# ON THE EQUILIBRIA OF SILVER AND LEAD, SILVER AND BISMUTH, AND BISMUTH AND LEAD WITH THEIR FLUORIDES AT 900° C.

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*Received* 15*th September*, 1943.

The study of equilibria of molten metals with their fused salts as exemplified by the equation

$$\mathrm{M_AX} + \mathrm{M_B} \rightleftharpoons \mathrm{M_A} + \mathrm{M_BX}$$

was inaugurated by Lorenz.[1]

It is scarcely necessary to observe that investigations of equilibria of this nature are of practical interest, as many metallurgical processes are based on reactions of molten metals with their fused salts (slag).[2]

The reactions are such as occur between two liquid phases—a salt phase, being a solution of two salts, and a metal phase, being a solution of two metals.

A reaction $a\mathrm{A} + b\mathrm{B} \leftrightarrows c\mathrm{C} + d\mathrm{D}$ has an equilibrium constant

$$K = \frac{a_{\mathrm{C}}^{\mathrm{c}} \cdot a_{\mathrm{D}}^{\mathrm{d}}}{a_{\mathrm{A}}^{\mathrm{a}} \cdot a_{\mathrm{B}}^{\mathrm{b}}}$$

where $a_{\mathrm{A}}$ is the activity of the substance A, etc. If the solutions are ideal, then $a_{\mathrm{A}} = N_{\mathrm{A}}$, $a_{\mathrm{B}} = N_{\mathrm{B}}$, etc., where $N_{\mathrm{A}}$, etc., are the mole fractions. Hence one obtains the following equation for the equilibrium constant

$$K_{\mathrm{N\ equil.}} = K = \frac{N_{\mathrm{C}}^{\mathrm{c}} \cdot N_{\mathrm{D}}^{\mathrm{d}}}{N_{\mathrm{A}}^{\mathrm{a}} \cdot N_{\mathrm{B}}^{\mathrm{b}}} \quad . \quad . \quad . \quad . \quad (1)$$

Equilibria between molten metals and their salts frequently obey, to a first approximation, the law of mass action for ideal solutions.[3]

Measurements of the e.m.f.s of cells such as $\mathrm{M_A/M_AX//M_BX/M_B}$—the substances being in a molten state—also enable equilibrium constants to be determined, and a comparison may be made between the values obtained by these two quite independent methods. But before one constant can be compared with the other, the relationship between $K_{\mathrm{electric}}$ and $K_{\mathrm{equilib.}}$ must be established. This was done by K. Jellinek and Siewers [3] who showed that

$$E_{\mathrm{O,\,A}} - E_{\mathrm{O,\,B}} = \frac{RT}{nF} \ln \frac{a_{\mathrm{C}}^{\mathrm{c}} \cdot a_{\mathrm{D}}^{\mathrm{d}}}{a_{\mathrm{A}}^{\mathrm{a}} \cdot a_{\mathrm{D}}^{\mathrm{d}}}$$

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[1] Lorenz and co-workers, *Z. anorg. Chem.*, 1923, **131**, 247; 1924, **138**, 204; 1925, **135**, 281; 1928, **170**, 247, 320, 324; 1928, **171**, 355; 1928, **177**, 1; 1929, **178**, 40, ; 337 *Ann. Chemie*, 1927, **453**, 338.

[2] Herasymenko, *Trans. Faraday Soc.*, 1938, **34**, 1245, 1254.

[3] K. Jellinek and Siewers, *Z. Elektrochem.*, 1934, **40**, 871; *cf.* also K. Jellinek and co-workers, *Z. anorg. Chem.*, 1925, **146**, 337; 1924, **139**, 233; *Zeitschr. f. phys. Chem.*, 1924, **110**, 192; **111**, 234; *Z. Elektrochem.*, 1925, **31**, 542; 1933, **39**, 444; see also K. Jellinek, *Lehrbuch der physikalischen Chemie*, Enke, Stuttgart, 1932, Vol. IV, p. 573, etc., and K. Jellinek, *Kurzes Lehrbuch der physikalischen Chemie*, Deventer, Holland, 1938, Vol. I, p. 311, and 1938, Vol. II, p. 143.

or, in the case of ideal solutions

$$E_{0,\,\mathrm{A}} - E_{0,\,\mathrm{B}} = \frac{RT}{nF} \ln K_{N\,\mathrm{equil.}} \quad . \quad . \quad . \quad (2)$$

$E_{0,\,\mathrm{A}}$ and $E_{0,\,\mathrm{B}}$ being the potential differences between each metal and its pure salt melt.

