# Communications

## The Influence of Oxygen Pressure and $P_2O_5$ on the Surface Tension of Liquid Iron Oxide at 1435 °C

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The influence of oxygen pressure on the surface tension of liquid iron oxide has been measured by Kidd and Gaskell[1] using Padday's cone technique, which involves measuring the maximum excess force, $f$, exerted on a cone during its immersion in or withdrawal from a liquid. The surface tension, $\gamma$, is then obtained from the relationship

$$\gamma = g\rho^{1/3}\left(\frac{f}{C}\right)^{2/3} \qquad [1]$$

where $g$ is the acceleration due to gravity, $\rho$ is the density of the liquid, and $C$ is the cone constant, which is obtained by measuring the maximum excess force exerted on the cone during its immersion in a liquid of known density and surface tension. As the two studies[2,3] of the variation, with composition, of the density of liquid iron oxide produced significantly differing results, application of Padday's cone technique could not produce an unambiguous relationship between surface tension and composition. The technique also involved the practical disadvantage that the observation of a maximum excess force exerted on a cone during its immersion in a liquid of given density and surface tension requires the use of a cone of some minimum length, which, in the case of liquid iron oxide, was calculated to be 1.92 cm. Consequently, a 2.5-cm depth of liquid iron oxide was used, which required up to 69 hours for equilibration with the $CO$-$CO_2$ atmosphere used to control the composition of the liquid.

In the present study, the influence of oxygen pressure and $P_2O_5$ on the surface tension of liquid iron oxide has been measured using the classical hollow cylinder technique.

The classical hollow cylinder technique involves measurement of the force, $f$, required to rupture the liquid meniscus attached to the lower end of a hollow vertical cylinder making contact with the surface of the liquid. The surface tension, $\gamma$, is then obtained from the expression

$$Fk' = \pi (d_1 + d_2)\,\gamma$$

where $d_1$ and $d_2$ are the inner and outer diameters of the cylinder and $k'$ is a correction factor that accounts for the weight of meniscus raised above the level of the free surface of the liquid at the point of rupture.[4] The correction factor is a function of $d^3/V$, where $V$ is the volume of liquid held up by the cylinder and $d$ is the average of $d_1$ and $d_2$. The values of $d_1$ and $d_2$ were determined by measurement at room temperature and knowledge of the coefficient of thermal expansion of the cylinder material.

**Table I. Surface Tensions of Iron Oxide and Iron Phosphate Melts at 1435 °C**

| $p_{CO_2}/p_{CO}$ | $p_{O_2}$ (Atm) | Mole Fraction $Fe_2O_3$ | Surface Tension (N/m) |
|---|---|---|---|
| 0.52 | $6.01 \times 10^{-9}$ | 0.042 | 0.565 |
| 3.15 | $2.20 \times 10^{-7}$ | 0.137 | 0.559 |
| 5.78 | $7.42 \times 10^{-7}$ | 0.170 | 0.558 |
| 7.07 | $1.11 \times 10^{-6}$ | 0.180 | 0.558 |
| 10.66 | $2.52 \times 10^{-6}$ | 0.205 | 0.559 |
| 14.00 | $4.35 \times 10^{-6}$ | 0.220 | 0.557 |

| Mole percent of $P_2O_5$ | 2.5 | 5.3 | 7.0 | 9.0 | 12.0 |
|---|---|---|---|---|---|
| $p_{CO_2}/p_{CO}$ | Surface Tension (N/m) | | | | |
| 3.15 | 0.474 | 0.454 | 0.421 | 0.407 | 0.409 |
| 5.78 | 0.472 | 0.452 | 0.404 | 0.407 | 0.399 |
| 7.07 | 0.470 | 0.452 | 0.396 | 0.397 | 0.399 |
| 10.66 | 0.470 | 0.452 | 0.397 | 0.397 | 0.403 |
| 14.00 | 0.466 | 0.452 | 0.403 | 0.480 | 0.402 |

A Pt-10 pct Rh cylinder 1.8 cm in length, with 1.52-cm o.d. and 1.31-cm i.d., was suspended from a Cahn 1000 electrobalance by means of a Pt-10 pct Rh chain, and a shallow melt was contained in a hemispherical Pt-10 pct Rh crucible of 4-cm diameter. The Cahn balance was mounted above a vertical molybdenum-wound resistance tube furnace, and the crucible was placed on an alumina pedestal cemented to the upper end of a mullite thermocouple protection tube, which, in turn, was introduced to the furnace through a gas-tight seal at the lower end of the alumina reaction tube. The lower end of the mullite tube was attached to a jack located below the furnace, and contact between the cylinder and the melt was effected by raising the jack.

