

A THERMOGRAVIMETRIC TECHNIQUE FOR CONTINUOUS QUANTITATIVE SULPHUR ANALYSIS AT ELEVATED TEMPERATURES

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(Received October 7, 1970)

The problems of conventional methods for determining sulphur content at elevated temperatures are discussed and a thermogravimetric technique for a direct continuous analysis is described. The technique is illustrated by employing the Cu–S system at 1200° and with a discussion of the necessary correction factors for buoyancy and volatilization being included.

Thermodynamical equilibrium properties have for a long time been the weapon of the chemical metallurgist for tackling steady state problems encountered in process metallurgy. Together with oxides, sulphide ores provide a valuable source for many metals (Cu, Ni, Zn, Pb, etc.) and thus an extensive knowledge of the thermodynamics of the sulphide systems at their process temperatures is essential if one wishes to perform study upon the extraction problems.

Typical of these sulphide systems is the Cu–S binary which for many years has excited interest in view of the fact that it can exist at a given temperature over an appreciable composition range. This range is completely dependent upon the partial pressure of the sulphur gas in equilibrium with the Cu–S phase. Thus, one finds that as the Cu : S ratio approaches and slightly exceeds that corresponding to stoichiometric Cu_3S , the partial pressure of sulphur gas in equilibrium approaches atmospheric pressure [1].

Consequently, due to the wide range of compositions of the Cu–S binary and also the fact that metallic copper has a reasonable partial pressure at elevated temperatures which could lead to volatilization problems, this system was chosen as a suitable example upon which to develop the gravimetric technique.

Conventional techniques

Copper–sulphur equilibria have been studied by numerous investigators covering a wide range of compositions and temperatures, including solid and liquid phases of both invariant and univariant equilibria. Relationships have been obtained between the various compositions and the equilibrium partial pressures of S_2 , most of which have been well reviewed by Kellogg [2].

Generally, the technique employed by these workers is to bubble gases containing a known partial pressure of sulphur p_{S_2} into the pure copper held in an inert vessel (usually high purity alumina) with the whole being maintained at a constant temperature. When equilibrium has been established, small samples are drawn off, cooled and chemically analysed for Cu and S. However, the techniques have several inherent drawbacks.

(i) Attainment of equilibrium

(a) By continuously analysing entrance and exit gases until they become the same and remain so for several hours, one can justifiably claim equilibrium has been established. However, the accuracy of this method depends upon the accuracy of analysis which tends to be rather poor, especially at low sulphur pressures. Also when the sulphur pressure is high, elemental sulphur tends to deposit on cooling and so even at equilibrium the entrance and exit gases will not be the same [3]. Thus, each determination involves many gas analyses and adjustments of ingoing gas compositions to find the equilibrium condition.

(b) Gocken [4] reported that the time taken to reach equilibrium is a mathematical function of the mass of the sample, bubbling rate, temperature, distance from equilibrium, as well as direction of equilibrium, and this time can vary from a few minutes to several days.

(c) As an alternative to frequent exit/entrance gas analyses and adjustments, or the adoption of a crude reaction rate equation, equilibrium points have also been reached by bubbling a constant p_{S_2} through the sample for several days and then assuming equilibrium has been obtained.

(ii) Partial pressure of S_2

There are two main techniques for applying a variable p_{S_2} .

(a) By producing a known H_2S/H_2 mixture at room temperature, the partial pressure of S_2 developed at the elevated temperature due to some dissociation of H_2S may be readily defined from a knowledge of the standard free energy change for the reaction:



since

$$K_1 = \text{antilog}_{10} \left(- \frac{\Delta G_1^0}{4.575 T} \right)$$

and

$$p_{S_2}^{1/2} = \frac{1}{K_1} \frac{P_{H_2S}}{P_{H_2}}$$

Two expressions for reaction (1) are offered, both based on data from JANAF [5]:

$$(1000-1400^\circ\text{K}) \Delta G_1^\circ = -21,268 + 0.6878 T \log T + 9.364 T$$

$$K_1 = \text{antilog}_{10}(4648.3/T - 0.1503 T \log T - 2.0467)$$

hence

$$(1340-1700^\circ\text{K}) \Delta G_1^\circ = -21,642 + 11.795 T$$

and

$$K_1 = \text{antilog}_{10}(4729.9/T - 2.5778)$$

However, there are other associated equilibria which should be considered:



