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THERMOCHEMISTRY OF THE Co-S-O SYSTEM FROM 950 TO 1200°K

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EXTRACTION METALLURGY DIVISION

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THERMOCHEMISTRY OF THE Co-S-O SYSTEM FROM 950 to 1200°K

T. R. Ingraham

Abstract

Total pressures produced by the decomposition of $CoSO_4$ and by the decomposition of mixtures of CoO and Co_3O_4 were measured, using a Pyrex bellows mercury manometer. At temperatures in excess of 782°C, in the presence of its gaseous decomposition products, $CoSO_4$ produces CoO. At temperatures less than 782°C, the oxide product is a mixture of CoO and Co_3O_4. Perhaps because of the high surface energy of the finely divided oxides, an irreversible metastable equilibrium can be observed during the initial part of an experiment for the measurement of the oxygen pressure over mixtures of CoO with Co_3O_4.

Free energies for the sulphate and oxide decomposition reactions were combined with published data on CoO, CoS, Co_9S_8, SO_3 and SO_2 to produce thermodynamic phase diagrams for the various univariant and bivariant equilibria existing between 950 and 1200°K.

The transition from β to α cobalt sulphate occurs at 675 ± 10°C and involves 0.60 ± 0.04 kcal/mole.

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INTRODUCTION

"The distribution of cobalt among sulphide minerals is a matter of considerable economic importance." (1) Even though large tonnages of cobalt are recovered annually from sulphide sources, the art involved in the recovery processes is substantially more advanced than its science. The deficiencies in present knowledge of the cobalt-sulphur-oxygen system include identification of some of the phases present at various temperatures, and information on the relative stability of the various phases.

In this paper, data will be reported for measurements of the dissociation pressures generated over cobalt sulphate and over mixtures of cobalt monoxide and tricobalt tetroxide. The results will be combined with established data for other cobalt, sulphur and oxygen compounds, to produce phase diagrams and to establish the thermodynamics of the univariant and bivariant equilibria existing in the cobalt-sulphur-oxygen system between 950 and 1200°K.

MATERIALS, APPARATUS AND PROCEDURE

The cobalt source material used in all experiments was Baker and Adamson reagent-grade hydrated cobaltous sulphate. for which the following analysis was supplied by the manufacturer: insoluble 0.01%, Cl 0.001%, Fe 0.03%, Ni 0.10%, NO_3 0.005%, Cu 0.005%, Pb 0.005%. alkali and earth metals 0.25%.

Anhydrous cobalt sulphate was obtained by dehydration of this material at 400°C for 48 hours in a muffle furnace. Tricobalt tetroxide was obtained by additional decomposition of the sulphate in the muffle furnace at 850°C for 50 hours. Cobalt monoxide was obtained by decomposition of tricobalt tetroxide under vacuum in a silica vessel at 850°C over a period of 24 hours. Material compositions were confirmed by X-ray analysis.

The experimental technique used was that of measuring the pressure produced at various temperatures by the decomposition, in an evacuated space, of cobalt sulphate and of mixtures of cobalt monoxide and tricobalt tetroxide. The apparatus used was a U-tube mercury manometer in which the mercury was protected from attack by corrosive gases by enclosure in a flexible Pyrex bellows. This apparatus and its use for measurement of a variety of equilibria have been described in earlier publications (2, 3, 4, 5).

Before beginning a run, the interior of the entire apparatus, including the bellows manometer and the Pyrex connecting tubing, was thoroughly washed in situ with acid and distilled water to remove any traces of reactants or products from a previous run. The apparatus was dried by sealing and evacuating for 10 hours at operating temperature. After cooling, the apparatus was opened and a previously dried sample contained in a platinum boat was introduced. The apparatus was then resealed and evacuated with a rotary pump for several hours. In the final period of 1 hour before the apparatus was isolated from the pump, the sample temperature was increased slowly until incipient decomposition had begun. This ensured the expulsion of the last traces of water from sulphate samples and the presence of sufficient reaction product to enhance the reversibility of the decomposition reaction. Equilibrium was established within 10 to 24 hours in both the sulphate and oxide systems.

