KINETICS OF THE CdS—CdO REACTION AND PREPARATION OF CADMIUM BY THE PROCESS

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The reaction between CdS and CdO as a means of preparing Cd metal was studied in the temperature range 750° to 900°C in nitrogen atmosphere as well as under reduced pressure (<1 mm Hg). A simple experimental set up was devised for rapid heating of the reactants and chilling of the products (Cd vapour and SO_2 gas) in order to minimise the highly feasible reverse reaction. From the kinetic studies carried out under nitrogen, it was found that the CdS--CdO reaction obeyed approximately a linear rate law. As the vapour pressures as well as the dissociation pressures of CdS and CdO were appreciable at the temperatures studied, various possible modes of reaction viz , solid-solid, gas-solid and gas-gas were examined and the reaction was suggested to be controlled by the interaction between strongly adsorbed CdS (and/or SO_2 gas formed by its dissociation) and sparsely adsorbed CdO (and/or O_2 gas formed by its dissociation) vapours on neighbouring sites in accordance with the Langmuir-Hinshelwood mechanism. The apparent activation energy of the process was found to be 47 ± 5 K cals/mole of SO_2. Optimum conditions for preparing high-purity cadmium (99.9%) were found to be reduction at 850°C for 2 hours under reduced pressure (<1 mm Hg) followed by vacuum distillation at 400°C. The residues from the reduction as well as the separation-refining experiments, could be further reprocessed as such or by mixing with a fresh batch of the charge for reduction.

In the production of copper, nickel and lead by the blowing of copper matte[1], nickel sulphide[2] and galena concentrates[3], respectively, the interactions between the concerned sulphides and oxides are known to play a vital role in the metal production However, the sulphide-oxide reaction as such as a means of producing metals has not received adequate attention of metallurgists. In recent years the authors conducted extensive investigations on the exploitation of sulphide-oxide reactions for the preparation of some metals and alloys and have been successful in preparing nickel[4], cobalt[5], nickel cobalt[6] and copper-nickel alloys[7-9]. The present paper is concerned with studies on the CdS – CdO reaction.

Tseft (cited in Chizhikov[10]), who conducted a qualitative study of the CdS—CdO reaction, reported that SO_2 pressure was significant in the temperature range 760 to 976°C. Chizhikov[10], on the other hand, found that the reaction occurs to a considerable extent even at 800°C. Okunev and Coworkers[11] determined the change in standard free-energy (ΔG°) with temperature (°K) for the reaction

$$CdS\ (s) + 2CdO\ (s) \rightleftharpoons 3Cd(vap) + SO_2\ (g)$$

to be $\Delta G^\circ = 159350 - 122.83T$. From the data presented in Appendix-I, the reaction appears to be thermodynamically feasible at 1025°C under standard conditions. However, as the products of the reaction are gaseous, it may be feasible at lower temperatures under reduced pressure or a flowing stream of inert gas For example, the CdS—CdO reaction may occur even at a temperature below 500°C under a reduced pressure of 10^{-2} mm Hg. However, owing to the appreciable vapour pressure of cadmium sulphide (Appendix-I), high temperatures or use of high vacuum have limited utility. Further, contamination of the product metal with its sulphide and oxide is also a problem owing to the high thermodynamic feasibility of the reverse reaction between Cd (vap) and $SO_2(g)$. It is also evident from Appendix—I that the simple thermal dissociation of CdS and CdO is very much less feasible (thermodynamically) than the CdS—CdO reaction and as such the possibility of formation of cadmium metal by the said dissociation reactions can be ignored at moderate temperatures.

In a preliminary study of the CdS—CdO reaction under a flowing stream of nitrogen, appreciable SO_2 evolution was detected at 600°C. A strong tendency for the reverse reaction was also noticed. Frents[10] has also reported that the reaction between $SO_2(g)$ and Cd is highly feasible even at 400°C. Our trials revealed that this reverse reaction between Cd (vap) and $SO_2(g)$ could be suppressed to a large extent (by heating the reaction mixture (CdS + CdO) in a furnace of short length) by rapid cooling of the products as they emerge out of the reaction zone. Results of the investigation on the kinetics of the CdS—CdO reaction under nitrogen and preparation of the metal under both nitrogen and reduced pressure are presented and discussed in this paper.