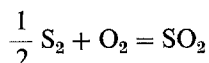
Braune et al. [12] and Richardson and Jeffes [13] have listed free energy data showing that the polymerization of S_2 according to Equ. (2) is insignificant. Variable data exists for the dissociation of S_2 in Equ. (3) [13-15] but even the most favourable does not provide enough monoatomic sulphur to significantly affect the composition of the gas mixture. Variable data also exists for the formation of HS. By assuming a negligible entropy change, since the volume change between reactants and products is small, the free energy of Equ. (4) is then equal to the enthalpy change which is taken as 8,700 cal. Though insignificant at low temperatures, above 1000°, the formation of HS should be taken into account. In this fashion it is possible to determine the input room temperature $p\text{H}_2\text{S}/p\text{H}_2$ ratio necessary to provide a given p_{S_2} at the elevated temperature. Equilibria requiring an extremely low p_{S_2} , e.g. at 1200°, $p_{\text{S}_2} = 10^{-6}$ atm is produced from an input $\text{H}_2\text{S}/\text{H}_2$ ratio $\approx 1/2500$. This extremely low ratio is critically controlled by initially diluting the H_2S by a known factor of inert argon as discussed in the Appendix. Apart from possible thermal segregation of H_2 and H_2S (mol. wt. 2 and 34, respectively) at the elevated temperatures, which may be reduced by using a relatively rapid gas flow, and also the associated problems of elemental sulphur decomposition in the cooler zones, none of the published reports using this gas mixture for sulphide investigations have forwarded any additional problems.

(b) Though experimentally a similar technique, an alternative to $\text{H}_2\text{S}/\text{H}_2$ gas mixtures, but less attractive for providing the p_{S_2} at elevated temperatures, is that of S_2-N_2 gas mixtures [6-8]. The mixture is prepared by bubbling purified nitrogen at about 150 cc/min through a bath of pure molten sulphur held in a thermostated bath of Wood's metal, and the gas mixture is led to the furnace system through heated Pyrex tubing. The S_2 partial pressure in the gas mixture is calculated from the following equation:

$$p_{\text{S}_2(T)} = p / \{1 + (2/x) [(p/p_{\text{S}_x}) - 1]\}$$

where p_{S_x} (atm) is the saturated vapour pressure of the liquid sulphur, x is the average number of sulphur atoms per molecule [9, 10] and p which is generally equal to 1 atmosphere is the total pressure at the temperature T . The experimental equilibrium and chemical analysis are identical to that for $p\text{H}_2\text{S}/p\text{H}_2$ gas mixtures.

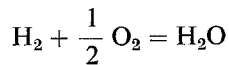
The results obtained by this alternative equilibrium tend to be in poor agreement with themselves and with the more conventional $\text{H}_2\text{S}/\text{H}_2$ techniques [8, 9]. The discrepancies may be attributed to the different methods of chemical analysis for %S, but as has been pointed out by Nagamori [11] it may also be due to the influence of a small partial pressure of oxygen in the system. At 1200° for nearly stoichiometric Cu_2S , the p_{S_2} in equilibrium with it varies from between 10^{-6} to slightly less than 1 atm, whereas the p_{O_2} in equilibrium with Cu_2O is approximately 10^{-5} atm (i.e. stable Cu_2O exists if $p_{O_2} > 10^{-5}$ atm). This represents similar competing powers of both S_2 and O_2 for elemental copper. Experiments by Rosenqvist using an S_2 - N_2 gas mixture showed the presence of SO_2 in the outlet gas. For in the case of $p_{S_2} = 1.1 \times 10^{-1}$ atm and assuming $p_{\text{SO}_2} = 0.001$, from the equilibrium:



$$K = \frac{p_{\text{SO}_2}}{p_{\text{S}_2} \cdot p_{\text{O}_2}} = 1.04 \times 10^{-1} \text{ at } 1200^\circ$$

the ensuing equilibrium $p_{\text{O}_2} \approx 10^{-12}$ atm.