RESULTS AND DISCUSSION

Decomposition of Cobaltous Sulphate

When anhydrous cobaltous sulphate is thermally decomposed in air and the process is observed by differential thermal analysis, three stages are identifiable. The first endotherm represents an apparently irreversible change in crystal structure (low temperature β to high temperature α) which occurs at 675 ± 10°C (when a 3°C per minute heating rate is used). The second endothermic peak occurs near 945°C and is caused by the decomposition of α cobaltous sulphate to cobalt monoxide.

The oxidation of cobalt monoxide to tricobalt tetroxide may be observed by cooling the sample. The exotherm for this oxidation occurs at 827°C. The reactions involved are:

$$\beta\ CoSO_4 \rightleftharpoons \alpha\ CoSO_4 \tag{1}$$

$$\alpha\ CoSO_4 \rightleftharpoons CoO + SO_3 \tag{2}$$

$$SO_3 \rightleftharpoons SO_2 + 1/2\ O_2 \tag{3}$$

$$3\ CoO + 1/2\ O_2 \rightleftharpoons Co_3O_4 \tag{4}$$

A crystal change in cobalt sulphate was reported by Warner (6), who identified, by X-ray diffraction studies, the crystal forms of cobaltous sulphate occurring below 613°C and above 620°C. The energy change for this recrystallization from β to α cobaltous sulphate has not been reported, but a value was estimated in this study, using the method described by Ingraham and Kellogg (4). In that method, a weighed amount of potassium sulphate is substituted for the usual alumina standard in a differential thermal analysis run. As the temperature is progressively increased, the endothermic peaks corresponding to each recrystallization appear on opposite sides of a centre base line. Since the area under each peak is proportional to the number of moles of material and the heat of its crystal change, the heat of the unknown crystal change may be readily calculated from the peak areas and the weights of material. The peak area can be determined within ± 1 per cent by weighing the cut-out of a photostat of the graph of the peak. By assuming that the heat of transition of potassium sulphate is 2.14 kilocalories per mole, it was estimated that the crystal transition of cobalt sulphate, which occurred at 675 ± 10°C, involved 0.60 ± 0.04 kilocalories per mole. This is small in comparison with most of the heats of crystal change for sulphates reported by Kubaschewski and Evans (7).

Table I

Total Gas Pressures Developed Over $CoSO_4$

t(° C)	P(atm)	t(° C)	P(atm)	t(° C)	P(atm)
699.1	0.00599	787.7	0.04761	861.7	0.22346
708.3	0.00770	794.6	0.05664	867.7	0.25826
718.0	0.01022	810.1	0.07322	871.1	0.27508
726.9	0.01277	814.1	0.08293	881.5	0.34558
736.6	0.01526	819.8	0.09529	895.6	0.44484
742.8	0.01830	824.5	0.11147	904.2	0.53033
747.6	0.01830	833.6	0.12733	909.1	0.59436
750.8	0.01998	838.9	0.14098	914.6	0.65167
758.0	0.02400	849.3	0.17867	922.0	0.75202
765.6	0.02978	857.5	0.21866	930.1	0.84519
771.8	0.03396			937.2	0.95173
780.1	0.04186				

The total gas pressures developed when cobaltous sulphate was decomposed are shown in Table I. When the results shown in Table I were converted to logarithm of total pressure and reciprocal temperature and plotted in Figure 1, it was evident from the abrupt change in slope at 782° C that two processes were involved. Similar but not so well defined changes in slope were observed by Warner (6) and by Marchal (8). Warner (6) assumed that the change in slope was due to an error in the pressure measurements caused by thermal segregation. The work of Ingraham and Kellogg (4) on zinc sulphate has indicated that thermal diffusion errors are likely to be small in the apparatus used to make these pressure measurements. It seems more likely that the change in slope is due to the formation of different cobalt oxides under different temperature conditions. This premise may be verified by calculating the sum of the partial gas pressures developed during decomposition at temperatures less than 782° C. The method of making the calculation is as follows:

(a) The equation for the partial pressure of sulphur trioxide is calculated from the total pressure data shown in Table I for temperatures in excess of 782° C. This calculation requires the equilibrium constant for sulphur trioxide dissociation and it assumes that the sulphur dioxide partial pressure in the system is twice that of oxygen, in agreement with Equation 3.

