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# Thermodynamic Studies of High Temperature Equilibria

## IV. Experimental Study of the Equilibrium Reaction $5PbO(s) + 1/2S_2(g) + 3/2O_2(g) \rightleftharpoons 4PbO.PbSO_4(s)$

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The equilibrium reaction

$$5PbO(s) + 1/2\ S_2(g) + 3/2\ O_2(g) \rightleftharpoons 4PbO.PbSO_4(s)$$

has been investigated in the temperature range 700 – 800°C by a flow method. At a certain temperature, PbO(s) was equilibrated with a gas phase with pre-set partial pressure values of $S_2$ and $O_2$ and the conversion of PbO to $4PbO.PbSO_4$ was followed by a thermobalance. The values obtained for the equilibrium constant ($K$, $atm^{-2}$) at different temperatures ($T$, in Kelvin) can be summarized by the equation

$$\log K = 43\ 260/T - 18.51$$

Using literature values of the equilibrium constant of formation, $K_f$, for PbO, the corresponding values for $4PbO.PbSO_4$ can be given by the relation

$$\log K_f = 99\ 120/T - 43.03$$

In order to calculate equilibrium compositions and heat generations for the reactions between PbS and various amounts of air (Wittung [1]), basic thermodynamic data must be available for all the products assumed to be formed. For the gases of current interest in these calculations, as well as for the condensed phases Pb, PbS, PbO, $PbSO_4$, $PbO.PbSO_4$, and $2PbO.PbSO_4$, the required data are available in the literature. On the other hand, data of satisfactory accuracy are lacking for the basic sulfate $4PbO.PbSO_4$.

There are earlier thermodynamic studies [2,3] of the phase $4PbO.PbSO_4$ but the results obtained, which were based upon a static method, are quite conflicting. Therefore, we found it most important to perform a re-determination. For this investigation, we developed a dynamic method which permits data of higher accuracy to be obtained.

## METHOD

The equilibrium reaction

$$5PbO(s) + 1/2\ S_2(g) + 3/2\ O_2(g) \rightleftharpoons 4PbO.PbSO_4(s) \qquad (I)$$

was studied by equilibrating the initial solid phase PbO with a gas phase of known composition and thus known values of the partial pressures of $O_2$ and $S_2$. By stepwise changing the gas composition, the reaction temperature being kept constant, the conditions for the co-existence of both solid phases could be traced. The gain in weight was indicated by using a thermobalance.

The reaction temperature was then successively changed in the interval 700 – 800°C. We intended to study the equilibrium reaction (I) up to 835°C, *i.e.* the eutectic temperature[4,5] in the system $PbO - 4PbO.PbSO_4$. However, the evaporation of PbO(s) became quite considerable at temperatures $\gtrsim$800°C, and the weight gain indications became quite uncertain. It could be mentioned that trials to run the reverse reaction were unsuccessful because of slow reactions.

By applying the law of mass action to equilibrium reaction (I), one obtains the relation

$$K = p_{S_2}^{-1/2}\, p_{O_2}^{-3/2} \qquad (1)$$

At 727°C (1000 K) the equilibrium constant is of the order $K = 10^{25}$ atm$^{-2}$. This means that both $p_{S_2}$ and $p_{O_2}$ will take quite low values so that gas-buffer systems must be used to obtain a satisfactory mass transport and to obtain high stability of the partial pressures in the system. In this study the following gas-buffer systems have been used

$$CO_2 \rightleftharpoons CO + 1/2O_2$$
$$H_2O \rightleftharpoons H_2 + 1/2O_2$$
$$SO_2 \rightleftharpoons 1/2S_2 + O_2$$

To establish the proper gaseous conditions for the formation of $4PbO.PbSO_4$ at around 1000 K, $p_{O_2}$ must exceed a value of about $10^{-12.5}$ atm (to avoid formation of Pb(l)) and $p_{S_2}$ has to be kept below about $10^{-12.0}$ atm (to avoid formation of the other basic Pb-sulfates). To provide for a satisfactory mass transport, the following approximate pressure values were found suitable at around 1000 K: $p_{O_2} \approx 10^{-12.0}$ atm and $p_{S_2} \approx 10^{-13.0}$ atm, corresponding to the initial conditions $CO_2/H_2 \approx 10^{4.0}$ and $p_{SO_2} \approx 10^{-3.5}$ atm. Unfortunately these values are not easily arranged by mixing pure gases. However, the mixing-up of the gas phase was facilitated by starting with pure $CO_2$ and pre-mixed gas mixtures of $CO_2/H_2$ and $CO_2/SO_2$.