EXPERIMENTAL

Materials: CdS powder of 99.5% purity (orange variety; Lunar Caustic make; — 00 mesh) and reagent-grade CdO powder (B.D H make; 99% purity; -65 mesh, 65% of which was -150 mesh) were used in this investigation.

Kinetic Studies under Nitrogen

In each run, 10 gms of an appropriate mixture of CdS and CdO was compacted in a die of 13 mm I.D. at 16 kg/mm^2. The resultant briquette was taken into a silica boat, dried and weighed. The boat was then introduced into the middle of a silica reaction tube (20 mm I.D x 750 mm long) which was placed symmetrically in a nichrome-wound tube furnace. The furnace was of short length (29 mm I.D x 140 mm long with a uniform temperature zone of ~ 32 mm) and was designed for an average heating rate of over 100°C per minute. The gap between the ends of the furnace tube and the reaction tube was packed with asbestos rope and provision was made to cool either end of the reaction tube (immediately projecting out of the furnace) with cold water. The reaction tube, containing the sample, was flushed with nitrogen gas which was purified by passing through a train consisting of alkaline pyrogallol, conc. sulphuric acid, anhydrous calcium chloride, a refractory tube containing copper turnings at 500°C and finally phosphorus pentoxide. After flushing, the gas rate was controlled to 10±0.5 litres/hr and the furnace was switched on and controlled within ±5°C of the required temperature (which was measured by keeping the thermocouple sheath in contact with the briquette) for a pre-determined period. The furnace was then switched off and the sample was taken out and weighed after cooling to room temperature. At each temperature the experiment was continued in successive intervals for a suitable cumulative period. The time of heating and cooling the sample was neglected because of rapid heating and cooling that was possible in these experiments.

The influence of temperature (750° to 900°C) and time (5 min. to several hrs.) on the amount of CdS reacted was investigated using stoichiometric mixtures (CdS:CdO = 1:2). Effect of variation in mole proportions of the reactants (CdS:CdO = 1:1 to 1:4) was also investigated at 800°C. An experimental reproducibility within ±5% of the values reported was observed.

At any specific temperature and duration, knowing the amount of CdS in the sample and the weight loss values, the mole percent CdS reacted was easily calculated by (a) applying volatility corrections for CdS and CdO and (b) utilizing the fact that 36.0% of the corrected weight loss represented the amount of CdS reacted (because a stoichiometric mixture of 1 mole CdS and 2 moles CdO contains 36.0% CdS by weight). Volatility corrections for CdS and CdO were made from a knowledge of their vapour pressures at the experimental temperature and the volume of nitrogen passed through the system during the particular period of reduction.

Preparation and Refining of Cadmium under Reduced Pressure

Reduction experiments were also conducted under reduced pressure in essentially the same manner as those carried out in nitrogen atmosphere. In this case a one-end closed silica reaction tube connected to an Edwards Speedivac Rotary pump and a calibrated vacuostat was used. [Kinetic studies were not conducted under vacuum owing to the high vaporization (and consequent loss from the reaction mixture) of CdS, as this would lead to variation in the mole ratio of the reactants in the mixture with time, particularly in experiments of long duration]. Thus, experiments under reduced pressure were carried out to prepare the metal on a 10 gm as well as 50 gm scale using compacting dies, reaction tubes and furnaces of suitable dimensions.

The metallic condensate deposited in the cooler portions of the tube was scraped, compacted in a die of 13 mm I.D. at 16 kg/mm^2 and vacuum distilled at 400°C (found to be optimum by trial and error) to obtain refined metal. For this distillation a one end closed silica reaction tube connected to a rotary pump and a vacuostat was used. The cooler portions of the distillation tube itself served as a condenser for the refined cadmium. The residues from the reduction experiments and refining operations were also recycled in order to increase the yield. The cadmium metal thus obtained was examined for its purity, lattice parameters, hardness and density.