The details of this type of calculation are discussed in references 4 and 5.

(b) The equation for the partial pressure of oxygen in the system is calculated from the dissociation of tricobalt tetroxide.

(c) The equilibrium constant for sulphur trioxide dissociation is used with the equation for sulphur trioxide pressure from (a) and oxygen pressure from (b) to calculate the sulphur dioxide pressure at any selected temperature below 782° C.

If the assumption of a mixed oxide product is correct, then the sum of the partial pressures from (a), (b) and (c) should, within experimental error, equal the experimentally determined total pressure shown in the first column of Table I.

Using the sigma calculation of Kelley (9) and the specific heat data of Kelley (10) for cobaltous sulphate, cobaltous oxide and sulphur trioxide, the following thermodynamic quantities were calculated from the results in the second and third columns of Table I, for the reaction:

$$CoSO_{4(\alpha)} \rightleftharpoons CoO + SO_3$$

$$\Sigma = -R\ln p_{SO_3} - 4.66 \ln T - 0.89 \times 10^{-3}T + 1.41 \times 10^{5}T^{-2} = \Delta H_0/T + I$$

$$\Delta H^{o}_{(\alpha)} = 61,665 - 4.66T - 0.89 \times 10^{-3}T^{2} - 2.82 \times 10^{5}T^{-1}$$

$$\Delta F^{o}_{(\alpha)} = 61,665 + 10.730T \log T + 0.89 \times 10^{-3}T^{2} - 1.41 \times 10^{5}T^{-1} - 80.026T$$

$$\text{or} \quad \Delta F^{o}_{(\alpha)} = 62,362 + 15.0T \log T - 92.784T \quad (950°-1200°K)$$

The foregoing equations are valid only within the range of stability of $CoSO_{4(\alpha)}$. To extrapolate the quantities to room temperature, it is necessary to consider the heat of the transition:

$$CoSO_{4(\beta)} \longrightarrow CoSO_{4(\alpha)} \; : \; \Delta H = 600 \text{ cal/mole}$$

Thus, for the reaction: $CoSO_{4(\beta)} \rightleftharpoons CoO + SO_3$, by summation on the assumption that the specific heat for the α form of $CoSO_4$ is the same as that for the β form, the enthalpy and free energy equations are:

$$\Delta H^{o}_{(\beta)} = 62,265 - 4.66T - 0.89 \times 10^{-3}T^{2} - 2.82 \times 10^{5}T^{-1}$$

$$\Delta F^{o}_{(\beta)} = 62,265 + 10.730T \log T + 0.89 \times 10^{-3}T^{2} - 1.41 \times 10^{5}T^{-1} - 80.026T$$

$$\Delta H^{o}_{298} = 59,850 \qquad \Delta F^{o}_{298} = 45,925$$

Although the foregoing calculations are in substantial disagreement with the early work and suggestions of Warner (6), a recent revision (11) of his data—based on (a) the presence of two cobalt oxides, (b) accurate results for the oxygen pressure of the CuO-Cu_2O couple, (c) and deletion of the concept of thermal diffusion—agrees within 0.5 kcal per mole with the above results.

From the heats and free energies of formation at 298.2°K given by Coughlin (12) for cobaltous oxide and sulphur trioxide, the following estimate has been made of the heat and free energy of formation of cobaltous sulphate:

$$\Delta H^{o}_{298} = -227,050 \text{ cal/mole} \qquad (-223,700)\#$$

$$\Delta F^{o}_{298} = -195,725 \text{ cal/mole} \qquad (-193,330)\#$$

When the literature was examined to obtain data on the dissociation of tricobalt tetroxide to combine with the foregoing free energy data for the dissociation of cobalt sulphate, the data shown in Table II were found. It is evident from an examination of Table II that there is sufficient disagreement to warrant additional study of the system.

