

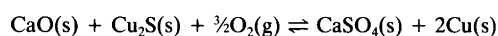
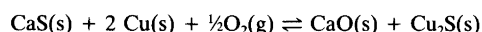
Solid-State Emf Studies of Equilibria in the System Ca-S-O, using the Solid Couple (Cu,Cu₂S) as Gas-Phase Buffer

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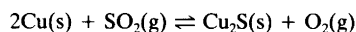
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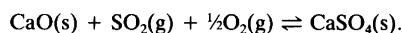
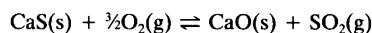
The equilibria



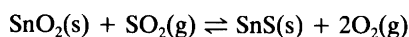
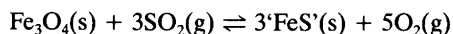
were studied by measuring the equilibrium oxygen pressures using galvanic cells involving calcia-stabilized zirconia as solid electrolyte material. The calculated Gibbs free energy values for these equilibria were combined with accurate literature values for the equilibrium reaction



to calculate ΔG° - T relationships for the following equilibrium reactions:

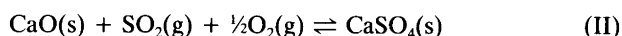
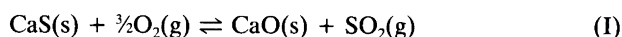


The solid-state galvanic cell technique employing stabilized zirconia has been used to study a number of equilibria in metal-sulfur-oxygen systems. As examples, the recent studies of the following equilibrium reactions can be mentioned^{1,2}

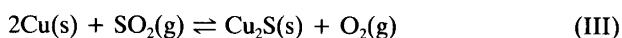


These equilibria were investigated by equilibration of the solid phases, i.e. (Fe₃O₄, 'FeS')¹ and (SnO₂, SnS)², respectively, with continuously flowing SO₂-Ar gas mixtures of known concentrations. The equilibrium oxygen partial pressures, $p(\text{O}_2)$, thus generated were determined through solid-state emf measurements. Quite accurate results could be obtained in these investigations (the uncertainties were about $\pm 0.02 \log p(\text{O}_2)$ units), but this technique using streaming SO₂ involves several experimental difficulties. One problem is to maintain a constant value of the SO₂ partial pressure throughout the emf measurements. Another difficulty occurs in systems where quite low SO₂ pressures are required, in which case the buffer capacities will be too low to maintain stable conditions. The present study aims to demonstrate the use of an auxiliary solid couple to attain stable equilibrium partial pressures in a

system involving low SO₂ pressures. To this end, data for the following equilibria of industrial importance will be determined:

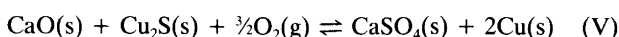
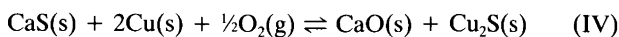


by using the solid phases Cu and Cu₂S to buffer the gas phase according to the equilibrium reaction



This equilibrium was studied carefully by Björkman and Fredriksson.³ It should also be mentioned that Kumar and Kay⁴ used the couple (Cu, Cu₂S) to fix the sulfur potentials in their investigation of equilibria in some metal-S-O systems.

The equilibria (I)–(III) are visualized in a stability diagram at 1200 K with $\log p(\text{SO}_2)$ and $\log p(\text{O}_2)$ as axes (Fig. 1). At each of the intersection points, four solid phases coexist in accordance with the equilibria (IV) and (V)



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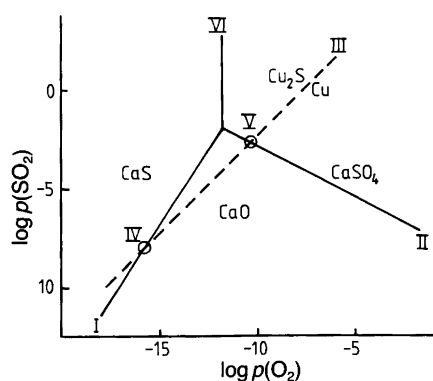
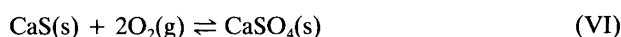


Fig. 1. Stability diagram for the system Ca-Cu-S-O at about 1200 K.

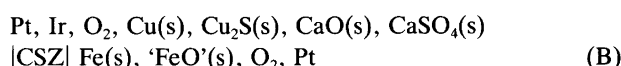
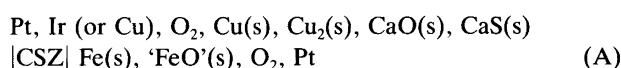
The equilibrium oxygen pressures generated by the four solid phases have been determined in the temperature range 1000–1300 K by means of solid state emf measurements. It should be pointed out that combination of the equilibria (IV) and (V) gives the “simple” equilibrium reaction (VI):



which has been studied thoroughly by means of solid-state emf measurements.⁴⁻⁶ It is thus feasible to check the overall results from the present study.

