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Solubility of Red Phosphorous in Lead

Sean E. Walker

Metallurgical Engineering

ABSTRACT

The determination of the solubility of red phosphorus in lead can be used to produce a plot of the solubility with respect to temperature and pressure. The plot is produced with experimental data, activity determination from present thermodynamic data, and compilation of the two sets of data into the semi-regular solution format. A lead-phosphorus solubility diagram is necessary to determine the amount phosphorus that will be absorbed by lead and will remain unreacted in a given process.

INTRODUCTION

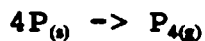
A lead-phosphorus solubility plot is needed for two specific processes. The production of lead grids and the removal of copper from lead.

A new method of producing lead grids for maintenance free lead acid batteries involves the introduction of phosphorus into the lead. The addition of phosphorus reduces the antimony content needed for increased strength. Grain refinement is also believed to occur due to the phosphorus. Resistance to cracking is another area the phosphorus could possibly improve. Presently a trial and error estimation of the amount of phosphorus soluble in lead is used for phosphorus addition determinations.

Phosphorus forms a compound with copper. When red phosphorus is placed in molten lead containing copper, the resulting compound of copper and phosphorus forms in the dross. A solubility plot could be used determined to the excess amount of phosphorus needed to exceed the solubility of lead and compound with all of the copper.

THERMODYNAMIC BACKGROUND

The solubility of red phosphorus in lead can be determined by controlling temperature and pressure within the lead-phosphorus system. Since phosphorus has a sublimation temperature of 431°C (704 K) at that temperature the reaction



occurs. Formation of phosphorus gas from solid phosphorus produces free energy of:

$$\Delta G^\circ = -RT \ln[P_{4(g)} / (a_{P(s)})^4] \quad (1)$$

In an atmosphere containing no other gases at the sublimation point the partial pressure of phosphorus will be one atmosphere. Therefore, with the free energy data interpolated past the sublimation temperature using the free energy of formation equation for phosphorus at temperatures greater than its boiling point, the activity of solid phosphorus in the lead can be determined.

Experimentally, controlling the temperatures of lead and phosphorus and indirectly the partial pressure of phosphorus, the mole fraction of phosphorus in the lead can be determined. Using the formula

$$a = \gamma * N \Rightarrow a/N = \gamma$$

$$\text{Log}(a') - \text{Log}(N') = \text{Log}(\gamma')$$

$$\text{Log}(a') = A' + B'/T \quad (2)$$

$$\text{Log}(N') = A'' + B''/T \quad (3)$$

$$\text{Log}(\gamma') = (A' - A'') + (B' - B'')/T$$

$$\text{Log}(\gamma') = A + B/T \quad (4)$$

the Logarithm of γ can be determined. From equation 2 the semi-regular solution can be completed as follows:

$$\text{Log}(\gamma) = (A + B/T) * (1-N)^2$$

$$\alpha = \text{Log}(\gamma) / (1-N)^2 = A' + B'/T \quad (5)$$

The standard graph for the solubility is 2.303α versus $10^4/T$ as shown in graph A.

EXPERIMENTAL PROCEDURE

A pure lead specimen of approximately 10 grams was placed in the tube at position A, while red phosphorus was placed in position B of the quartz tube in figure 1. The two C's denote dimples in the quartz which limited movement of the two specimens and kept the molten lead from flowing thin or mixing with the solid phosphorus. The position marked D was where Ti-Zr is introduced into the system and held in place by steel wool.