Table II

Linear Equations for Oxygen Pressure Over Co_3O_4

$$2\ Co_3O_4 \rightleftharpoons 6\ CoO + O_2$$

Source	Log p_{O_2}	ΔH
Kubaschewski and Evans (7)	$15.472 - 1.914 \times 10^4/T$	87.6 kcal
Watanabe (13)*	$13.349 - 1.677 \times 10^4/T$	76.7 kcal
Watanabe (13)**	$12.355 - 1.580 \times 10^4/T$	72.3 kcal
Foote and Smith (14)	$12.352 - 1.535 \times 10^4/T$	70.2 kcal
Roiter and Paladino (15) and Aukrust and Muan (16)	$13.900 - 1.585 \times 10^4/T$	72.5 kcal

The above equations were calculated from the published data * for 100 mole per cent Co_3O_4 and ** for 50 mole per cent each of CoO and Co_3O_4.

Decomposition of Tricobalt Tetroxide

Experiments on the decomposition were made in the same apparatus as was used to study the decomposition of the sulphate. Since the work of Watanabe (13) had indicated a strong possibility of solid solution formation in the 0-10 and 90-100 mole per cent ranges for mixtures of cobaltous oxide and tricobalt tetroxide, the size and composition of the sample used for study were carefully selected. One-to-one molar ratios of the two oxides were used in amounts sufficient to maintain the composition of the residual sample within the 30-to-70 mole per cent region for each oxide, at the maximum amount of decomposition studied. The results of a series of experiments are shown in

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\# The bracketed values are estimates made from the data of Kelley (9), based on S_2 as the standard state of sulphur at 298°K.

Tables IIIa and IIIb and in Figure 1. The results represented by the closed black circle in Figure 1 do not represent true equilibrium. They were not reproducible after the sample had been heated above about 890° C. The points represented by the open triangles could be reproduced at will on excursions from high to low temperature or vice versa. The equations for the two linear relationships are as follows:

(1100-1160°K) $\log p_{O_2} = 15.065 - 1.843 \times 10^4/T$ $\Delta H = 84.3$ kcal/mole

(1086-1219°K) $\log p_{O_2} = 12.809 - 1.580 \times 10^4/T$ $\Delta H = 72.3$ kcal/mole

