabilized by impurities

claimed that the $C2/c$ space group is the correct one for $\alpha F_2$. The interpretation of [1970Pau] is generally accepted; however, several theoretical models and interpretation of Raman spectra favored $C2/m$ in some reports [1980Kob, 1987Nau] and $C2/c$ in others [1974Eng, 1986Kir, 1987Sch, 1989Kir]. Energy calculations indicate that the stabilities of the two possible structures differ only slightly ($\leq 0.4\%$).

The lattice parameter of $\beta F_2$ was determined by [1964Jor] from x-ray diffraction of a single crystal of unspecified purity.

The elementary cell dimensions for $Hg_2F_2$ were obtained from x-ray diffraction of powders [1933Ebe, 1956Grd, 1968Gab] or single crystals [1971Dor, 1990Emu, 1992Sch]. [1997Lia] performed quantum chemical calculations of the interatomic distances in solid $Hg_2F_2$ and came to the conclusion that their results are in reasonable agreement with the experimental data of [1970Dor] and [1992Sch]. Therefore, the results of [1992Sch] may be recommended. Interpretation of NMR spectra by [1968Gab] indicate that the Hg-F bond in $Hg_2F_2$ is ionic with a large charge separation.

[1990Emu] found a second crystalline form of $Hg_2F_2$ to be monoclinic. Since his crystal was twinned, he could not completely determine its structure. The lattice parameter data of this form of $Hg_2F_2$ approximates the lattice parameter data of $\alpha F_2$; however, it is impossible to imagine a decomposition of stable $Hg_2F_2$ with a formation of unstable $\alpha F_2$ crystal at room temperature and normal pressure; Fig. 1.

$HgF_2$ lattice parameter data were determined by [1933Ebe] and [1963Swa] from x-ray diffraction from powders. The first data were obtained from a sample of unspecified purity with lower precision than in the later, more careful investigation by [1963Swa] who used 99.9+% pure material. Therefore, the results of the latter investigation are recommended. $HgF_2$ shows a distinctly ionic structure [1959McI].

The lattice parameter data for Hg are quoted from the assessment of [1992Gum].

## Thermodynamics

[1952Koe] measured emf of cells of the type, M, $MF_2$/HF (NaF)/$Hg_2F_2$/Hg, where M = Cd, Cu, or Pb. These measurements were used to calculate the Gibbs energy of formation of $Hg_2F_2$ equal to −437.5 kJ/mol at 10 °C. [1959Blo] investigated the temperature dependence of the equilibrium:

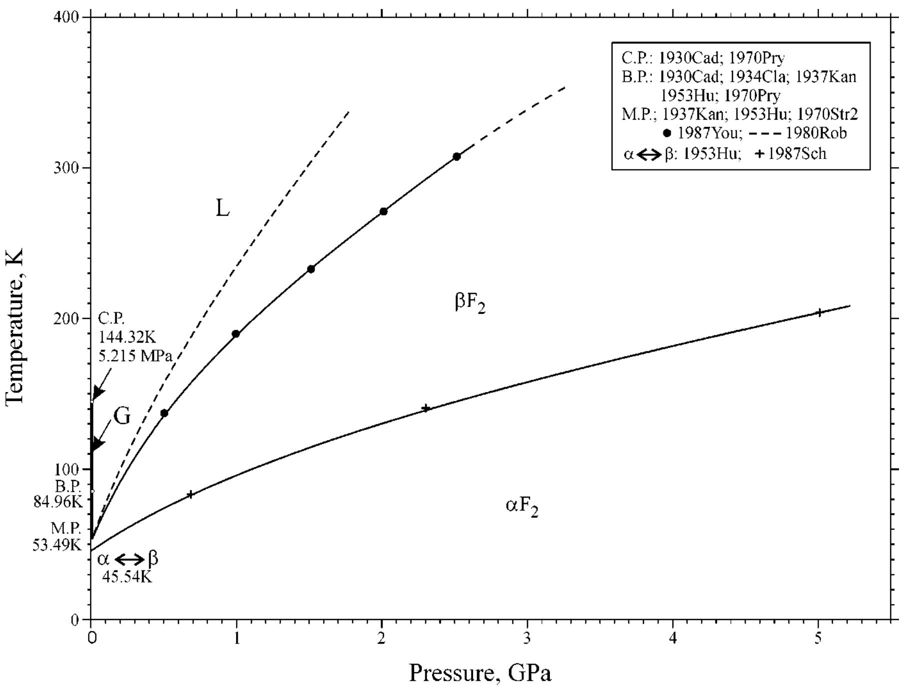

**Fig. 1** Assessed $F_2$ unary P-T phase diagram. The solid lines are based upon the indicated experimental data, while the dashed line represents a theoretical calculation of the $\beta F_2 \leftrightarrow$ L transformation

$TiF_4(G) + Hg(L) <-> 1/2Hg_2F_2(s) + TiF_3(s)$ and, with the help of thermodynamic values tabulated in the literature, they found the enthalpy and free energy of $Hg_2F_2$ formation at 25 °C equal to −492.4 and −440.5 kJ/mol, respectively. The agreement between the Gibbs energy values from the two determinations is satisfactory, taking into account the temperature difference in both determinations. Authors of [1965JAN] refined the above data using selected auxiliary thermodynamic values and came to the following results at 25 °C: −485.7 kJ/mol for the enthalpy of formation and −427.8 kJ/mol for the Gibbs energy of formation. The earlier values of −322 kJ/mol for the enthalpy of formation and −243 kJ/mol for the Gibbs energy of formation calculated by [1959Mas] with their own empirical relations are rejected.

There are no experimental thermodynamic data for the formation of $HgF_2$. Several values were calculated from empirical models comparing thermodynamic features of mercury halides; however, one should notice that $HgF_2$ possesses distinctly different physical properties than analogous halides and such corelations may fail. For the standard enthalpy of $HgF_2$ formation, one may find in the literature the following predictions: −402 [1948Yat], −330 [1953Lon], ∼−419 [1956Kar], −291 [1959Mas], and −423 kJ/mol [1965JAN]. For the Gibbs energy of $HgF_2$ formation at 25 °C, one may find: −393 [1954Kar] and −374 kJ/mol [1965JAN]. Values in [1965JAN] are most commonly used, but they are not based on experimental data.

## Pressure

The melting temperatures of $\beta F_2$ were measured also at elevated pressures. [1970Str2] extended the investigations up to 13.7 MPa, [1987You] to 2.5 GPa, and [1987Sch] to 3 GPa. [1987You] observed the melting process by visual and Raman spectroscopy methods. Experimental difficulties (reaction of $F_2$ with diamond, diamond breaking, and $F_2$ explosion) limited the precision of their temperature estimation to ±23 K at 2.5 GPa. [1987Sch] investigated the $F_2$ melting and the $\alpha F_2 <-> \beta F_2$ phase transition with the use of the Raman technique. The melting curve was established as lying between two limiting curves, thus having even poorer precision than in the experiments of [1987You]. However, the $\alpha F_2 <-> \beta F_2$ phase boundary of [1987Sch] was determined with a precision better than ±10 K. [1980Rob] calculated the $F_2$ melting curve based on the Lenard-Jones model and a Devonshire equation of state; the calculations, when compared to experiment, clearly overestimated melting temperatures. The unary phase diagram of $F_2$ at high pressures is shown in Fig. 1. The behavior of Hg under high pressure was assessed in [1992Gum].

Studies of the influence of pressure on $HgF_2$ properties were carried out. No inversion of the $HgF_2$ structure, typical of other Hg(II) halides, was observed in x-ray diffraction and electric resistance measurements at pressures applied up to 5 GPa and temperatures up to 400 °C [1967Sei].

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