Alternatively consider the corresponding equilibria for $\text{H}_2\text{S}/\text{H}_2$ gas mixtures represented by



$$K = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} \cdot p_{\text{O}_2}^{1/2}} = 7.4 \times 10^5 \text{ at } 1200^\circ,$$

the $p_{\text{O}_2} \approx 10^{-18}$ atm. Consequently, $\text{H}_2\text{S}/\text{H}_2$ gas mixtures provide an impurity p_{O_2} gas level that is many orders of magnitude lower than that of S_2 - N_2 mixtures. Fortunately, in the case of Cu-S studies the p_{O_2} impurity level would not be expected to produce any extensive adverse effects upon the equilibrium, but in the case of other metal-sulphur studies, the oxidation may be considerable.

(iii) Sampling and analysing

All workers have expressed difficulties experienced in sampling techniques and in chemically analysing for the sulphur. Sampling involves lowering a Vycor or silica tube into the melt and drawing up several grams of sample. Sulphur losses

on cooling and contamination may be significant, especially in two phase regions where a sample of each phase is required. Different types of chemical analysis for the sulphur have been performed, including:

- (1) Dissolution in bromine-- HNO_3 , and application of Allen and Bishop's method.
- (2) Dissolution in KClO_3 -- HNO_3 and sulphur determined as BaSO_4 .
- (3) Determination of %Cu and obtaining %S by difference (a very poor method).

The direct analytical techniques [1, 2] involving a long time to dissolve the melt, and a corresponding risk in losing the sulphur as H_2S or SO_4^{2-} evaporation, have resulted in poor reproducibilities for percent S. Analysis of the metal, whether by a chemical, electrolytical or by an atomic absorption technique have been reported as satisfactory.

The three major aspects of conventional techniques applied to the Cu-S binary may be applied to any other metalsulphur system.

Thermogravimetric technique for sulphide studies

In order to minimise the errors and inherent difficulties experienced by the techniques described previously, a thermogravimetric technique was developed and applied for studying not only the Cu-S system which is described in detail in this paper, but sulphide systems in general.

By continuously monitoring the weight of a sample of known metal content suspended at a particular temperature in a known $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ mixture, variations in weight due to either sulphur loss or gain created by the defined p_{S_2} atmosphere may be continuously recorded. Hence at equilibrium, i.e. when the weight of the sample remains constant for a given p_{S_2} , the amount of sulphur present is directly known at that temperature without the necessity of sampling and chemical analysis. The same sample is then subjected to a different $\text{H}_2\text{S}/\text{H}_2$ mixture and a new equilibrium point established. In this manner it is possible to establish a whole range of equilibrium points at different temperatures with a minimum of effort and time and with a high degree of accuracy, all from the same original metal sample.

Experimental

Apparatus

A schematic diagram of the apparatus is illustrated in Figs 1, 2a and 2b. The alumina supporting rod and crucible were suspended from a Cahn RH Automatic Electrobalance capable of detecting a weight change of one part per million

which in this case was one millionth part of 15 g, i.e. 0.015 mg. The electrobalance signal was continuously recorded on a Speedomax W/L chart recorder set to the 1 mV range. Thermal fluctuations were dampened by selecting an appropriate electronic filter. Baffles were carried by an internal column to act as both a heat shield and to reduce rapid gas convection. The whole unit was housed in a round bottom alumina tube O.D. 1.7 cm, I.D. 1.4 cm, that was connected to the electrobalance glass column by means of a water cooled brass adaptor.