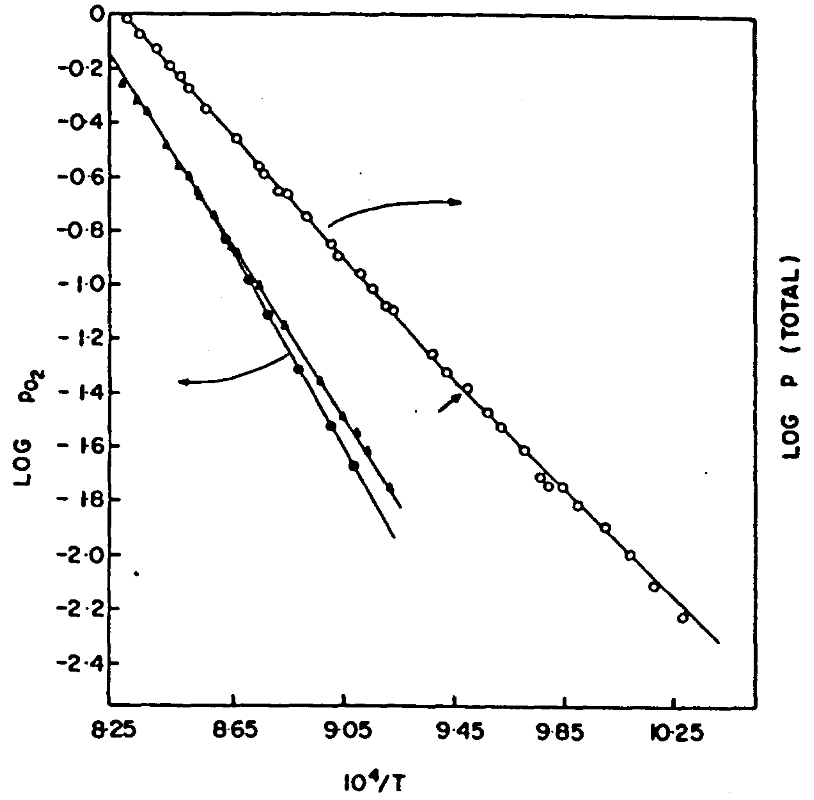

Figure 1. Log pressure versus reciprocal temperature relationships

● metastable equilibrium CoO – Co_3O_4

▲ reversible equilibrium CoO – Co_3O_4

○ reversible equilibrium $CoSO_4$ – CoO (from $10^4/T$ = 8.26 to 9.48)

○ reversible equilibrium $CoSO_4$ – Co_3O_4 (from $10^4/T$ = 9.48 to 10.35)

A comparison of these equations with those shown in Table II leads to the conclusion that the data selected by Kubaschewski and Evans (7) probably refer to the irreversible metastable equilibrium between the two oxides. The results of Foote and Smith (14), Roiter and Paladino (15) and Aukrust and Muan (16), and some of the results of Watanabe (13), agree with our results for

Table IIIa

Oxygen Pressures Developed Over 1:1 CoO:Co_3O_4
on the Initial Increase of Temperature

t(°C)	P(atm)	t(°C)	P(atm)
828.0	0.02115	865.1	0.07685
837.0	0.02962	875.2	0.10407
852.4	0.04849	886.3	0.14695

Table IIIb

Oxygen Pressures Developed Over 1:1 CoO:Co_3O_4
when Equilibrium is Established on Temperature Increase and Decrease

t(°C)	P(atm)	t(°C)	P(atm)	t(°C)	P(atm)
812.6	0.01789	870.3	0.09942	904.3	0.25927
822.2	0.02456	880.9	0.13161	909.8	0.27642
827.2	0.02848	885.0	0.14138	914.4	0.32612
832.8	0.03228	892.2	0.18039	925.6	0.44459
842.6	0.04470	899.2	0.21176	930.0	0.48092
859.8	0.07116	900.1	0.21573	937.8	0.56158
				945.6	0.67821

the reversible equilibrium between the two oxides. Although the difference between the two sets of data can be explained by the solid solution proposal of Watanabe (13), the recent work of Roiter and Paladino (15) and Aukrust and Muan (16) seems to indicate conclusively that "the two phases were stoichiometric within experimental error" (15). The argument against solid solution is reinforced by our observation that the beginning of an experiment relates to a metastable equilibrium. The existence of these metastable equilibria is well established. It has been suggested by Kelley (17) that the high surface energies of finely divided oxides can lead to erroneous free energy determinations because the free energy of the finely divided material may differ by as much as 5 kilocalories per mole from that for coarsely crystalline material. Since 8 moles of oxides are involved in the production of a mole of oxygen by Reaction 4, the deviation from 72.3 kcal/mole for the stable oxides to 84.3 kcal/mole for the metastable oxides is quite reasonable.

When the foregoing results for the equilibrium dissociation of tricobalt tetroxide were combined with results for the dissociation of cobalt sulphate and the equilibrium constant for the dissociation of sulphur trioxide, an equation for the total dissociation pressure was obtained. This is shown as the line drawn in Figure 1 between the temperatures 693°C and 782°C ($10^4/T = 9.48$ to 10.35). The excellent agreement between this theoretical line and the experimental points supports the conclusion that the inflection in the curve is caused by a change in the reaction product rather than by the effects of thermal diffusion.

Construction of Phase Diagrams

Following the method suggested by Kellogg and Basu (18) in their study of the lead-sulphur-oxygen system, thermodynamic phase diagrams have been constructed for the cobalt-sulphur-oxygen system, showing the stable univariant and bivariant equilibrium relationships.

The univariant equilibria in the ternary system are shown enclosed by the appropriate tie lines in Figure 2. Choice of the compound Co_9S_8 was based on the work of Rosenqvist (19). The individual chemical reactions and the equilibrium constants required for the calculation of the univariant equilibria are shown in Table IV, and the results from calculation of the logarithms of the univariant equilibrium constants are shown in Table V. The results are shown in Figure 3 for the equilibrium relationship for reactions A, B, C and D in Table V.