RESULTS AND DISCUSSION

Kinetic Studies under Nitrogen Atmosphere

Results of the progress of reduction using stoichiometric mixtures (CdS:CdO = 1:2) are shown in Fig.1, where the cumulative mole percent CdS reacted (N) is plotted against time (t) at various temperatures. The reaction is seen to be greatly influenced by temperature. In all the cases, the mole percent CdS reacted is a linear function of time up to about 80% reduction (within experimental limitations), beyond which there is some deviation from linearity.

The influence of variation in mole ratios of the reactants at 800°C is shown in Fig. 2, from which the slopes of the mole percent CdS reacted vs time plots

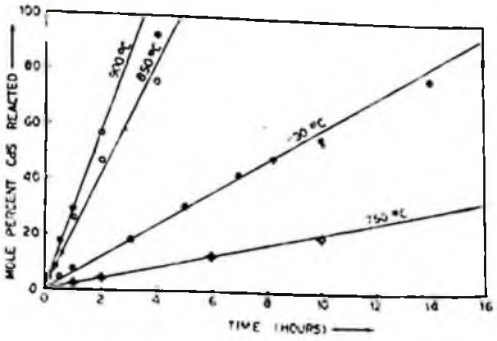


Fig. 1. Effect of temperature and time on the CdS—CdO (mole ratio 1:2) reaction under nitrogen atmosphere.

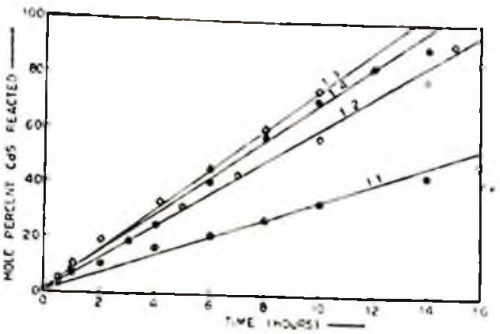


Fig. 2. Influence of varying mole ratios of reactants (CdS:CdO) on the CdS—CdO reaction under nitrogen atmosphere at 800°C.

are found to be nearly the same (within experimental limits) for mole ratios of CdS.CdO = 1:2, 1:3 and 1:4. The slope of the line (in other words the rate of reaction) for CdS:CdO = 1:1 is nearly half of that of the others suggesting, thereby, that 1 mole of CdS requires 2 moles of CdO to yield the metal. On the whole, the variation in mole ratios of the reactants appears to result in no significant change in the rate of reaction, which may be considered to proceed according to the rate law $N = Kt$ where K stands for the linear rate constant. The values of v ($v = dN/dt = K$; units mole sec^{-1}) at various temperatures are recorded in Table I. As a linear relationship is generally indicative of surface reaction, in this case diffusion is unlikely to be a rate-determining process.

Mechanism of the Reaction

Since the rate of reaction in the present study has been found to increase with temperature, the reasoning for selecting the proper mechanism is based on the assumption that the specific reaction rate constant values at various temperatures should follow the Arrhenius equation. This means that for any valid mechanism, the apparent rate constant k^1 should increase consistently with temperature. As k^1 bears a definite relationship with the specific rate constant (k), it can be utilized to calculate the activation energy.

As the vapour pressures of the reactants are appreciable (Appendix—I) at the temperatures of study, vapours of CdS and CdO are likely to participate actively in the reaction. Thus the reaction between CdS and CdO may occur between (i) both the solid reactants (ii) both the reactants in the gaseous phase and (iii) one solid reactant and the other gaseous reactant. Within this scope, different possibilities regarding the mode of reaction are discussed below :

(A) Reaction between solid CdS and solid CdO :—

$$CdS(s) + 2CdO(s) \rightarrow 3Cd(g) + SO_2(g)$$

Such termolecular reactions are known to be generally very difficult. Further as reactions involving vapours of CdS and/or CdO are likely to proceed more easily, progress of the reaction by interaction between solids is considered insignificant.