In order to test the apparatus, some preliminary runs of the equilibrium reaction

$$Pb(l) + 1/2O_2(g) \rightleftharpoons PbO(s)$$

were performed in the same temperature interval. It proved necessary, at least for the lower reaction temperatures, to pre-heat the reaction gas mixture to ensure an approach to an equilibrium state of the gas phase.

## EXPERIMENTAL SET-UP

A sketch of the apparatus is given in Fig. 1 and the reactor compartment is shown in more detail in Fig. 2.

*The gas phase.* The reaction gas mixture was successively mixed from 3 gas sources (see Fig. 1), *viz.* pure $CO_2$, the mixture $CO_2/H_2$ (containing about 0.1 % $H_2$) and $CO_2/SO_2$ (containing about 1.0 % $SO_2$). The exact content values of $H_2$ and $SO_2$, respectively, in the pre-mixed gases were given by delivery with an indicated uncertainty of 1 – 5 %. All gases were of high quality (impurities of the order 10 ppm) but nevertheless they were freed from traces of $H_2O$ by passing a tube containing $P_2O_5$-granules. After purification and flow rate measurements, the gases were passed, *via* a preheating reactor kept at about 850°C, to the reactor compartment. Here also an $N_2$-stream was added which partly passed upwards (see Fig. 2), and partly downwards to the balance compartment. Also $N_2$ was freed from $H_2O$ and also from oxygen by passage through a tube containing hot activated copper on kieselguhr at about 180°C.

The flow rates ($J$, ml/min) were measured using rotameters (Brooks Shorate) calibrated against a soap-film meter and a gas calibrator (Brooks Vol-u-meter). The calibration values for all gases could be reproduced within a maximum deviation of about 1.0 %. The flow rates were always adjusted by gas regulators so as to satisfy the following relation

$$J(5) = J(1) + J(2) + J(3) + \alpha\, J(4) \qquad (2)$$

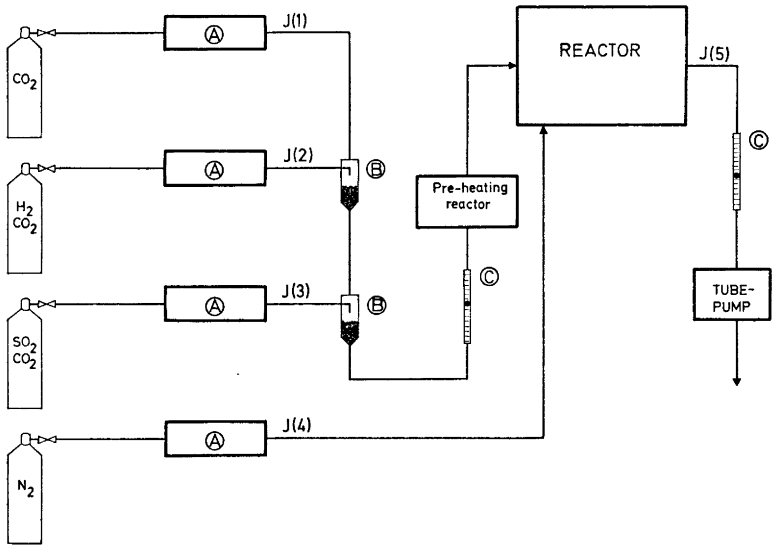


*Fig. 1.* Sketch of the apparatus. A = Purification unit and rotameter. B = Gas-mixer. C = Rotameter. Concerning symbols for gas flow-rates, see text after eqn. (2).