In Table VI, the logarithm of the equilibrium constant is shown for the bivariant equilibria in the system at 950°K and 1200°K. The temperature of 950°K was selected as being the most representative of commercial roasting practice on cobaltiferous pyrite (20). It has been reported, for example, that maximum sulphation of cobalt is obtainable in a fluid bed roaster at 925-975°K, using a gas containing 8 per cent sulphur dioxide and 4 per cent oxygen. The temperature of 1200°K was selected to illustrate the instability of cobalt sulphate in normal roaster gas atmospheres at elevated temperatures. The univariant and bivariant equilibria for both temperatures are shown in Figure 4, in which the solid line represents the 950°K data and the broken line represents the 1200°K data. The solid circle near the right centre of the diagram was positioned to represent 5 per cent each of sulphur dioxide and oxygen - a rough average roaster gas composition. From the solid lines, it is evident that at 950°K the stable phase corresponding with a gas composition of 5 per cent of sulphur dioxide and oxygen is cobalt sulphate. It is evident, however, that at 1200°K, because of the migration of the bivariant equilibria boundaries to the upper right-hand side of the diagram, cobalt sulphate is not a stable phase in normal roaster gas compositions. Cobalt monoxide is the stable phase.

Table IV. Equilibrium Constants for Basic Reactions in Co-S-O System

Reaction	log K					
	950°K	1000°K	1050°K	1100°K	1150°K	1200°K
$1/2\ O_2 + SO_2 \rightleftharpoons SO_3$ (ref. 21)	0.517	0.257	0.022	-0.189	-0.382	-0.557
$1/2\ S_2 + O_2 \rightleftharpoons SO_2$ (ref. 21)	16.089	15.092	14.194	13.376	12.629	11.943
$Co + 1/2\ O_2 \rightleftharpoons CoO$ (ref. 12)	9.138	8.479	7.883	7.341	6.846	6.392
$9/4\ Co + S_2 \rightleftharpoons 1/4\ Co_9S_8$ (ref. 7)	9.528	8.617	7.792	7.043	6.358	5.731
$CoO + SO_3 \rightleftharpoons CoSO_4$ (author)	3.833	3.186	2.606	2.083	1.607	1.174
$3\ CoO + 1/2\ O_2 \rightleftharpoons Co_3O_4$ (author)	1.912	1.496	1.120	0.778	0.466	0.179

Table V. Stable Univariant Equilibria in the Co-S-O System

Point	Reaction	log K					
		950°K	1000°K	1050°K	1100°K	1150°K	1200°K
A	$Co_9S_8 + 16\ CoO \rightleftharpoons 25\ Co + 8\ SO_2$	-6.952	-6.175	-5.468	-4.827	-4.241	-3.706
B	$Co_9S_8 + 25\ CoSO_4 \rightleftharpoons 34\ CoO + 33\ SO_2$	+1.975	+2.342	+2.657	+2.957	+3.229	+3.478
C	$30\ CoSO_4 + 51\ CoS_2 \rightleftharpoons 9Co_9S_8 + 60\ SO_2$	+2.454	+2.800	+3.113	+3.401	+3.664	+3.903
D	$CoSO_4 + 2\ CoO \rightleftharpoons Co_3O_4 + SO_2$	-2.435	-1.947	-1.505	-1.115	-0.760	-0.435