(B) Reaction between CdS vapour and solid CdO :—

$$CdS(g) + 2CdO(s) \rightarrow 3Cd(g) + SO_2(g)$$

In such a case, the rate of reaction should be proportional to p_{CdS}. Thus k^1, the apparent rate constant, will be equal to v/p_{CdS}. Examination of the values given in Table I shows that the variation of k^1 with temperature is not consistent and this mechanism is considered unlikely.

(C) Reaction between CdO vapour and CdS solid :—

$$CdS(s) + 2CdO(g) \rightarrow 3Cd(g) + SO_2(g)$$

In such a case, $k^1 = v/p^2CdO$. As k^1 falls off with temperature (Table I), this mechanism is also not considered probable.

(D) Reaction between vapours of CdS and CdO :—

$$CdS(g) + 2CdO(g) \rightarrow 3Cd(g) + SO_2(g)$$

This is a homogeneous gaseous reaction involving three moles. As such termolecular reactions are rare, this probability is discarded.

(E) Heterogeneous reactions between adsorbed and unadsorbed CdS and CdO vapours :—

As vapourisation is a fast process, the existence of vapours of CdS and CdO at the experimental temperatures over the sulphide and oxide may be assumed One of the possibilities is that vapours of one of the reactants may get adsorbed and subsequently react with the

TABLE I: **Mechanism of CdS–CdO Reaction under Nitrogen**

Values of $\nu = dN/dt$ in mole sec.$^{-1}$ are 5.81×10^{-4}, 16.50×10^{-4}, 56.69×10^{-4} & 79.341×0^{-4} at 750, 800, 850 and 900°C, respectively (from Fig.1)

Reaction between	Apparent rate constant (k')	Numerical values of k' at various temperatures (°C)			
		750	800	850	900
1	2	3	4	5	6
CdS(vap) and 2CdO(s)	$\frac{dN/dt}{p_{CdS}}$ in mole sec.$^{-1}$ atm.$^{-1}$	6.6	5.8	6.8	3.6
$\frac{1}{2}S_2$(vap) and CdO(s)	$\frac{dN/dt}{p_{S_2}^{\frac{1}{2}}}$ in mole sec.$^{-1}$ atm.$^{-\frac{1}{2}}$	0.11	0.17	0.37	0.32
CdS(s) and 2CdO(vap)	$\frac{dN/dt}{p^2_{CdO}}$ in mole sec.$^{-1}$ atm.$^{-2}(\times 10^4)$	253	66	33	7
CdS(s) and O_2(g)	$\frac{dN/dt}{p_{O_2}}$ in mole sec.$^{-1}$ atm.$^{-1}$	66	98	100	46
$\frac{1}{2}$ S_2(vap and O_2(g)	$\frac{dN\ dt}{p_{S_2}^{\frac{1}{2}}\ p_{O_2}}$ in mole sec.$^{-1}$ atm.$^{-3}(\times 10^3)$	12	10.3	6.5	1.9
Langmuir—Ridlel Mechanism					
Adsorbed and unadsorbed vapours of CdS and CdO	$\frac{dN/dt}{p_{CdS}\ p_{CdO}}$ in mole sec.$^{-1}$ atm.$^{-2}(\times 10^4)$	43.8	11.6	5.1	1.1.
Adsorbed and unadsorbed S_2(vap) and O_2(g)	$\frac{dN/dt}{p_{S_2}\ p_{O_2}}$ in mole sec.$^{-1}$ atm.$^{-2}(\times 10^4)$	218	108	42	7.6
Strongly adsorbed CdS(vap) and unadsorbed CdO(vap)	$\frac{dN/dt}{p_{CdO}}$ in mole sec.$^{-1}$ atm.$^{-1}$	38.4	32.9	43.0	24.0
Strongly adsorbed S_2(vap) and unadsorbed O_2(g)	$\frac{dN/dt}{p_{O_2}}$ in mole sec.$^{-1}$ atm.$^{-1}$	66	98	100	46
Langmuir Hinshelwood Mechanism					
Sparsely adsorbed CdS(vap) and sparsely adsorbed CdO(vap)	$\frac{dN\ dt}{p_{CdS} \cdot p_{CdO}}$ in mole sec.$^{-1}$atm.$^{-2}(\times 10^4)$	43.8	11 6	5.1	1.1
Sparsely adsorbed S_2(vap) and sparsely adsorbed O_2(g)	$\frac{dN/dt}{p_{S_2} \cdot p_{\ 2}}$ in mole sec.$^{-1}$atm.$^{-2}(\times 10^4)$	218	108	42	7.6
Strongly adsorbed CdS(vap) and sparsely adsorbed CdO(vap)*	$\frac{dN/dt}{p_{CdO}/p_{CdS}}$ in mole sec.$^{-1}(\times 10^{-3})$	3.4	9.3	36	53.4
Strongly adsorbed S_2(vap) and sparsely adsorbed O_2(g)*	$\frac{dN/dt}{p_{O_2}\ /\ p_{S_2}}$ in mole sec.$^{-1}(\times 10^{-3})$	2.0	8 9	24	28