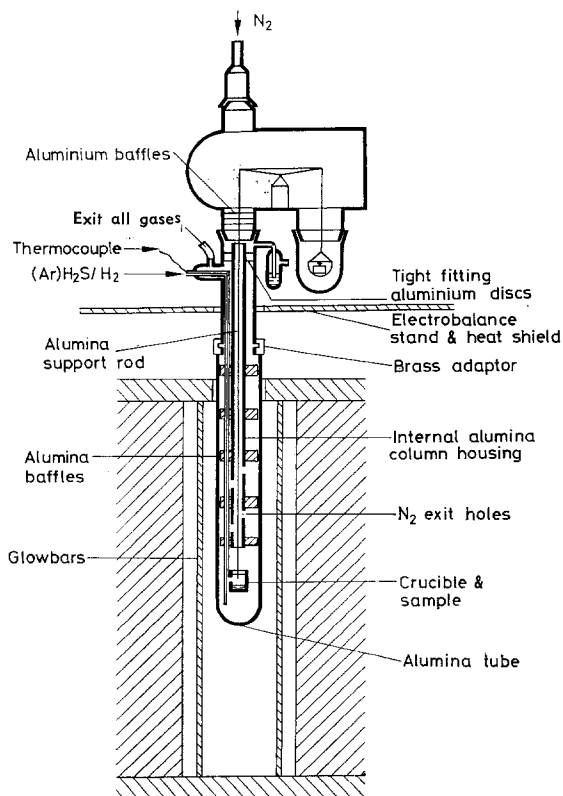
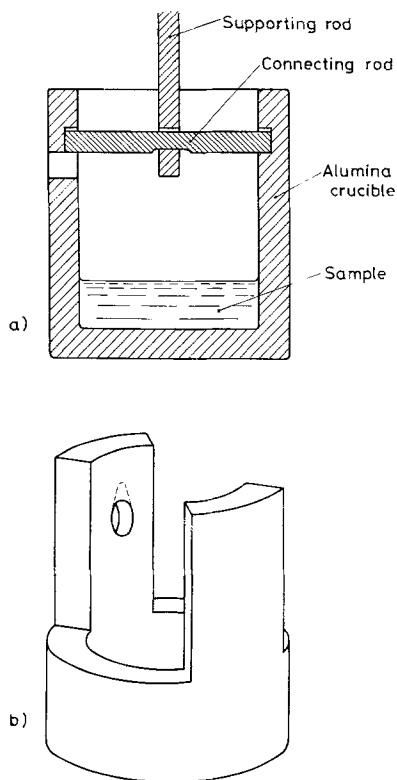


Fig. 1. Schematic diagram of the thermogravimetric apparatus

The $\text{H}_2\text{S}/\text{H}_2$ ratio was obtained from calibrated 'constant head' capillary flow meters carrying dibutyl phthalate as the inert low pressure medium, and directed into the reaction down through an alumina tube 0.6 cm O.D., 0.3 cm I.D. In order to eliminate thermal segregation of the H_2 and H_2S experienced at low flow rates the flow rate was maintained in excess of 150 ml/min. Different $\text{H}_2\text{S}/\text{H}_2$ ratios vary in density and change the actual flow rate and affect the recorded weight change of the sample. These were accounted for by applying a 'buoyancy correc-

tion' described later. In order to establish low partial pressures of S_2 with a good degree of accuracy the H_2S gas was initially diluted in argon before mixing with H_2 . Argon was chosen since its molecular weight is near to that of H_2S and its solubility in Cu/Cu_2S is small.

Two major problems associated with the sulphur atmosphere, namely, (i) diffusion of gaseous sulphur up into the electrobalance and consequent chemical



Figs. 2a, 2b. Reaction crucible and supporting rod connection

attack of the electronics, and (ii) deposition at lower temperatures of elemental sulphur on the supporting rod which would produce an invalid weight increase, were both entirely eliminated by passing dry nitrogen gas through the electrobalance and down the central column. To eliminate the influence of nitrogen on the defined p_{S_2} , holes were drilled in the lower region of the column through which the inert gas could readily diffuse. Thus only the lower part of supporting rod experienced a sulphur atmosphere and this was well above the deposition temperature (444.6°). The reaction tube was maintained at the elevated temperatures by means of a SiC resistance furnace controlled by three Pt-13% Rh, Pt thermocouples

in series connected to a Gardsman controller via a 40° cold-junction. The temperature in the reaction zone was monitored by two more Pt-13% Rh, Pt thermocouples which had been previously calibrated at the melting point of copper (1083°) and a continuous recording of the temperature indicated control to within less than $\pm 0.5^\circ$. The absolute temperature was determined by use of a Cambridge 44 228 potentiometer.

Procedure

Approximately 2 g of copper were suspended in the alumina crucible from the calibrated electrobalance. Two grams of copper represented an amount large enough for good data accuracy (weight change range approx. 10 mg/l atom-percent S in 99 percent Cu region and approx. 22 mg/l atom-percent S in the Cu_2S region), and yet small enough for fairly rapid equilibrium (maximum of 2 hours in the low sulphur region). The apparatus was set up as illustrated in Fig. 1 and the furnace was established at a constant temperature for at least 24 hours, during which time a steady state situation had been well attained. Throughout the experimental run the optimum flow rate of N_2 was kept constant, optimum being defined by a flow rate fast enough to prevent upward sulphur diffusion inside the column and yet slow enough not to influence the p_{S_2} in the sample region. By trial and error the optimum N_2 flow rate was determined to be 50 ml/min.