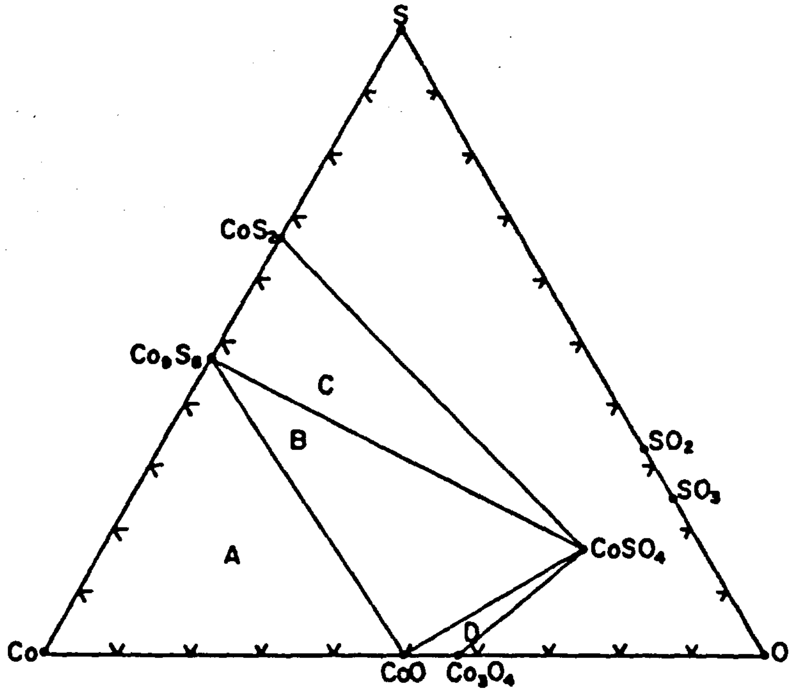

Figure 2. Tie line relationships for stable Co–S–O compounds in the range of temperature from 950°K to 1200°K.

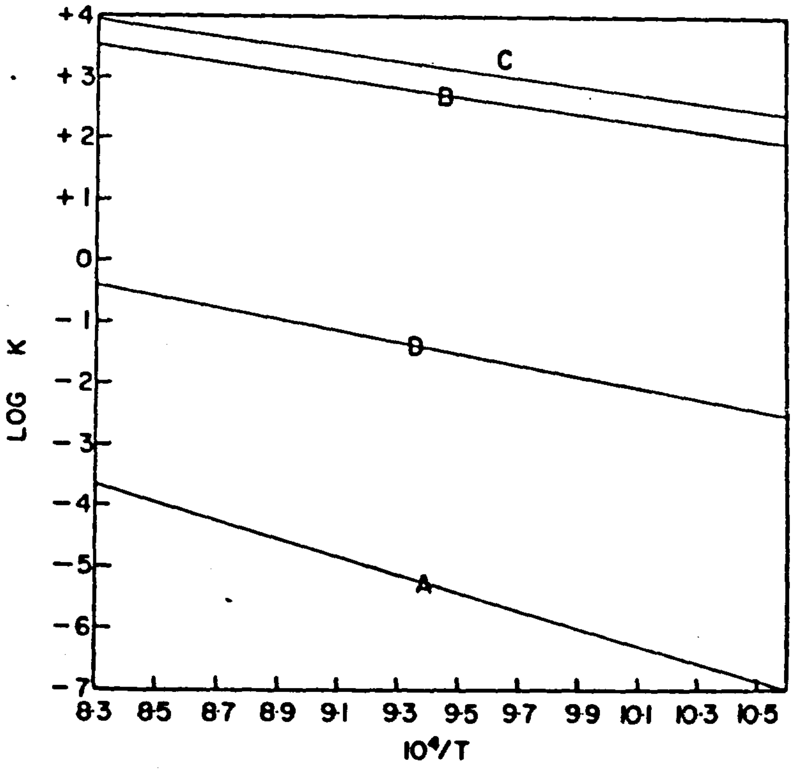

Figure 3. Variation of logarithm of equilibrium constant with reciprocal temperature for the stable univariant equilibria in Table V.