Experimental

Galvanic cells used. To study equilibria (IV) and (V), the following galvanic cells, involving calcia-stabilized zirconia (CSZ) as a solid electrolyte, were arranged



As the Pt wire, normally used as electrode material, will be corroded by sulfide phases, the terminal part in contact with the sample mixture was replaced by Ir or Cu. The construction of the galvanic cells has been described in detail by Pejryd.⁷

Chemicals. The sulfide CaS (Fisher, *p.a.*) was dried at 420 K. Cu₂S was made by reacting Cu (Merck *p.a.*) and sulfur (granular, Kvarntorp) in evacuated ampoules, first at 470 K for 24 h and then at 670 K for 70 h after an intermediate grinding. The oxide ‘FeO’ was synthesized by mixing the proper amounts of Fe (Merck *p.a.*) and Fe₂O₃ (Merck *p.a.*) and firing at 1100 K in an evacuated Al₂O₃ ampoule. The sulfate CaSO₄ was prepared from CaSO₄·2H₂O by heating in air at about 700 K, and the oxide CaO from CaCO₃ (Riedel-deHaën AG, *p.a.*) by heating at about 1300 K.

The phases were examined by X-ray powder diffraction.

Cell operation. Prior to the measurements, the half-cells were evacuated and sealed. The measurements were performed as a “temperature titration” by changing *T* in steps of 10–15 K and waiting for equilibrium to be attained (5–10 h). The cells were heated in a vertical resistance furnace with non-inductive coils maintaining a 50 mm long uniform temperature zone, the temperature being measured with a Pt/Pt (10 mass % Rh) thermocouple. Both temperature and emf measurements were made with a high input impedance digital voltmeter (Solartron 7075).

Results and calculations

Emf values obtained. The emf values obtained at various temperatures (*E*_{exp}/mV, *T*/K) from cell (A) and cell (B) are given in Table 1 and Table 2, respectively. The values in

Table 1. The experimental data, *E*_{exp}/mV and *T*/K, and calculated values $\Delta E = E_{\text{exp}} - E$, obtained for cell A.

<i>T</i> /K	<i>E</i> _{exp} /mV	ΔE /mV
1046.5	-39.30	0.38
1063.3	-36.55	0.67
1077.3	-35.60	-0.45
1089.2	-33.27	0.11
1104.5	-31.50	-0.42
1108.1	-30.30	0.23
1117.0	-29.35	-0.17
1133.4	-29.56	-0.90
1135.2	-25.80	0.59
1143.0	-25.40	-0.22
1149.3	-24.10	0.10
1156.8	-23.87	-0.84
1158.7	-22.30	0.43
1160.6	-22.20	0.23
1164.8	-22.72	-0.95
1172.0	-20.85	-0.21
1182.3	-18.50	0.51
1186.2	-18.08	0.31
1186.0	-19.61	-1.35
1193.8	-16.60	0.58
1196.0	-17.11	-0.28
1203.3	-15.05	0.61
1209.4	-15.43	-0.76
1214.0	-13.40	0.53
1224.4	-12.76	-0.52
1228.6	-11.24	0.32
1229.7	-10.60	0.78
1236.8	-11.02	-0.80
1247.0	-7.57	0.97
1249.6	-8.23	-0.11
1255.0	-6.18	1.04
1267.3	-5.85	-0.67
1271.1	-3.42	1.13
1271.2	-5.04	-0.51
1277.3	-3.90	-0.38
1280.9	-1.74	1.17
1287.7	-0.69	1.08
1293.3	-1.68	-0.85
1298.0	1.11	1.14
1302.8	0.12	-0.66
1309.4	0.98	-0.92
1322.4	3.15	-0.97

Table 2. The experimental data, E_{exp}/mV and T/K , and calculated values $\Delta E = E_{\text{exp}} - E$, obtained for cell B.

T/K	$-E_{\text{exp}}/\text{mV}$	$\Delta E/\text{mV}$
1012.9	-310.49	-0.33
1040.5	-316.10	-0.25
1063.1	-320.44	-0.17
1084.4	-324.55	0.00
1094.5	-326.38	0.10
1108.9	-329.00	0.21
1124.2	-331.87	0.18
1125.2	-331.84	0.39
1142.0	-335.07	0.22
1151.8	-336.65	0.40
1159.5	-338.10	0.32
1167.2	-339.15	0.62
1171.4	-341.30	-0.80
1177.8	-340.99	0.62
1178.9	-341.27	0.53
1190.1	-343.13	0.59
1200.1	-345.39	0.02
1216.6	-349.00	-0.84
1219.9	-349.05	-0.35
1225.3	-350.61	-1.02
1227.5	-350.04	-0.10
1250.5	-354.73	-1.11
1251.4	-353.80	-0.03
1259.6	-355.28	-0.23
1268.3	-356.50	-0.09
1277.7	-357.63	0.22
1277.7	-357.92	-0.07
1275.6	-358.00	-0.47
1290.2	-359.82	-0.08
1303.4	-362.21	-0.50
1304.1	-361.78	0.03
1314.6	-362.80	0.55
1315.2	-361.93	1.51
1323.6	-364.73	-0.07