* It is the only mechanism where k' is increasing consistently with temperature, in both the molecular as well as elemental approaches.

unadsorbed species of the other. The rate of a reaction, v, occurring in accordance with the Langmuir-Rideal mechanism [13] can be derived to be

$$v = k\,\theta_1.p_2 \quad \text{or} \quad k.\theta_2.p_1$$

$$= \frac{k\,K_1\,C^0_s\,p_1p_2}{1+K_1.p_1+K_2.p_2} \quad \text{or} \quad \frac{k.K_2.C^0_s.p_1p_2}{1+K_1p_1+K_2.p_2}$$

where θ_1 and θ_2 represent the fractions of surface sites covered by gases 1 and 2, respectively; k, the rate constant; K_1 and K_2, the equilibrium constants for adsorption of gases 1 and 2 on the surface sites, and C^0_s, the total number of original surface sites. Now, three special cases of interest arise in this mechanism:

(i) Sparse adsorption: If one constituent is sparsely adsorbed and the other is unadsorbed, the denominator in the above equation will be nearly equal to unity and it can be shown that apparent rate constant k^1 will be equal to $v/p_{CdS}.p_{CdO}$. In this case, k^1 is found to be falling with temperature and the possibility of this mechanism being the rate controlling one may be discarded.

(ii) One reactant more strongly adsorbed than the other: As the vapour pressure of CdS is much larger than that of CdO (Appendix–I), it is quite likely that it is more strongly adsorbed than CdO. In such a case, the adsorbed complex (CdS on CdO sites) may react with the unadsorbed CdO vapour and it can be shown that if this mechanism is valid, k^1 should be equal to v/p_{CdO}. As the variation of k^1, thus calculated, is inconsistent with increase in temperature (Table I), this possibility may also be discarded.

(iii) One reactant is not at all adsorbed: The result of such a treatment comes out to be the same as special case (ii) discussed above.

(F) Heterogeneous reaction between adsorbed CdS and CdO vapours:

The CdS-CdO reaction may be visualised to occur by interaction of adsorbed CdS and CdO vapours on neighbouring sites. The rate of a reaction occurring in accordance with the Langmuir-Hinshelwood mechanism[13] can be derived to be

$$v = k\,\theta_1\,\theta_2 = \frac{k\,K_1\,K_2.C^{*S}\,p_1p_2}{(1+K_1\,p_1+K_2\,p_2)}$$

where the symbols have the same meaning as in the earlier case The following two special cases are now worth considering:

(i) Reaction between sparsely adsorbed CdS and CdO vapours: In this case the denominator becomes nearly equal to one and hence this leads to a relationship $k^1 = v/p_{CdS}\,p_{CdO}$. As k^1 is found to decrease with rise in temperature (Table I). this probability is ruled out.