The sample was equilibrated in a stream of pure hydrogen. The weight of this starting point was considered the standard from which the difference of all other equilibration weights were measured. Equilibration points increasing in sulphur content were established, the first point being but a few mg from the standard. Rather than pass in a given $\text{H}_2\text{S}/\text{H}_2$ ratio and wait for equilibration it was found more convenient at low S contents to initially provide a mixture slightly rich in H_2S , establish a predetermined amount of sulphur content, then vary the $\text{H}_2\text{S}/\text{H}_2$ ratios and find that mixture for which the weight remained constant. Care had to be taken that mixtures too dilute in H_2S were not mistaken for equilibrium mixtures since it was found that sulphur removal was approximately ten times lower than sulphur addition. During an eight hour period it was possible to determine up to eight equilibrium points at low sulphur contents and considerably much more for high sulphur contents (i.e. around Cu_2S region) since equilibration of the latter was fairly rapid. From the phase diagram of the Cu– Cu_2S system shown in Fig. 3, it can be seen that the two phase region $\text{Cu}_{(l)}-\text{Cu}_2\text{S}_{(l)}$ is wide. Thus it was comparatively easy to assess the equilibrium $\text{H}_2\text{S}/\text{H}_2$ mixture since any mixture only slightly rich or dilute from the equilibrium values produced a rapid continuous weight change. Care was taken, especially in the high sulphur region, that the exit did not become blocked with elemental sulphur deposits; a process that would cause a backflush of the corrosive atmosphere into the electrobalance.

In the liquid regions most metal sulphides exhibit a fairly wide miscibility gap that separates the relatively narrow metal rich region (liquid I) from that of the

sulphur rich region (liquid II). In view of the narrow extent of liquid I it is not unreasonable to assume that the activity of the metal remains constant across this region; e.g. in the Cu–S system at 1200° the range of a_{Cu} varies from 1 to 0.98. Thus a constant flow rate of gas passing over the crucible containing the liquid I would be expected to produce a constant evaporation rate of Cu. The volatilization factor $Va_{liq I}$ (mg/hour) was determined by passing H_2 over pure

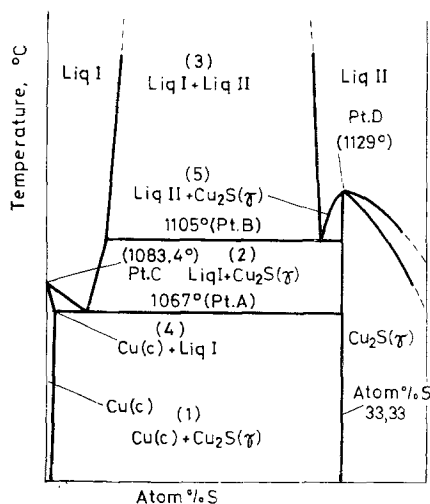


Fig. 3. The system Cu–S; high temperature portion only, not to scale [2]

Cu for several hours and then this factor was applied to correct subsequent equilibrium readings. A check was made after studies were performed for several hours on the liquid I region by reducing the sample to the pure copper state and it was found that the overall weight loss agreed exactly with that predicted from the volatilization factor previously determined. Volatilization corrections applied to the liquid II region may be calculated from a knowledge of the vapour pressures of the metal and of the sulphide.

Since

$$\frac{p_{Cu}^{\circ}}{p_{Cu_2S}^{\circ}} = \frac{Va_{liq I}}{Va_{liq II}}$$

where p° refers to the vapour pressure of the pure components and Va to the volatilization factors for a given temperature at a given flow rate.

Fortunately most metal sulphide systems exhibit fairly small vapour pressures, especially just above the melting point of the metal [16], so volatilization corrections may not be necessary for work that is not too accurate.

A dummy run substituting an inert alumina dead weight for the copper was made in order to apply a gas density buoyancy correction (approximately 0.05

mg for very dilute H_2S mixtures and 2.4 mg for pure H_2S). An additional buoyancy correction due to the increase in size of the sample on going from pure metal to metal sulphide was also taken into account. The nature of the buoyancy correction would remain similar for all metal sulphide studies on the same apparatus.