The e.m.f. of such a cell is also given by the Gibbs-Helmholtz equation

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_{p,\,N} \quad . \quad . \quad . \quad . \quad (3)$$

The potential difference at the interface of the two salt melts being neglected in equations (2) and (3).

On the subject of the equilibria between molten metals and their fused fluorides, only two papers are to be found in the literature. These are by Rinck,[4] dealing with the reaction $K + NaF \rightleftharpoons KF + Na$, and by Jander[5] on the equilibrium $3Na + AlF_3 \rightleftharpoons 3NaF + Al$.

To obtain further information in this subject preliminary experiments on the equilibria of silver and bismuth, silver and lead, and lead and bismuth with their fluorides were carried out.

## Apparatus and Technique.

An initial difficulty—that of finding a material resistant to the molten fluorides—was overcome by using graphite crucibles: they had an ash content of 0·5 %, consisting of silica and silicon carbide. The crucible, of inner diameter 3 cm. and height 8 cm. and covered by a nickel lid through which a graphite rod could be inserted in the melt, was enclosed in an electric furnace. The whole experiment was carried out in a pure nitrogen atmosphere to prevent oxidation. Care was taken to ensure an even temperature distribution in the furnace, and temperatures were measured by a Pt-Pt Rh thermocouple which had been calibrated by the boiling-point of sulphur and the melting-point of NaCl. The thermal e.m.f. was measured on a Siemens-Halske millivoltmeter (304 $\Omega$). During an experiment the temperature was kept constant to ± 2° C.

The furnace containing the crucible, with the metal or metals in question, was heated to the desired temperature, the fluoride or fluorides added and the temperature again brought up to that required. It was then left for about fifteen minutes, during which it was frequently stirred with the graphite rod. Finally the equilibrium was frozen by removing the crucible from the furnace and pouring its contents on to a cold copper sheet. The metals and fluorides were subsequently carefully separated and analysed.

## Preparation of Substances.

(*a*) *Lead* was an " Analar " product.

(*b*) *Silver* was prepared from Ag residues and an analysis of the product —determined as AgCl—showed a purity of 99·8 %.

(*c*) *Bismuth* (99·9 % by analysis as phosphate) was prepared by the method described by Mylius and Groschuff.[6]

(*d*) *Lead fluoride* was prepared by Ruff's method.[7] The dry lead fluoride obtained was rapidly fused in portions in a Pt crucible at 900° C. to destroy the lead fluoride fluorine hydrate. Analysis showed

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[4] Rinck, *Ann. Chim.*, 1932, **18**, 395.

[5] Jander and co-workers, *Z. anorg. Chem.*, 1937, **232**, 39, 56; 1938, **239**, 65; *cf.* also Krings and co-workers, *ibid.*, 1931, **200**, 46; 1931, **202**, 99; 1932, **206**, 337; **209**, 385; and F. Körber and co-workers, *Mitt. Kaiser Wilh. Institut für Eisenforschung*, 1932, **14**, 119, 181; 1933, **15**, 271; 1935, **17**, 39, 231; 1936, **18**, 109, 89, 131.

[6] Mylius and Groschuff, *Z. anorg. Chem.*, 1916, **96**, 246.

[7] Ruff, *Chemie d. Fluors*, p. 33.

that if the material was only dried on a sand bath the resultant product had a lead content several per cent. lower than that required by the formula $PbF_2$. If it was fused for too long a time, however, the lead content was too high. Analysis of the material actually used gave Pb —determined as $PbSO_4$—as 84·56 %, the theoretical value being 84·50 %.

(*e*) *Bismuth fluoride*.—The method of preparation is that described by Gott and Muir.[8] Drying at 100° C., as recommended by the authors, yielded a product with too small a Bi content, but when it was fused, as previously described for $PbF_2$, analysis showed that a satisfactory material had been obtained. The Bi content—determined as phosphate —was 78·3 % compared with a theoretical value of 78·57 %.

## The Equilibrium of Lead and Bismuth with their Fluorides.

The experimental method was that described above and the resultant melt appeared to be homogeneous—the melting-point of $BiF_3$ was estimated to be 850° C. The analysis was carried out according to a method by Moser and Maxymowicz.[9] Table I contains the analytical results—experiments nos. 1-5 were carried out at 900° C., and no. 6 at 1000° C.