(ii) Reaction between strongly adsorbed CdS and sparsely adsorbed CdO: As mentioned earlier, CdS may be more strongly adsorbed than CdO because of its higher vapour pressure and also because the adsorption of an unlike species on the adsorption centres is more probable than a like one. Thus, it is quite probable that vapours of CdS strongly adsorbed on CdO. may react as a whole with sparsely adsorbed CdO vapours on neighbouring sites. It can be easily seen that a consideration of this mechanism leads to the conclusion that

$$k^1 = \frac{v}{p_{CdO}/p_{CdS}}$$

The values of k^1 are found to increase consistently with increase in temperature (Table I). As this happens to be the only mechanism that shows such a behaviour, this is considered to be the most probable one. From a plot of log k^1 with $1/T°K$ shown in Fig. 3 (the relationship is seen to be obeyed well within experimental

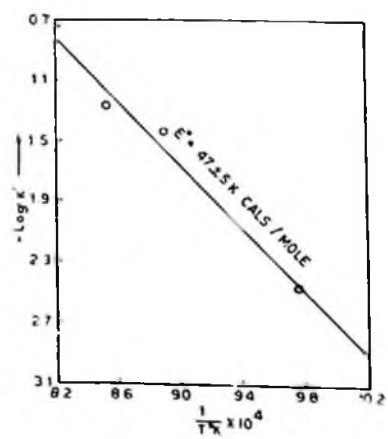


Fig. 3. Activation energy plot for the CdS-CdO reaction.

lim ts) the apparent activation energy for the reaction has been calculated to be 47±5 K. cals/mole of SO_2

As the dissociation pressures of CdS and CdO are appreciable, there is a possibility of sulphur vapour and oxygen gas (formed by such dissociation) taking part in the reaction to yield cadmium metal (Mass spectrometric studies show that the vapours of CdS and CdO are essentially composed of the elements[14]). Similar mechanisms, as in the above molecular approach, with S_2

and/or O_2 (formed by dissociation) as reactants (Elemental approach) have been considered and k^1 values for each case, calculated at various temperatures, have also been recorded in Table I. By examining these results, it is again observed that the most probable rate-determining mechanism is the heterogeneous reaction between strongly adsorbed S_2 vapour and sparsely adsorbed O_2 gas on neighbouring sites.

Summing up the above, one may conclude that the CdS-CdO reaction (under nitrogen atmosphere) in the temperature range 750 to 900°C involves an apparent activation energy of 47 ± 5 K. cals per mole of SO_2 and that the reaction is controlled most probably by the interaction between strongly adsorbed CdS (and/or sulphur) and sparsely adsorbed CdO (and/or oxygen) vapours on neighbouring sites in accordance with the Langmuir-Hinshelwood mechanism.

Table II. Preparation of Cadmium Metal by CdS-CdO Reaction

(Stoichiometric Mixture)

Temperature (°C)	Time (hrs.)	Percent weight loss* under Nitrogen (10lit./hr.) 10 gms sample*	Reduced Pressure (< 1mm) 10 gms. sample	Reduced Pressure (< 1mm) 50 gms sample**
	2	5.0	...	...
	4	..	32.0	...
750	6	13.2	...	...
	8	17.0	52.4	50.09
	10	20.9	...	...
	1	8.1	...	
	2		40.0	...
	3	19.5		
	4	25.7	63.2	6.0
800	5	31.9	...	...
	7	43.5	...	...
	8	49.9	84.4	
	10	56.3		...
	16	81.9	...	...
	1	26.9	43.0	...
	2	46.0	61.5	56.2
850	4	72.8		...
	6	...	93.1	...
	1	28.5	...	...
900	2	54.5	...	
	4	83.7	..	...

* No correction has been applied for volatility losses.

* The condensate obtained in the 10 gms. scale runs under nitrogen contains about 60% of free cadmium metal.