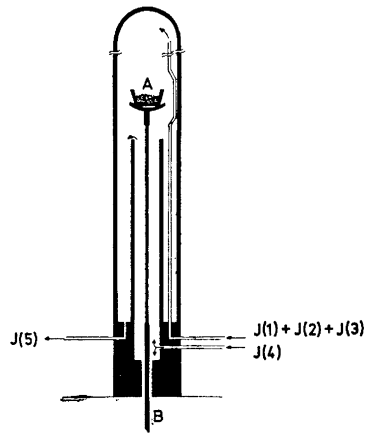


*Fig. 2.* Sketch of the reactor compartment. Arrows indicate gas streams.

where the flow-rate symbols are $J(1)$ for pure $CO_2$, $J(2)$ for the mixture $CO_2/H_2$, $J(3)$ for the mixture $CO_2/SO_2$, $J(4)$ for $N_2$, and $J(5)$ for the outlet flow rate. The flow rate of $N_2$ was kept practically constant through all runs, $J(4) \approx 40$ ml min$^{-1}$, and the value of $J(5)$ was regulated by a tube-pump with adjustable suction capacity. To eliminate air diffusion into the reactor compartment and to avoid contact between the corrosive reaction gas mixture and the balance, values $0 < \alpha < 1$ should be chosen. In order to minimize the dilution of the reaction gas with $N_2$, the quantity $\alpha$ was chosen as low as practically possible, normally $\alpha \approx 0.2$, which means that the reaction gas was diluted with approximately 5 % of $N_2$.

*Table 1.* Basic experimental data and calculated values of log $K$ for the equilibrium reaction $5PbO(s) + 1/2S_2(g) + 3/2O_2(g) \rightleftharpoons 4PbO.PbSO_4(s)$.