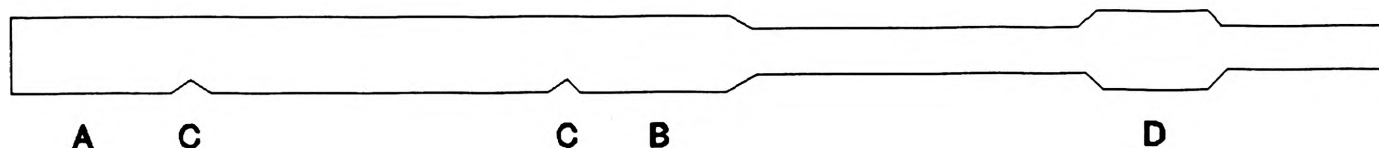


FIGURE 1. Reaction Tube

Once the lead, phosphorus, and titanium were in position the end of the tube nearest the lead was sealed. The narrow end was then hooked to a vacuum pump and the air was removed. Internal pressures of $< 10 \mu\text{atm}$. were the lowest pressures obtainable. After reaching the lowest pressure attainable the tube was flushed three times with argon gas to remove as much oxygen as possible. The tube was then sealed while in a near vacuum state. Next the titanium-zirconium was heated with a Bunsen burner to remove the remaining oxygen down to a negligible partial pressure. Finally, the tube was sealed near point A on figure 1 so that only the large diameter section with the two samples is left and under a vacuum.

A prepared reaction tube was then placed within a larger tube and into a tube furnace with a three region temperature control. The larger tubes were sealed with rubber stoppers to retain heat. Thermocouples were used for temperature measurements and as a temperature control device. Two thermocouples were placed at positions A, B, and directly between A and B in figure 1. One thermocouple at each position was connected to a power source which controls the heating elements, and the other thermocouple was connected to an electronic temperature readout for data collection. The readout set of thermocouples were placed inside the larger tube and directly on the reaction tube. This produced greater readout accuracy than the furnace control thermocouples which were on the outside of the larger tube.

After heating the lead and phosphorus for 24 hours at the desired temperatures, the reaction tube was removed from the furnace and quenched to retain the phosphorus in that had diffused into the lead at the elevated temperature. Lead and phosphorus samples were then removed from the cooled tube. The used phosphorus was saved for later use.

Lead samples were digested in nitric acid and the solution is analyzed by gas atomization for the phosphorus content. Since concentrations were small gas atomization was one of only a few processes capable of determining the phosphorus content accurately.

The lead digestion began by cutting the lead pieces into 1 gram samples and the actual weight is recorded. The 1 gram samples were then placed into a 150 ml beaker with 50 ml concentrated nitric acid and 50 ml of deionized water. The beaker and contents were then heated just below the boiling point of water. The temperature was sustained until all of the lead was dissolved. Once the lead was dissolved, the beaker was allowed to cool to room

temperature and was diluted to 250 ml in a volumetric flask. The solution was then shaken until equilibrium was obtained. Finally, a sample of the solution was placed in the gas atomizer and the phosphorus concentration in the solution was determined. Using the weight of the sample and the concentration of the lead nitrate solution the atomic percent of phosphorus was determined as follows:

$$F*250/Twt = wt\% P$$

$$\text{using 100 g basis} \rightarrow (100*wt\% P/100)/GFW P = \#P \text{ moles}$$

$$(100*(1-wt\% P/100)/GFW Pb = \#Pb \text{ moles}$$

$$N_p = \#P \text{ moles}/(\#P \text{ moles} + \#Pb \text{ moles})$$

EXPERIMENTAL THEORY

At the phosphorus end of the tube the reaction is the same as at the lead end, however, the phosphorus is in contact with an excess amount of solid phosphorus which produces:

$$a_p = 1 \rightarrow \Delta G^\circ = -RT \ln[P_{M(g)}/1]$$

The reaction at the phosphorus end of the tube is the pressure controlling reaction. Therefore the temperature controls the pressure. The temperature of the lead, since the pressure is known and constant due to the phosphorus temperature, can be varied to produce a variation in a_p within the lead. a_p is not 1 within the lead. A solid or liquid phase is not actually present, however, unreacted phosphorus is present within the molten lead. a_p in lead is useful for determination of γ as previously described.

DATA PROCESSING

The data collected from the gas atomizer had several possible errors involved. Specimens that showed greater than average amounts of phosphorus concentrations per temperature can be explained by the following. When the lead was removed from the furnace and quenched the solidified lead was in the shape of a bead with surface area exposed to the phosphorus atmosphere. Most of the time the tube fractured upon quenching and solid phosphorus formed on the lead's surface. Since the concentration of the phosphorus on the surface was much larger than the concentration within the lead, it must be removed. If the molten lead was jostled during the quench, ripples in the lead were solidified, causing removal of phosphorus with a steel brush extremely tough.