Table VI

Stable Bivariant Equilibria in the Co-S-O System

Reaction	log K	
	950°K	1200°K
$Co_9S_8 + 8\ O_2 \rightleftharpoons 9\ Co + 8\ SO_2$	+ 90.599	+ 72.622
$9\ CoO + 8\ SO_2 \rightleftharpoons Co_9S_8 + 25/2\ O_2$	-172.845	-130.152
$CoSO_4 \rightleftharpoons CoO + SO_2 + 1/2\ O_2$	- 4.347	- 0.615
$3\ CoSO_4 \rightleftharpoons Co_3O_4 + 3\ SO_2 + O_2$	- 11.129	- 1.666
$Co_9S_8 + SO_2 + 17\ O_2 \rightleftharpoons 9\ CoSO_4$	+211.970	+135.689
$9\ CoS_2 + 10\ O_2 \rightleftharpoons Co_9S_8 + 10\ SO_2$	+150.444	+121.144
$CoS_2 + 3\ O_2 \rightleftharpoons CoSO_4 + SO_2$	+ 40.268	+ 28.537

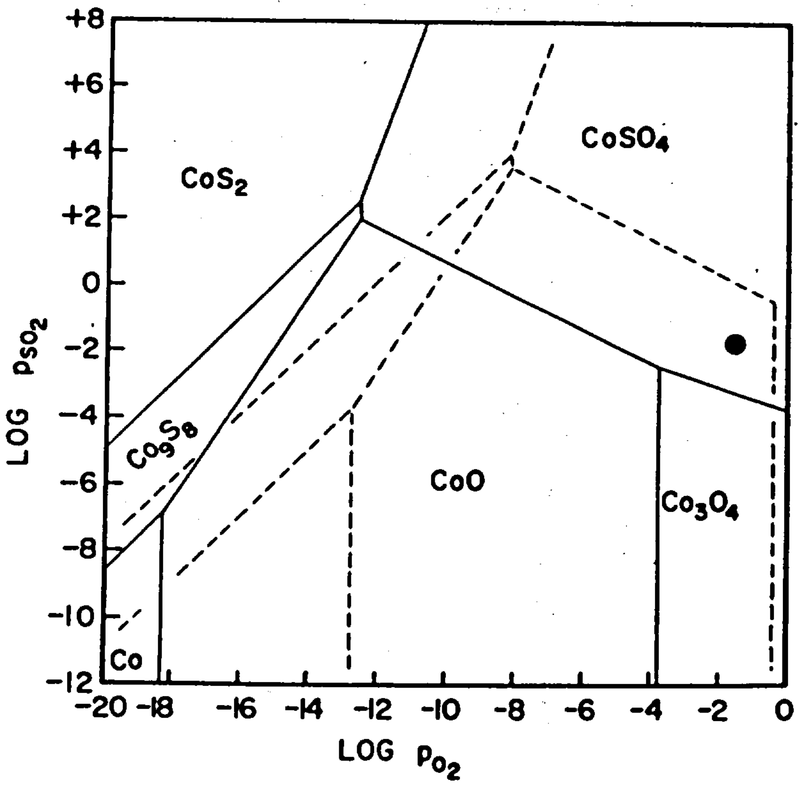

Figure 4. Predominance-area diagram showing the stable univariant equilibria and stable bivariant equilibria in Tables V and VI for temperatures of 950°K and 1200°K. Solid line 950°K, broken line 1200°K.

Figure 4 can also be used to make thermodynamic predictions of the phases which might be expected to occur during the roasting of a sulphide at 950°K. If, for example, a horizontal line is drawn to the left across the diagram from the solid circle, it is possible to predict that, at a constant sulphur dioxide pressure of say 5 per cent, as the oxygen pressure increases at the interface during roasting, the first transition to occur is from CoS_2 to Co_9S_8. The next phase to form is CoO, produced by the oxidation of Co_9S_8. The final phase to appear is $CoSO_4$, which is formed by the sulphation of CoO. It is evident that at 950°K, unless the sulphur dioxide pressure were kept below 1 per cent ($\log p_{SO_2} = -2$), Co_3O_4 would not occur as a thermodynamically stable phase. By a similar argument, it can be established that it would be entirely unlikely for metallic cobalt to be formed during normal roaster operations.

The diagram can also be used to expose one of the recurring fallacies in metallurgical text books regarding the formation of some sulphates directly from sulphides. In the cobalt system it is evident that the direct conversion could occur only at partial pressures of sulphur dioxide in excess of 260 atmospheres ($\log p_{SO_2} = +2.4$). The conversion directly from sulphides is entirely improbable in the range of normal operations.

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