| $t$, °C | $J(CO_2)$ ml min$^{-1}$ | $J(H_2)$ ml min$^{-1}$ | $J(SO_2)$ ml min$^{-1}$ | Solid phase[a] | log $p_{O_2}$ | log $p_{S_2}$ | log $Q$ | $10^4/T$ | log $K$ | $\Delta$ log $K$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 700.7 | 134 | 0.0243 | 0.0439 | PbO | −13.75 | −10.67 | 25.96 | 10.268 | 25.91 ± 0.05 | 0 |
| | 135 | 0.0243 | 0.0562 | 4:1 | −13.74 | −10.49 | 25.86 | | | |
| 703.8 | 157 | 0.0343 | 0.0462 | PbO | −13.82 | −10.52 | 25.98 | 10.235 | 25.91 ± 0.07 | 0.15 |
| | 160 | 0.0343 | 0.0647 | 4:1 | −13.80 | −10.26 | 25.84 | | | |
| 705.3 | 160 | 0.0198 | 0.0439 | PbO | −13.28 | −11.59 | 25.71 | 10.220 | 25.66 ± 0.05 | −0.04 |
| | 160 | 0.0198 | 0.0554 | 4:1 | −13.28 | −11.39 | 25.61 | | | |
| 706.2 | 141 | 0.0284 | 0.0770 | PbO | −13.67 | −10.17 | 25.59 | 10.210 | 25.57 ± 0.02 | −0.09 |
| | 143 | 0.0287 | 0.0870 | 4:1 | −13.67 | −10.08 | 25.54 | | | |
| 719.0 | 125 | 0.0154 | 0.0447 | PbO | −12.86 | −11.67 | 25.12 | 10.079 | 25.02 ± 0.09 | −0.07 |
| | 127 | 0.0147 | 0.0670 | 4:1 | −12.80 | −11.44 | 24.93 | | | |
| 731.0 | 141 | 0.0143 | 0.0447 | PbO | −12.33 | −12.37 | 24.68 | 9.958 | 24.60 ± 0.07 | −0.03 |
| | 142 | 0.0138 | 0.0616 | 4:1 | −12.29 | −12.19 | 24.53 | | | |
| 733.7 | 153 | 0.0156 | 0.0539 | PbO | −12.26 | −12.33 | 24.55 | 9.931 | 24.43 ± 0.12 | −0.02 |
| | 156 | 0.0156 | 0.0932 | 4:1 | −12.24 | −11.90 | 24.31 | | | |
| 742.5 | 142 | 0.0172 | 0.0616 | PbO | −12.15 | −12.03 | 24.24 | 9.845 | 24.22 ± 0.02 | 0.14 |
| | 143 | 0.0172 | 0.0678 | 4:1 | −12.14 | −11.97 | 24.20 | | | |
| 756.0 | 122 | 0.0264 | 0.171 | PbO | −12.28 | −10.28 | 23.56 | 9.718 | 23.49 ± 0.07 | −0.04 |
| | 127 | 0.0264 | 0.237 | 4:1 | −12.24 | −10.10 | 23.42 | | | |
| 758.5 | 125 | 0.0275 | 0.226 | PbO | −12.22 | −10.08 | 23.37 | 9.693 | 23.31 ± 0.06 | −0.11 |
| | 132 | 0.0275 | 0.304 | 4:1 | −12.17 | −9.97 | 23.24 | | | |
| 759.1 | 104 | 0.0154 | 0.0825 | PbO | −11.86 | −11.49 | 23.54 | 9.687 | 23.47 ± 0.07 | 0.08 |
| | 108 | 0.0165 | 0.121 | 4:1 | −11.88 | −11.15 | 23.40 | | | |
| 759.4 | 136 | 0.0314 | 0.223 | PbO | −12.24 | −10.09 | 23.40 | 9.684 | 23.33 ± 0.07 | −0.05 |
| | 143 | 0.0314 | 0.308 | 4:1 | −12.19 | −9.95 | 23.26 | | | |
| 760.8 | 143 | 0.0380 | 0.336 | PbO | −12.32 | −9.56 | 23.27 | 9.671 | 23.23 ± 0.04 | −0.09 |
| | 148 | 0.0380 | 0.396 | 4:1 | −12.29 | −9.52 | 23.19 | | | |
| 770.8 | 156 | 0.0171 | 0.108 | PbO | −11.27 | −12.38 | 23.10 | 9.579 | 23.06 ± 0.03 | 0.13 |
| | 155 | 0.0176 | 0.131 | 4:1 | −11.31 | −12.13 | 23.03 | | | |
| 771.3 | 150 | 0.0176 | 0.180 | PbO | −11.32 | −11.78 | 22.87 | 9.574 | 22.81 ± 0.05 | −0.09 |
| | 155 | 0.0176 | 0.237 | 4:1 | −11.29 | −11.63 | 22.76 | | | |
| 771.8 | 122 | 0.0145 | 0.0803 | PbO | −11.32 | −12.28 | 23.13 | 9.569 | 23.02 ± 0.10 | 0.14 |
| | 133 | 0.0182 | 0.163 | 4:1 | −11.44 | −11.50 | 22.92 | | | |
| 771.9 | 166 | 0.0157 | 0.125 | PbO | −11.12 | −12.57 | 22.97 | 9.568 | 22.90 ± 0.06 | 0.02 |
| | 172 | 0.0157 | 0.166 | 4:1 | −11.09 | −12.41 | 22.84 | | | |
| 772.4 | 148 | 0.0182 | 0.204 | PbO | −11.33 | −11.60 | 22.80 | 9.564 | 22.75 ± 0.05 | −0.11 |
| | 155 | 0.0176 | 0.254 | 4:1 | −11.27 | −11.58 | 22.69 | | | |
| 795.0 | 116 | 0.0145 | 0.198 | PbO | −10.75 | −11.81 | 22.03 | 9.362 | 21.94 ± 0.09 | −0.05 |
| | 126 | 0.0145 | 0.306 | 4:1 | −10.68 | −11.64 | 21.85 | | | |
| 797.1 | 158 | 0.0182 | 0.215 | PbO | −10.63 | −12.19 | 22.03 | 9.343 | 21.97 ± 0.06 | 0.06 |
| | 165 | 0.0189 | 0.305 | 4:1 | −10.63 | −11.92 | 21.90 | | | |

[a] 4:1 refers to $4PbO.PbSO_4$.