At 1435 °C, the liquid iron oxide phase field extends from saturation with iron at $p_{CO_2}/p_{CO} = 0.22$ to saturation with magnetite at $p_{CO_2}/p_{CO} = 15.40$.[5] Consequently, the liquid iron oxide was equilibrated with $CO$-$CO_2$ gas mixtures with ratios $p_{CO_2}/p_{CO}$ in the range 0.52 to 14.0. After changing the composition of the equilibrating gas mixture, measurements were made until the surface tension became constant, and it was found that equilibration of the melt with the gas was achieved in 12 hours.

The iron phosphate melts were produced from mixtures of reagent-grade iron pyrophosphate and wustite of $Fe^{3+}/Fe^{2+} = 0.10$, produced by oxidizing a pure iron bar in an induction coil at a temperature higher than the melting temperature of wustite and quenching the droplets of liquid oxide onto a steel plate. The $P_2O_5$ contents of the iron phosphate melts were determined by chemical analysis.

The experimental results are listed in Table I and are shown in Figures 1 and 2. The electrobalance gave an accuracy measurement of $\pm 5 \times 10^{-3}$ g, which, for a surface tension of 0.565 N/m, gives an uncertainty of $\pm 0.005$ N/m. As seen in Figure 1, the surface tensions measured directly in the present work have values which lie between those calculated by Kidd and Gaskell, and oxygen pressure has very little influence on the surface tension of liquid iron oxide. The variation of surface tension with oxygen pres-

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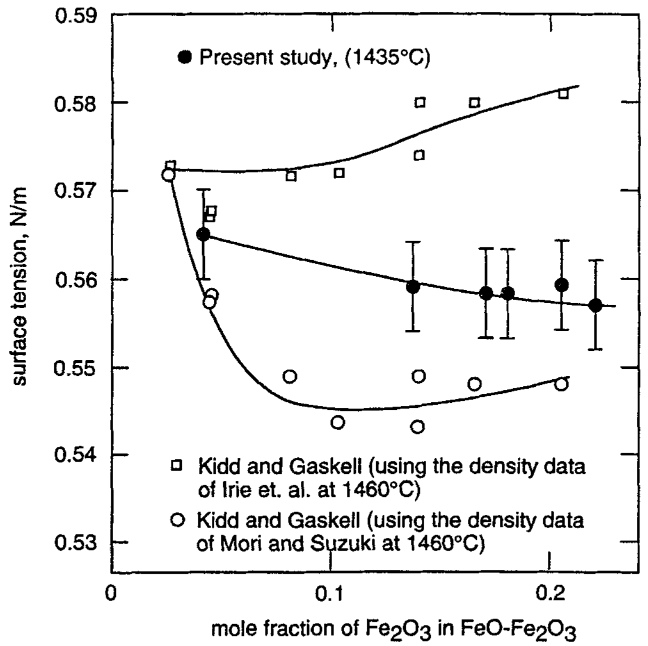

Fig. 1—The measured surface tensions of melts in the system FeO-$Fe_2O_3$ at 1435 °C and comparison with the values calculated by Kidd and Gaskell.[1]

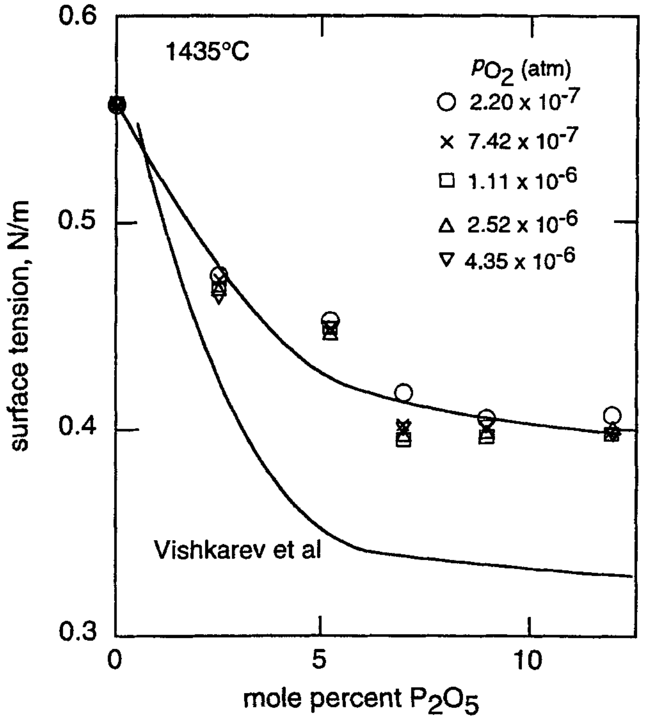

Fig. 2—The influence of $P_2O_5$ and oxygen pressure on the surface tension of liquid iron oxide at 1435 °C.