** The condensate obtained in the 50 gms. scale runs under reduced pressure contains about 45% of free cadmium metal.

Preparation and Refinding of Cadmium Metal

The progress of the CdS-CdO reaction under nitrogen as well as reduced pressure (< 1 mm Hg) has been summarised in Table II. where the percent weight loss is tabulated at various temperatures and durations. The weight loss under reduced pressure was found to be 1.3 to 3 times that under nitrogen the effect being more pronounced at shorter reduction times. The larger weight loss obtained in the former case is possibly due to (a) higher degree of reaction as the gaseous products are removed faster than under nitrogen, and (b) higher vaporization losses of the reactants (particularly CdS) under reduced pressure

The condensed products (possessing dull grey to orange-grey colour) were found to contain metallic cadmium as well as its sulphide and oxide and were essentially in the form of loose sponge, powder and thin irregular sheets. In general, the products obtained under nitrogen were found to contain a higher percentage of the metal (≈60%) than those obtained under reduced pressure (≈45%). This may be accounted for by the higher volatilization of the reactants under reduced pressure. In order to separate the metal from its sulphide and oxide, vacuum distillation of the products at 400°C was found to be a successful operation. The residues from such separation-refining operations and the unreacted portions from the reduction experiment (both the residues are composed of CdS and CdO) could be mixed, compacted and retreated or recycled with a fresh batch of the charge for reduction resulting in essentially similar results. Keeping in view the overall metal recovery achievable per reduction experiment and the desirability of retreatment recycling of residues, a temperature of 850°C and a duration of 2 hrs are considered optimum for reduction under reduced pressure as well as flowing nitrogen. In each trial conducted on a 50 gm scale under the above conditions, 12 gms of the metal and a total residue of 35.5 gms were obtained This represents an overall metal recovery of 8.5% for one cycle of reduction and refining. In a typical run, treatment of 44 gms of the mixture in 5 successive cycles of reduction and refining

resulted in 31 gms of pure metal and an overall residue of 6 gms. The total yield for the 5 cycles thus comes to be 97%, the balance 3% representing handling losses in the various operations.

Properties of the Product Metal

The product obtained by the CdS-CdO reaction on vacuum distillation at 400°C resulted in cadmium metal (deposited in the form of irregular flakes, thin sheets and sponge in the silica distillation tube) which was highly lustrous, silver-grey in colour and quite ductile. The metal was easily compacted to a high density (8.38 gms/cc at 32 kg/mm²) and melted in a vacuum sealed pyrex glass tube resulting in lustrous buttons. Chemical and spectrochemical analysis of the distilled cadmium are given in Table III. The metal is seen to be highly pure (99.9%) with trace amounts of S, As, Fe, Si and Zn as the main impurities. For further purification, the cadmium was redistilled and the analyses of this metal is also given in Table III. Redistillation has resulted in no significant purification except for a slight lowering in the sulphur content. The higher silicon content of the redistilled metal is attributed to the additional condensation and scraping operation involved in the experiments as the silica tube itself functioned as the distillation tube as well as the condenser. Lattice parameters (a = 2.9782A°, c = 5.617A°), hardness (22 DPH) and density (8.59 gms/cc) of the cadmium metal (Table III) are in very close agreement with those of high-purity cadmium[10] prepared by conventional techniques

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Table III. Properties of Cadmium Metal Obtained by Cds–CdO Reaction under Reduced Pressure at 850°C

Property/Analysis	After separation-refining at 400°C	After redistillation at 400°C
Appearance	Extremely bright, highly lustrous and silver-grey flakes, irregular strips and sponge	Extremely bright, highly lustrous and silver-grey flakes, irregular strips and sponge
Density, gms./c.c.	8.58	8.59
Hardness, D.P H.	22	22
Lattice parameters		
a	2.9782A°	...
c	5.6170A°	...
Sulphur content	<0.05%	<0.0 %**
Spectrochemical analysis in parts per million		
As	< 100	< 100
Co	< 10	< 10
Sb	< 10	< 10
Fe	25	10
Pb	< 5	< 5
Sn	< 5	< 5
Ni	< 5	< 5
Mg	< 10	< 10
Bi	< 5	< 5
Al	10	< 10
Si	50	100
Cu	< 10	< 10
Zn	< 50	< 50

** Calculated taking into account (a) the residue left behind in redistillation and (b) the sulphur content of the single distilled metal used for re-distillation.