The flow rates of the different components making up the reaction gas mixture were thus continuously measured. By assuming this gas mixture to reach an equilibrium state in the reactor compartment, the values of $p_{S_2}$ and $p_{O_2}$ could be calculated with a computer program, SOLGAS, derived by Gunnar Eriksson.[6] The thermodynamic data to be required for these calculations were interpolated from values given in JANAF-tables.[7]

*The solid phase.* The solid substance PbO (Fischer *p.a.*) was used without further purification. After screening (grain sizes with diameters of 0.045 – 0.065 mm were used) the sample was placed in a low crucible of $Al_2O_3$. The weight of the solid sample was continuously recorded using a Netzsch thermobalance, type 409. During each run about 200 mg PbO was dosed, then, by stoichiometry, a weigth gain of about 15 mg was expected. In practice it was found that a weight gain of about 1 mg/h was obtained. As the sensitivity of the thermobalance was about 0.5 mg, it was thus necessary to run 1 – 2 h for each gas composition in order to obtain a safe indication.

In some runs the equilibrated solid sample was quenched and examined by X-ray powder analysis. No phases other than PbO and $4PbO.PbSO_4$ could be identified.

*Reaction temperature.* The reaction temperature was measured with a Pt-Pt (10 % Rh) thermocouple. The thermo-emf obtained was continuously recorded to indicate approximate temperature values. For more precise temperature values, reliable within ± 1°, the thermo-emf was from time to time separately measured using a precision potentiometer (Leeds and Northrup, K-3 universal potentiometer). The temperature around the solid sample could easily be controlled within ± 1° of a constant, desired temperature.

## RESULTS AND DISCUSSION

*Comments to results obtained.* Basic experimental data and some calculated values from the study of equilibrium reaction (I) are given in Table 1. The quantities $J(CO_2)$, $J(H_2)$ and $J(SO_2)$ are the calculated values of actual flow rates for each of $CO_2$, $H_2$ and $SO_2$, respectively. The symbol $Q$ is equivalent to the equilibrium constant $K$ (*cf.* eqn. (1)), but valid for conditions other than the equilibrium state

$$Q = p_{S_2}^{-1/2}\ p_{O_2}^{-3/2} \tag{2}$$

For every experimental run two log $Q$-values are given. The first value corresponds to the last gas composition, where PbO is the only solid present, while the second log $Q$-value corresponds to the conditions immediately after a weight gain. For a certain experimental run, the log $K$-value has been calculated as the average of the two indicated log $Q$-values. The log $K$-values thus obtained were fitted to a straight line ($T$, in Kelvin)

$$\log K_{calc} = 43260/T - 18.51 \tag{3}$$

by a least squares treatment. The deviation $\Delta \log K = \log K - \log K_{calc}$ was calculated and is included in Table 1. As seen, the log $K$-values are gathered around the straight line within the range ± 0.15 log-units.

*Some thermodynamic calculations.* The log $K_f$-temperature relation

$$\log K_f = 11172/T - 4.904 \tag{4}$$

was calculated for PbO on the basis of fundamental thermodynamic data given by Wittung.[1] The estimated uncertainty was ± 0.05 logarithmic units. By combining eqns. (3) and (4), the log $K_f$ for $4PbO.PbSO_4$ can be calculated and written according to the relation

$$\log K_f = 99120/T - 43.03 \tag{5}$$

with an estimated error of ± 0.25 logarithmic units. The corresponding relation for the free energy of formation of $4PbO.PbSO_4$ can be written ($\Delta G_f^\circ$ in cal $mol^{-1}$, 1 cal = 4.1840 J):

$$\Delta G_f^\circ = -453\,500 + 196.9\,T \qquad (6)$$

It could be mentioned that the $\Delta G_f^\circ$-value at 1000 K will be $-256\,600 \pm 1400$ cal while the literature values are $-250\,060$ cal $mol^{-1}$ (Kellogg and Basu [2]) and $-254\,800$ cal $mol^{-1}$ (Lloyd [3]), respectively.

The heat evolved for the same equilibrium reaction (I) in the temperature range studied can be calculated by applying the relationship

$$\Delta H = -R \ln 10 \frac{d(\log K)}{d(1/T)} \qquad (7)$$

to eqn. (3). The following value is obtained in the temperature range studied: $\Delta H^\circ = -198\,000 \pm 4000$ cal.

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