Results and discussion

The rate of volatilization of pure Cu at 1200° in a flow rate of 250 ml/min of hydrogen was 0.33 mg/hour, compared with a loss in weight at stoichiometric Cu_2S of 0.23 mg/hour in the same flow rate of the required H_2S/H_2S mixture.

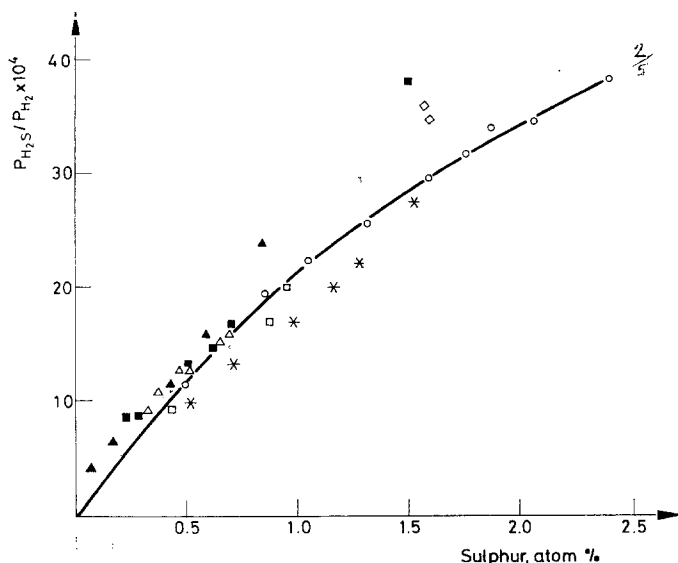


Fig. 4. H_2/H_2S ratios in equilibrium with the Cu—S liquid I region in the vicinity of 1200° . \circ Present study at 1200° ; \square Yagihashi [20] at 1100 and \triangle at 1250° . * Alcock [17] at 1100 and \diamond at 1256° . \blacksquare Sudo [18] at 1247° . \blacktriangle Hirakoso et al. [19] at 1247°

Since the activity of copper in Cu_2S is approximately 0.5, the predicted weight loss of elemental copper at this composition is $0.33 \times 0.5 = 0.17$ mg/hr, together with 0.0415 mg/hr loss of elemental sulphur to maintain the stoichiometric balance. Hence the total predicted weight loss is 0.21 mg/hr, compared with the measured value of 0.23 mg/hr. The discrepancy may be attributed to the volatilization of compound ' $Cu_2S_{(g)}$ ' or ' $CuS_{(g)}$ ', but is probably more likely due to the fact that the metallic copper tends to form a globule which presents a smaller surface area than that of the Cu_2S , hence volatilization of the latter would be greater than the estimated value. All results were corrected for elemental copper and sulphur

Table 1
Results for Cu-S at 1200°C

Run number	Buoyancy correction (mg)	Volatilization correction (mg)	Corrected Cu-mass (g)	Corrected S-mass (g)	% S	$\log p_{S_2}^{1/2}$
B 1	0.10	0.36	2.4146	0.00596	0.49	3.568
A 1	0.15	0.30	2.4117	0.01045	0.85	3.345
B 2	0.20	0.66	2.4143	0.01296	1.05	3.282
A 2	0.20	0.66	2.4113	0.01616	1.31	3.225
B 3	0.20	1.00	2.4140	0.01950	1.58	3.160
A 3	0.25	1.00	2.4110	0.02185	1.76	3.131
C 1	0.30	0.40	2.4044	0.02290	1.85	3.095
A 4	0.30	1.30	2.4107	0.02530	2.04	3.083
A 5	0.30	1.40	2.4106	0.02980	2.39	3.047
D 1	Immiscibility gap		—	—	—	2.99
D 2	0.45	0.80	1.9372	0.4761	32.76	2.87
E 11	0.50	1.55	2.47975	0.61525	32.96	2.72
E 10	0.60	1.25	2.48015	0.61895	33.09	2.70
E 9	0.65	1.00	2.4803	0.62150	33.18	2.61
D 3	0.65	1.10	1.9369	0.48535	33.19	2.56
E 8	0.70	0.85	2.48045	0.62515	33.10	2.44
D 4	0.75	1.20	1.9368	0.48765	33.29	2.40
E 7	0.75	1.20	2.4805	0.62870	33.43	2.23
D 5	0.80	1.30	1.9367	0.4895	33.38	2.20
D 6	0.10	1.40	1.9366	0.49325	33.54	1.87
E 1	0.10	0.25	2.48105	0.6313	33.52	1.79
D 7	0.15	1.40	1.9366	0.49445	33.60	1.76
E 2	0.25	0.40	2.4809	0.6350	33.65	1.61
D 8	0.20	1.50	1.9365	0.4965	33.69	1.53
E 3	0.40	0.40	2.4809	0.6370	33.73	1.46
D 9	0.40	1.60	1.9364	0.4984	33.78	1.38
E 4	0.40	0.40	2.4809	0.6411	33.87	1.23
D 11	0.50	1.65	1.93635	0.4994	33.82	1.22
E 5	0.60	0.50	2.4807	0.6444	33.98	1.09
D 11	0.70	1.65	1.93635	0.50245	33.96	1.07
E 6	1.00	0.60	2.4806	0.6488	34.14	0.90
D 12	1.00	1.70	1.9363	0.5064	34.14	0.84
D 13	1.10	1.70	1.9363	0.5077	34.19	0.76
D 14	2.40	1.80	1.9362	0.5207	34.78	0.38