Table 1 are obtained from two different runs, while those in Table 2 are from three different runs. The measured values were smoothed by a least-squares treatment to evaluate the following $E(T)$ relationships (E in mV, T in K)

$$E(\text{A}) = -76.59 - 0.73023T + 0.25349T \log T \quad (1)$$

(1050 < T/K < 1325)

$$E(\text{B}) = 151.14 - 2.1556T + 0.56570T \log T \quad (2)$$

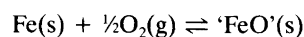
(1000 < T/K < 1325)

The relationships (1) and (2) correspond to the assumption of a constant (but non-zero) value of ΔC_p for the equilibrium reactions considered. Calculated values of the deviations $\Delta E = E_{\text{exp}} - E$ are also given in Tables 1 and 2. The mean errors are: $\sigma E(\text{A}) = \pm 0.73$ mV, $\sigma E(\text{B}) = \pm 0.54$ mV.

Calculation of oxygen pressures. The equilibrium oxygen pressures [$p(\text{O}_2)/\text{atm}$] for the equilibria studied are related to the emf (E/mV) and temperature (T/K) values and the reference oxygen pressures $p^*(\text{O}_2)$ by the equation

$$\log p(\text{O}_2) = \log p^*(\text{O}_2) - \frac{4F}{R \ln 10} \cdot \frac{E \cdot 10^{-3}}{T} \quad (5)$$

where R is the gas constant and F the Faraday constant. The reference oxygen pressures $p^*(\text{O}_2)$, which originate from the equilibrium reaction



can be expressed by the equation²

$$\log p^*(\text{O}_2) = -0.8839 - \frac{26506}{T} + 2.2012 \log T \quad (6)$$

The uncertainty in $\log p^*(\text{O}_2)$ is ± 0.004 at 1000 K. By combining eqns. (1), (5) and (6), and (2), (5) and (6), respectively, the following relationships may be derived:

$$\log p(\text{O}_2, \text{IV}) = 13.837 - \frac{24962}{T} - 2.9089 \log T \quad (7)$$

$$[1050 < T/\text{K} < 1325, \delta \log p(\text{O}_2, \text{IV}) = \pm 0.011]$$

$$\log p(\text{O}_2, \text{V}) = 42.571 - \frac{29553}{T} - 9.2028 \log T \quad (8)$$

$$[1000 \leq T/\text{K} < 1325, \delta \log p(\text{O}_2, \text{V}) = \pm 0.009]$$

Calculated values of $\log p(\text{O}_2, \text{IV})$ and $\log p(\text{O}_2, \text{V})$ at $T = 1100, 1200$ and 1300 K are given in Table 3.

By the application of basic thermodynamics to equilibria (IV)–(VI), it can be shown that

$$\log p(\text{O}_2, \text{VI}) = 0.5 \{0.5 \log p(\text{O}_2, \text{IV}) + 1.5 \log p(\text{O}_2, \text{V})\} \quad (9)$$

Introducing eqns. (7) and (8) into eqn. (9), the following relationship can be evaluated:

$$\log p(\text{O}_2, \text{VI}) = 35.388 - \frac{28406}{T} - 7.630 \log T \quad (10)$$

$$[1050 < T/\text{K} < 1325, \delta \log p(\text{O}_2, \text{VI}) = \pm 0.01]$$

Calculated values of $\log p(\text{O}_2, \text{VI})$ at $T = 1100, 1200$ and 1300 K are given in Table 3, together with corresponding values from the literature.

Calculation of ΔG° values. The Gibbs free energies (ΔG°) for the various equilibrium can be evaluated from the general expression

$$\Delta G^\circ = -R \ln 10 \cdot T \log K \quad (11)$$

where the equilibrium constant K can be substituted as follows:

$$\log K(\text{IV}) = -0.5 \log p(\text{O}_2, \text{IV}) \quad (12)$$

$$\log K(\text{V}) = -1.5 \log p(\text{O}_2, \text{V}) \quad (13)$$

Using the eqns. (7), (8), (12) and (13), the following relationships are derived:

Table 3. The calculated values of oxygen pressures for equilibria (IV), (V) and (VI) from the present study and from data given in the literature.