For this reaction two equations are possible (*cf.* K. Jellinek and Siewers [3]).

$$(1)\quad 2\ BiF_3 + 3\ Pb \rightleftharpoons 3\ PbF_2 + 2Bi$$

or

$$(2)\quad 2\ BiF_3 + 3\ Pb \rightleftharpoons 3\ PbF_2 + Bi_2.$$

TABLE I

| Experiment. | Metal-phase. | | | | Salt-phase. | | Equil.-constants. Mole-fractions. | |
|---|---|---|---|---|---|---|---|---|
| | Bi. | Pb. | $Bi_2$. | Pb. | $BiF_3$. | $PbF_2$. | $K_{Bi}$. | $K_{Bi_2}$. |
| | Atom %. | Atom % | Mole %. | Atom%. | Mole %. | Mole %. | | |
| 1 | 74·6 | 25·4 | 59·5 | 40·5 | — | 100 | — | — |
| 2 | 95·0 | 5·0 | 90·5 | 9·5 | 1·0 | 99·0 | $7·0 \times 10^7$ | $1·0 \times 10^7$ |
| 3 | 99·0 | 1·0 | 98·0 | 2·0 | 6·3 | 93·7 | $2·0 \times 10^8$ | $2·5 \times 10^7$ |
| 4 | 99·4 | 0·6 | 98·8 | 1·2 | 12·0 | 88·0 | $2·2 \times 10^8$ | $2·7 \times 10^7$ |
| 5 | 98·9 | 1·1 | 97·8 | 2·2 | 5·9 | 94·1 | $1·8 \times 10^8$ | $2·2 \times 10^7$ |
| 6 | 90·6 | 9·4 | 82·9 | 17·1 | 0·3 | 99·7 | $1·1 \times 10^8$ | $1·8 \times 10^7$ |

Constants are obtained for either formulation

$$\left(K_{Bi} = \frac{Bi^2PbF_2{}^3}{Pb^3BiF_3{}^2}\,;\quad K_{Bi_2} = \frac{Bi_2PbF_2{}^3}{Pb^3BiF_3{}^2}\right)$$

which vary by a factor of about three, and if experiments 3, 4 and 5 only are taken into account the deviations from the mean are not more than about 10 % for Bi and $Bi_2$. Considering that the amounts of Pb in the metal phase vary as 1 : 8 and the amount of $BiF_3$ in the salt phase as 1 : 12 and that the reaction is rather one sided, the constancy appears to be satisfactory. One has to conclude, therefore, that the salt and metal phase are ideal solutions to a first approximation, provided that the deviations from ideality do not just compensate each other (*cf.* K. Jellinek

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[8] Gott and Muir, *J. Chem. Soc.*, 1888, **53**, 139.

[9] Moser and Maxymowicz, *Z. anal. Chem.*, 1925, **67**, 248.

and Siewers,[3] who investigated the equilibria $Zn + Cd\,Cl_2 \rightleftharpoons ZnCl_2 + Cd$ and $Zn + CdBr_2 \rightleftharpoons ZnBr_2 + Cd$ in this respect). From these experiments it cannot be decided which of the two formulations (Bi or $Bi_2$) is correct. Fig. 1 shows the $Pb/PbF_2$ isotherm for the first formulation (Bi). Experiment 1 was started with pure Pb and $BiF_3$, experiment 2 with pure Bi and $PbF_2$. This shows that the equilibrium could be reached from either side. Experiments 3, 4 and 5 were started with pure Bi, $PbF_2$ and different small amounts of $BiF_3$ (metals *ca.* 20 g., salts *ca.* 12 g.). Experiment 6 was carried out at 1000° C. beginning with Bi, Pb and $PbF_2$ together with a small amount of $BiF_3$.

At 1000° C. the fluorides have a high vapour pressure, especially $BiF_3$, which seemed to evaporate until its concentration in the salt phase was small. Thus the only equilibrium states which could be reached were those with small $BiF_3$ contents in the salt phase and comparatively large amounts of Pb in the metal phase. Hence, any analytical or other experimental errors, however slight, could lead to erroneous results and no conclusions could be drawn from experiment 6.

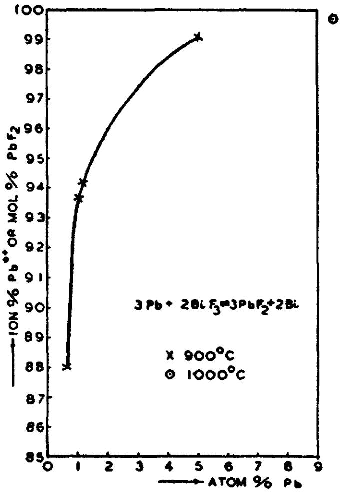

FIG. 1.