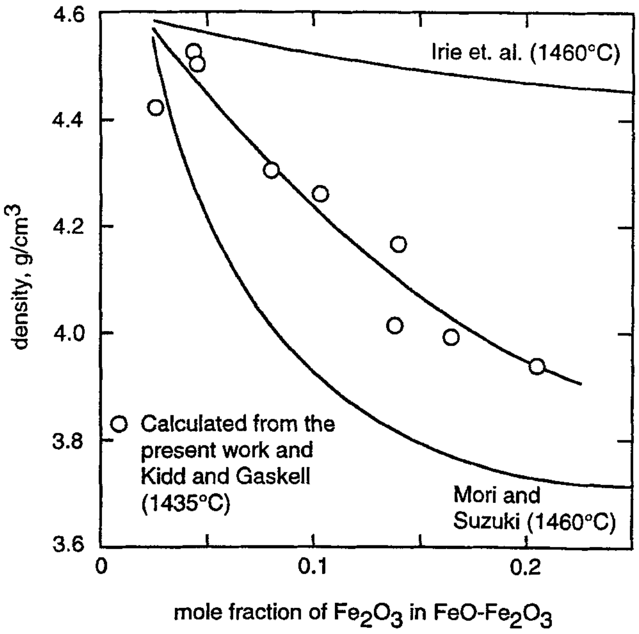

Fig. 3—The densities of iron oxide melts calculated from the measured surface tensions and the measurements made by Kidd and Gaskell.[1]

sure gives a surface excess concentration of oxygen of 1.15 × $10^{-7}$ g moles/m.[2]

Figure 2 shows that the addition of up to approximately 7 mole percent of $P_2O_5$ to liquid iron oxide decreases the surface tension from 0.56 to 0.40 N/m and that further additions in excess of 7 pct have little further effect. The oxygen pressure also has very little influence on the surface tensions of iron phosphate melts. Although the thermodynamic data required for calculating the surface excess concentration of $P_2O_5$ are not available, the behavior shown in Figure 2 indicates that the surface becomes saturated with $P_2O_5$ at 7 pct. Also shown in Figure 2 is the variation, with concentration of $P_2O_5$, of the surface tension of iron-saturated iron phosphate melts measured by Vishkarev *et al.*[6] However, as Kozakevitch[7] has pointed out, at saturation with iron, $P_2O_5$ in iron phosphate melts is rapidly reduced to phosphorus vapor, which casts doubt on the validity of the measurements of Vishkarev *et al.*

The surface tensions measured in the present work were combined with the measurements made by Kidd and Gaskell to calculate the density of liquid iron oxide as a function of composition using Eq. [1]. The values obtained, which are shown in Figure 3, lie between those measured directly by Irie *et al.*[2] and Mori and Suzuki.[3]

In summary, the following conclusions are presented.

1. At 1435 °C, the surface tensions of iron oxide and iron phosphate melts are not significantly influenced by changes in oxygen pressure.
2. The initial addition of $P_2O_5$ to liquid iron oxide at 1435 °C causes the surface tension to decrease from 0.56 to 0.40 N/m at 7 mole pct $P_2O_5$, and further additions have little influence.

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# Vacuum Evaporation of KCl-NaCl Salts: Part I. Thermodynamic Modeling of Vapor Pressures of Solid and Liquid Solutions