T/K	log [$p(\text{O}_2, \text{IV})/\text{atm}$]		log [$p(\text{O}_2, \text{V})/\text{atm}$]		log [$p(\text{O}_2, \text{VI})/\text{atm}$]			
	This work eqn. (7)	Ref. 4	This work eqn. (8)	Ref. 4	This work eqn. (10)	Ref. 5	Ref. 6	Ref. 4
1100	-17.703	-17.79	-12.285	-12.31	-13.64	-13.60	-13.54	-13.64
1200	-15.922	-16.18	-10.394	-10.43	-11.78	-11.74	-11.70	-11.83
1300	-14.423	-14.81	- 8.819	- 8.84	-10.22	-10.15	-10.15	-10.30
Uncertainties	± 0.011	± 0.04	± 0.009	± 0.05	± 0.01	± 0.02	± 0.02	± 0.08

$$\Delta G^\circ(\text{IV}) = -238944 + 132.44 T - 27.846 T \log T$$

$$[1050 < T/\text{K} < 1330, \delta\Delta G(\text{IV}) \approx \pm 150 \text{ J} \cdot \text{mol}^{-1}]$$

$$\Delta G^\circ(\text{V}) = -848682 + 1222.5 T - 264.27 T \log T$$

$$[1000 < T/\text{K} < 1330, \delta\Delta G(\text{V}) \approx \pm 350 \text{ J} \cdot \text{mol}^{-1}]$$

Finally, using the results obtained by Björkman and Fredriksson³ in their investigation of equilibrium (III)

$$\Delta G^\circ(\text{III}) = 58120 + 1155.0 T - 342.53 T \log T \quad (14)$$

$$[1025 < T/\text{K} < 1340, \delta\Delta G(\text{VI}) \approx \pm 600 \text{ J} \cdot \text{mol}^{-1}]$$

the ΔG° relationships of equilibria (I) and (II) can be calculated

$$\Delta G^\circ(\text{I}) = -297064 - 1022.6 T + 314.68 T \log T$$

$$1050 \leq T/\text{K} < 1325, \delta\Delta G(\text{I}) \approx \pm 600 \text{ J} \cdot \text{mol}^{-1} \quad (15)$$

$$\Delta G^\circ(\text{II}) = -790562 + 2377.5 T - 606.80 T \log T$$

$$1050 < T/\text{K} \leq 1325, \delta\Delta G(\text{II}) \approx \pm 800 \text{ J} \cdot \text{mol}^{-1} \quad (16)$$

Discussion

Table 3 shows the values of $\log p(\text{O}_2)$ obtained in the present study at the temperatures 1100, 1200 and 1300 K for the equilibria (IV), (V) and (VI), as well as the corresponding values from the literature. The values obtained for equilibria (IV) and (V) can be compared with those presented by Kumar and Kay,⁴ who also studied these equilibria by solid-state emf measurements. However, they used air instead of the couple (Fe, 'FeO') as reference system. This means that the differences in the oxygen pressures between sample and reference mixtures were quite high in their cells, in which cases oxygen can diffuse from one side of the electrolyte to the other, giving rise to erroneous emf values. The results obtained by Kumar and Kay⁴ deviate insignificantly from the present values for equilibrium (V), but significantly for equilibrium (IV), where the deviation amounts to 0.26 $\log p(\text{O}_2)$ units at 1200 K.

A check of the reliability of the overall results can be accomplished by a comparison of the calculated values of equilibrium (VI) with corresponding values determined directly.^{4,6} From Table 3 it can be seen that the present values fit in nicely between those given in the literature. This good agreement proves the successful use of the auxiliary couple (Cu, Cu₂S) to determine oxide-sulfide and oxide-sulfate equilibria in the system Ca-S-O. Work is now in progress using the (Cu, Cu₂S) couple to study equilibrium conditions in some other metal-S-O systems.

By considering the accurate ΔG° - T relationship of equilibrium (III), as determined by Björkman and Fredriksson³ (with a stated uncertainty of ± 600 J), the ΔG° values presented here for equilibria (I) and (II) are judged to be reliable to well within ± 1000 J. By way of example, eqn. (15) gives at 1200 K the value $\Delta G^\circ(\text{I}) = -361.4 \pm 0.6$ kJ, and eqn. (16) the value $\Delta G^\circ(\text{II}) = -179.7 \pm 0.8$ kJ. The corresponding $\Delta G^\circ(\text{I})$ value evaluated from Ref. 8. is -363.2 ± 5 kJ, and the $\Delta G^\circ(\text{II})$ value from Barin *et al.*⁹ is -170.1 ± 5 kJ. It can thus be stated that the present study has yielded quite improved values for the industrially important equilibria (I) and (II).

Acknowledgement. This work was supported financially by the Swedish Natural Science Research Council.

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