According to the equation

$$E_{0},{}_{\mathrm{Bi}} - E_{0},{}_{\mathrm{Pb}} = \Delta E = \frac{RT}{6F} \ln\text{·}K$$

the e.m.f. of the cell $Bi/BiF_3//PbF_2/Pb$ can be calculated.

One obtains for

$$K_{\mathrm{Bi}} : \Delta E = 0{\cdot}32 \text{ volt}$$

and

$$K_{\mathrm{Bi_2}} : \Delta E = 0{\cdot}286 \text{ volt.}$$

The change of heat content for the two formulations of the reaction can be roughly calculated from the Gibbs-Helmholtz equation, neglecting the temperature coefficient :

$$\Delta H_{\mathrm{Bi}} = -\ 44 \text{ K cal.} \qquad \Delta H_{\mathrm{Bi_2}} = -\ 40 \text{ K cal.}$$

44 K cal. and 40 K cal. respectively are liberated if the reaction proceeds as follows :

$$2\ BiF_3 + 3\ Pb \rightarrow 2\ Bi + 3\ PbF_2.$$

Since the change in heat content for this reaction is given by the difference in the heats of formation of 2 × $BiF_3$ and 3 × $PbF_2$, the heat of formation for $BiF_3$ can be calculated if the heat of formation for $PbF_2$ is known. The latter was found to be – 155·6 K cal. at 748° C.[10]

One obtains, therefore, for the heat of formation of $BiF_3$ a value for each of the formulations given above :

$$-\ 211 \text{ K cal. (for Bi).} \qquad -\ 213 \text{ K cal. (for Bi}_2\text{).}$$

Comparison with the known heat of formation for $SbF_3 = -\ 216{\cdot}5$ K cal. supports the values found for $BiF_3$. (The heats of formation for $SbCl_3$ and $BiCl_3$ are – 91·4 K cal. and – 90·6 K cal. respectively.)

[10] K. Jellinek and Rudat, *Z. anorg. Chem.*, 1928, **175**, 298; *cf.* also *Z. Elektrochem.*, 1936, **42**, 401.

## The Equilibria of Silver and Bismuth, and Silver and Lead with their Fluorides.

The equilibrium of Ag and Bi with their fluorides could not be studied successfully as the vapour pressures, especially that of the AgF, are too high. A lower temperature could not be employed since the melting-points of the salts are in the region of 900° C. Several experiments were carried out in which attempts were made to keep the time of reaction as short as possible, but only equilibria states with very small Ag content (about 0·1 %) in the salt phase could be obtained. The Bi content in the metal phase, starting from Ag and $BiF_3$ was considerable (about 8 %). This shows that Ag goes into the salt phase but apparently the AgF evaporates quickly.

The equilibrium constant

$$K = \frac{Ag^3 BiF_3}{Bi AgF^3}$$

for this reaction can be calculated knowing the heats of formation of the salts. The heat of formation of AgF was found to be $-$ 50·1 K cal.[11] and the value for $BiF_3$ is given above. The change in heat content for the reaction is thus $-$ 63 K cal. which gives an e.m.f. for the cell $Bi/BiF_3//AgF/Ag$ of 0·913 volt, and the equilibrium constant calculated from equation (2) is $5 \times 10^{11}$.

To complete the series of the equilibria of Ag and Pb with their halides,[12] an attempt was made to determine the equilibrium constant of Ag and Pb with their fluorides at 900° C. From the known heats of formation of the salts the constant

$$K = \frac{Ag^2 PbF_2}{Pb AgF^2}$$

was calculated to be about $10^{10}$. Only traces of AgF could be found in the salt phase.

It should be possible to study these equilibria successfully in a sealed reaction vessel which would enable still higher temperatures to be used, provided that a suitable material could be found.

## Summary.

(1) The equilibrium of Bi and Pb with their fluorides was studied at 900° C. It is shown that Bi is much nobler than Pb in this reaction. The metal and salt phases respectively are ideal solutions to a first approximation. The heat of formation of $BiF_3$ is calculated.

(2) The equilibria of Bi and Ag, and Ag and Pb with their fluorides were found to be unsuitable for investigation in an open reaction vessel as the vapour pressures of the salts at the required temperatures are too high. A theoretical estimation of the equilibrium constants for these reactions is given.

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[11] v. Wartenberg, *Z. anorg. Chem.*, 1926, **151**, 326.
[12] K. Jellinek and Hewskij, *Z. Elektrochem.*, 1933, **39**, 444.