loss, together with the necessary buoyancy correction, and are listed in Table 1 in increasing percent content.

The results are tabulated for three separate runs in the liquid I region and two separate runs in the liquid II region, and in Figs 4 and 5 are compared with established data.

The results show reasonable agreement with established data but in view of the inherent inaccuracies of these techniques as explained previously, and the excellent reproducibility of the thermogravimetric technique, one must conclude that

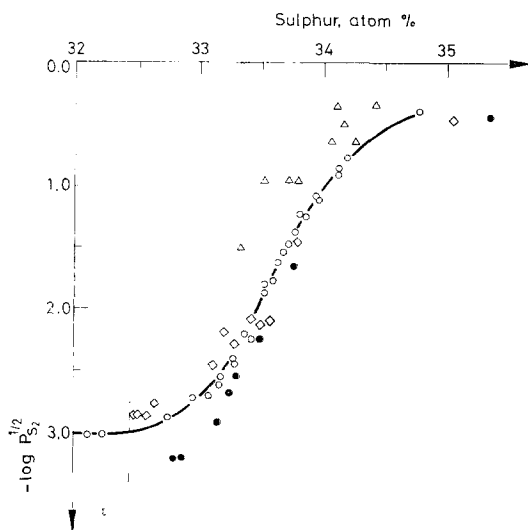


Fig. 5. Partial pressures of S_2 in equilibrium with Cu—S liquid II region in the vicinity of 1200°C ; \circ Present study at 1200° ; \diamond Schuhmann and Moles [3] at 1250° , \bullet and 1150° . \triangle Nagamori and Rosenqvist [8] at 1200°

this technique which directly measures the sulphur content at the required temperature instead of analysis at room temperatures provides one with the most accurate sulphur analytical method to this date.

Conclusion

The thermogravimetric technique has been developed and tested on the Cu—S binary at 1200° . Gas density buoyancy and volatilization corrections have been made and the results obtained have shown to be highly reproducible and in good agreement with established data.

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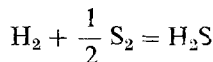
One of the authors, C. W. B., is grateful to the Noranda Research Centre for a graduate fellowship. We are also grateful to the Canadian National Research Council for financial assistance.

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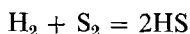
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Appendix



$$\text{Equilibrium constant } K_1 = \frac{p_{\text{H}_2\text{S}}}{(p_{\text{S}_2})^{1/2} \cdot p_{\text{H}_2}} \quad (1)$$



$$\text{Equilibrium constant } K_2 = \frac{(p_{\text{HS}})^2}{p_{\text{H}_2} \cdot p_{\text{S}_2}} \quad (2)$$

For a given volume of gas containing 1 mole H_2 , n moles H_2S , and x moles Ar (all measured at room temperature), n represents the input $\text{H}_2\text{S}/\text{H}_2$ ratio.