Specimens that showed less than average phosphorus concentrations can be explained by losses in the nitric acid digestion. The specimens while being digested in the nitric acid did not digest completely or some of the phosphorus was lost as vapor.

While one of the tubes for the 750°C was being sealed some of the phosphorus oxidized. The tube was heated anyway. As shown in the data table, the presence of oxidized phosphorus cut the solubility in half.

RESULTS

From the data collected equation five parameters have been determined:

$$\text{Pressure} = 1 \text{ atm.} \rightarrow 2.303*\alpha = 1752/T - 1.338 \quad (6)$$

$$\text{Pressure} = .2 \text{ atm.} \rightarrow 2.303*\alpha = 1957/T - 1.292 \quad (7)$$

Equations 6 and 7 are used to plot the Phosphorus Solubility In Lead graph. The standard error in equation 6 is .9% for B and .7% for A. This produces a random error of 1.1%. Only two points are present at .2 atm., therefore error determination is pointless.

NOMENCLATURE

G	free energy
R	gas constant (1.986 cal/mol)
T	temperature Kelvin
N	mole fraction
a	Raoultian activity
γ	activity coefficient
A,B	constants
α	alpha function
F	grams phosphorus per ml solution
wt%	weight percent
GFW	gram formula weight
Twt	total sample weight

atm.	atmospheres
Log	logarithm to base 10
Ln	logarithm to base e
Superscripts:	
f	fusion
s	saturated solution

ACKNOWLEDGEMENTS

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REFERENCES

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2. Davey T.R.A. "Derivation Of Activities From Metal Solubilities."

DATA TABLE

Sample	wt %P	AVE. %P	pp. P	Temp C	Element
1	0.0563	0.0582	1	431	P
	0.0506			431	Pb
	0.0678				
2	0.0815	0.0857	1	431	P
	0.0982			500	Pb
	0.0775				
3	0.0189	0.0343	0.9	429	P
	0.0497			500	Pb
4	0.1752	0.1366	1	431	P
	0.0644			431	Pb
	0.1701				
5	0.1055	0.0904	1	431	P
	0.0863			550	Pb
	0.0794				
6	0.0638	0.0638	0.2	383	P
	0.0638			600	Pb
7	0.0921	0.0856	1	431	P
	0.0841			600	Pb
	0.0805				
8	0.0302	0.0221	0.2	383	P
	0.0188			500	Pb
	0.0174				
9	0.0854	0.0878	1	431	P
	0.1026			550	Pb
	0.0755				
11	0.8865	0.937	1	435	P
	0.9029			902	Pb
	0.8816				
	0.9529				
	0.9696				
	0.9988				
	0.9681				
	1.4456				

DATA TABLE

12	0.4968	0.734	1	437	P	
	0.9511			900	Pb	
	0.7290					
	0.7805					
	0.7141					
13	1.5736	1.850	1	434	P	
	2.2318			Pb	904	Pb
	1.7450					
	0.5972					
14	1.5053	1.595	>1	441	P	
	1.2419			851	Pb	
	1.6850					
	1.9474					
15	0.6871	0.687	1	433	P	
				800	Pb	
16	4.0591	0.637	1	432	P	
	0.8573			800	Pb	
	0.6498					
	0.4029					
17	0.1697	0.172	1	432	P	
	* 0.1659			750	Pb	
	0.1800					
	0.9800					
	3.6631					
	1.8587					
18	4.8182	0.310	1	433	P	
	2.2733			750	Pb	
	0.2927					
	0.3163					
	0.3185					
	0.2976					
	0.3083					
	0.3257					

note.

* The phosphorus on this run was partially oxidized.

pp. is partial pressure

AVE. is an average excluding extremely high or low values.

Phosphorus Solubility In Lead