REFERENCES

1. A Butts, "Copper" (Reinhold Publishing Co., New York) (1954)112
2. P. Queneau C E.O.Neill, A. Illis and J.S. Warner; J. Metals, 22(7) (1969)35.
3. F.T. Fuller, J. Metals, 20(12) (1968)26
4. P M Prasad and P K Jena Met. Trans , 2(1971) 1651
5. S.K Jain, P M Prasad and P.K. Jena, Trans. Ind. Inst. Metals, 24(3) (1971)28.
6. S K. Jain, P M. Prasad and P.K. Jena, Ind. J. Tech., 10(1972)340.
7. P M. Prasad and P.K. Jena, Ind. J. Tech. 9(8) (1971)297.
8. Shamsuddin and P.M. Prasad, Curr. Sci., 41(22)(1972)797.
9. Shamsuddin and P.M. Prasad, Met Trans., 8B(1977)86.
10. D.M. Chizhikov, "Cadmium" (Pergamon Press, London, 1966).
11. A.K Okunev, A.K. Kir'yanov and B.I Sergin, Dokl. Akad. Nauk SSSR. 125(1) (1959)147.
12. O. Kubaschewski E LL. Evans and C.B. Alcock, "Metallurgical Thermochemistry" (Pergamon Press, New York, 1967) p422.
13. K J. Laidler, "Chemical Kinetics" (McGraw-Hill, New York 1965).
14. H.H. Kellogg, Trans. TMS-AIME, 236(1966)602.

Appendix I : Thermodynamics of CdS-CdO Reaction and Vapour Pressures of Cd, CdS and CdO

(A) Thermodynamics of CdS-CdO Reaction*

$CdS(s) + 2CdO(s) = 3Cd(vap) + SO_2(g)$ $\quad \Delta G^\circ = 159350 - 112.83T$

$CdS(s) = Cd(vap) + 1/2S_2(g)$ $\quad \Delta G^\circ = 71476 - 40.24T$

$CdO(s) = Cd(vap) + 1/2O_2(g)$ $\quad \Delta G^\circ = 87250 - 49.95T$

Temperature(°C)	For CdS-CdO reaction**			For thermal dissociation of Cds			For thermal dissociation of CdO		
	ΔG° K.cals.	p_{SO_2} mm.	p_{Cd} mm	ΔG° K.cals.	p_{S_2} mm.	p_{Cd} mm.	ΔG° K.cals.	p_{O_2} mm.	p_{Cd} mm.
750	33.8	5.2	15.6	30.3	0.023	0.046	36.2	0.0067	0.0134
800	27.6	13.2	39.7	28.3	0.069	0.137	33.7	0.0128	0.0257
850	21.4	30.6	91.8	26.3	0.185	0.370	31.2	0.0430	0.0860
900	15.3	65.2	195.6	24.3	0.461	0.923	28.7	0.1314	0.2628

* Calculated from the data taken from references 11 and 12. Available data extrapolated to the temperatures under consideration.

** For the CdS-CdO reaction (i) $\Delta G^\circ = 0$ at 1024°C, (ii) $pSO_2 = 10^{-2}$ mm Hg at 500°C, and (iii) $pSO_2 = 10^{-5}$ mm Hg at 340°C.

(B) Vapour Pressures of Cd, CdS and CdO (mm Hg)*

Substance	Temperature (°C)									
	400	500	600	700	750	765	800	850	900	950
CdS	—	0.0013	—	—	0.067	—	0.215	0.635	1.694	4.178
CdO	—	—	—	—	0.011	—	0.035	0.100	0.252	0.557
Cd	1.2	13	83	344	627	760	—	—	—	—

* Calculated from the data available in Ref. 10.