Assuming a total pressure, p_{total} , of 1 atmosphere (daily fluctuations are ignored), dissociation will take place to form $(1 + \alpha)$ moles H_2 , $(n - b)$ moles H_2S , $(2b - 2\alpha)$ moles HS, $\left(\alpha - \frac{b}{2}\right)$ moles S_2 , and x moles Ar, at the elevated temperature, where α and b are unknowns but dependent upon the temperature and the input ratio n . Hence the total number of gaseous moles from the original input is now defined by

$$n_T = \left(1 + n + \frac{b}{2} + x\right) \quad (3)$$

Hence

$$p_{\text{S}_2} = \frac{n_{\text{S}_2}}{n_T} \times p_{\text{total}} = \frac{(\alpha - b/2)}{\left(1 + n + \frac{b}{2} + x\right)} \quad (4)$$

$$\alpha = \left(p_{\text{S}_2} + np_{\text{S}_2} + \frac{b}{2} + xp_{\text{S}_2} + \frac{b}{2}\right) \quad (5)$$

$$K_1 = \frac{(n - b)}{(1 + \alpha) \cdot p_{S_2}^{1/2}} \quad (6)$$

Substituting α from Eq. (5) into Eq. (6) and simplifying, leads to:

$$b = nI - J \quad (7)$$

where

$$J = \frac{(1 + p_{S_2} + x p_{S_2})}{\left(\frac{p_{S_2}}{2} + \frac{1}{2} + \frac{1}{K_1 \cdot p_{S_2}^{1/2}}\right)} \quad (8)$$

and

$$I = \frac{\left(\frac{1}{K_1 \cdot p_{S_2}} - p_{S_2}\right)}{\left(\frac{p_{S_2}}{2} + \frac{1}{2} + \frac{1}{K_1 \cdot p_{S_2}^{1/2}}\right)} \quad (9)$$

Substituting Eq. (7) into Eq. (5) simplifies to

$$\alpha = nK + H \quad (10)$$

where

$$L = \left(p_{S_2} + \frac{I}{2} p_{S_2} + \frac{I}{2}\right) \quad (11)$$

and

$$H = \left(p_{S_2} - \frac{J p_{S_2}}{2} + x p_{S_2} - \frac{J}{2}\right) \quad (12)$$

Since

$$K_2 = \frac{(2b - 2\alpha)^2}{(\alpha + 1) \left(\alpha - \frac{b}{2}\right)}$$

Substituting Eqs (7) and (10) for b and α , and rearranging gives

$$Pn^2 + Qn + R = 0 \quad (13)$$

where

$$P = \left(L^2 K_2 - 4L^2 - 4I^2 + 8LI - \frac{K_2}{2} LI\right)$$

$$Q = \left(2LHK_2 - 8LH + 8IJ + (HI - JL) \left(8 - \frac{K_2}{2}\right) + K_2L - \frac{K_2}{2} I\right)$$

$$\text{and } R = \left(K_2 H^2 - 4H^2 - 4J^2 - 8JH + \frac{K_2}{2} JH + K_2 H + \frac{K_2}{2} J\right)$$

Eq. (13) gives

$$n = \frac{-Q \pm \sqrt{Q^2 - 4PR}}{2P} \quad (14)$$

Thus, for a given value of p_{S_2} , and knowing K_1 and K_2 at the elevated temperature, it is possible to determine the required input H_2S/H_2 ratio for varying amounts of argon.

The values were determined by the use of a digital computer programmed in double precision.

RÉSUMÉ — On discute les problèmes posés par les méthodes conventionnelles pour doser le soufre aux températures élevées et l'on décrit une méthode thermogravimétrique pour l'analyse directe en continu. La technique est illustrée sur l'exemple du système Cu—S à 1200°; on discute les facteurs correctifs que l'on doit appliquer pour tenir compte de la poussée et de la volatilisation.

ZUSAMMENFASSUNG — Es werden die Probleme der üblichen Methoden der Schwefelbestimmung bei hohen Temperaturen erörtert und eine thermogravimetrische Methode zur direkten kontinuierlichen Analyse vorgeschlagen. Das Verfahren wird an dem Beispiel des Systems Cu—S bei 1200° gezeigt mit Hinweis auf die infolge Auftrieb und Verflüchtigung nötige Korrektur.

Резюме — Обсуждены проблемы обычных методов определения содержания серы при высоких температурах и описан термогравиметрический метод ее прямого непрерывного анализа. Метод иллюстрирован использованием системы Cu—S при 1200° с обсуждением необходимых поправочных факторов.