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Pyrochemical methods which are routinely carried out for processing plutonium commonly use chloride salts as their processing media.[1,2,3] In electrorefining to purify plutonium scraps and alloys, typically an equal molar KCl-NaCl mixture is used as the molten electrolyte through which the oxidized Pu ions are transported to the cathode where the pure plutonium is produced and settles by gravity to the bottom of the molten salt.[1,2] In molten salt extraction, molten KCl-NaCl salt or KCl-NaCl salt containing $MgCl_2$ is used to extract Am from molten Pu.[1,3] Americium is a decay product of $^{241}$Pu and emits high energy gamma radiation. It is removed to reduce radiation exposure to workers handling Pu. The usage of these pyrochemical processes dates back almost 30 years,[2,3] and over the years, the spent salts from these processes have accumulated in substantial quantities throughout various plutonium processing sites. These salts contain plutonium and plutonium decay products. Their associated radioactivities and the large quantities present serious waste problems. A promising way to reduce storage space and disposal cost of these pyrochemical salts is by first converting the actinide species in the waste salts to oxides through oxygen sparging and then separating the salts from the actinides *via* a vacuum evaporation process. The separation is possible because of the large difference in the vapor pressure between the chloride salts and the actinide oxides. For example, at 1123 K (850 °C), the vapor pressures of NaCl and KCl are $10^{-0.063}$ and $10^{-0.23}$ torrs,[4] whereas the vapor pressures of $PuO_2$ and $AmO_2$ are $10^{-15.7}$ and $10^{-15.0}$ torrs,[5] respectively, which are orders of magnitude smaller than that of the salt components. Therefore, the condensate from the evaporation process would consist of practically pure salts which can be discarded at low cost, while the unevaporated residue concentrated in actinides is significantly reduced in volume.

To aid the optimization of this evaporation separation process and process equipment design, an effort to model the evaporation-condensation process of molten KCl-NaCl solutions was initiated. This article will present the first part of the modeling work in developing vapor pressure relations of the KCl-NaCl system for the full range of binary compositions and a wide temperature range covering both the solid and liquid solution temperatures. Both KCl and NaCl have the same crystalline structure and can form complete solid solution at temperatures greater than about 773K (500 °C), as shown in the KCl-NaCl phase diagram (Figure 1).[6] Figure 1 also shows that formation of solution lowers the melting point of the solid. At 50 mol pct NaCl, the salt mixture melts congruently at 933 K (650 °C), which is about 100 K lower than the melting point of KCl, the lower melting component. In the following, the methodology of using fundamental thermodynamic relations and data to model the vapor pressure equations for the solid and liquid solutions of the KCl-NaCl system will be presented, and the vapor pressures calculated from the model equations will be compared with the available experimental data. How the model equations are useful in predicting condensate compositions will also be discussed.

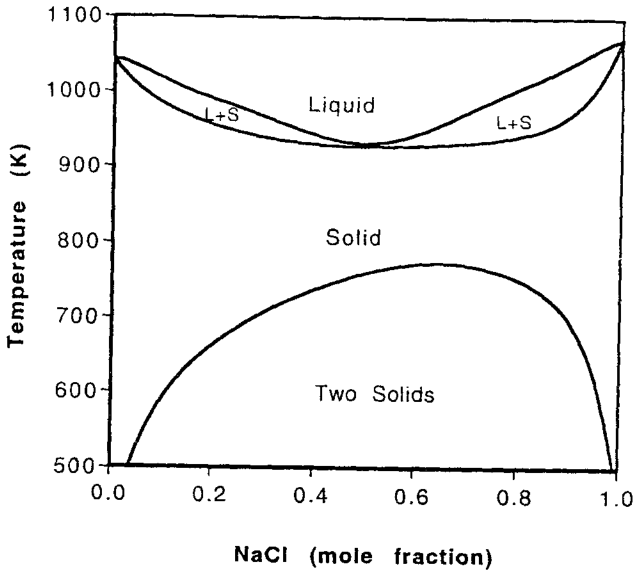

Fig. 1—Phase diagram of KCl-NaCl binary system.

Past studies[7–12] have shown that in the vapor phase over these salts, the vapor species consist of both monomers (KCl and NaCl) and dimers ($K_2Cl_2$ and $Na_2Cl_2$). Moreover, mixed dimer $NaKCl_2$ molecules are also present in the vapor phase over the binary KCl-NaCl system.[13]

The thermodynamic activities, *a*, of KCl and NaCl in the solid or liquid solutions are related to the partial molar free energies of these components (Eq. [27]) and defined as the ratio of vapor pressures between pure and solution states.[14] The activities can be determined from known thermochemical data (Eqs. [28] and [29]) and are composition and temperature dependent. We thus model the vapor pressures of KCl and NaCl over the solid and liquid solutions by the relations

$$P_{\text{A(over mixture)}} = a_{\text{A}} P^{\circ}_{\text{A (over pure A)}} \qquad [1]$$

and

$$P_{\text{B(over mixture)}} = a_{\text{B}} P^{\circ}_{\text{B (over pure B)}}, \qquad [2]$$

where *P* is pressure and the subscripts A and B denote KCl and NaCl, respectively. The equilibrium constants of for-

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