

# Phys8500

## Solution Homework #3

1.

for reaction 1:  $\Delta H_f^\circ$ :  $\text{H}_2\text{S}(\text{g}) = -20.5 \text{ [KJ} \cdot \text{mol}^{-1}]$ ;  $\text{Zn}(\text{s}) = 130.4 \text{ [KJ} \cdot \text{mol}^{-1}]$ ;

$\text{ZnS}(\text{s}) = -205.9 \text{ [KJ} \cdot \text{mol}^{-1}]$ ;  $\text{H}_2(\text{g}) = 0 \text{ [KJ} \cdot \text{mol}^{-1}]$ ;

$\Rightarrow$  Enthalpy change  $\Delta H < 0$

for reaction 2:  $\Delta H_f^\circ$ :  $\text{H}_2\text{S}(\text{g}) = -20.5 \text{ [KJ} \cdot \text{mol}^{-1}]$ ;  $\text{Cd}(\text{s}) = 111.8 \text{ [KJ} \cdot \text{mol}^{-1}]$ ;

$\text{CdS}(\text{s}) = -162 \text{ [KJ} \cdot \text{mol}^{-1}]$ ;  $\text{H}_2(\text{g}) = 0 \text{ [KJ} \cdot \text{mol}^{-1}]$ ;

$\Rightarrow$  Enthalpy change  $\Delta H < 0$

So, both reactions are exothermic! An alternative way is the following:

Form  $\Delta H^0 = \Delta G^0 + T \cdot \Delta S^0$  and  $\Delta S^0 < 0$  follow that  $\Delta H^0 < 0$  if  $\Delta G^0 < 0$

Reaction 1:  $\Delta G^0 = -76400 + 82.1 \cdot T - 5.9 \cdot T \cdot \ln(T) =$

(@T = 680°C = 953K) = -36728 [cal / mol] = -152588 [J / mol]

Reaction 2:  $\Delta G^0 = -50000 + 82.2 \cdot T - 6.64 \cdot T \cdot \ln(T) =$

(@T = 600°C = 873K) = -17494 [cal / mol] = -73256 [J / mol]

a) both reactions are exothermic!! If you go extreme high temperature, the reaction may become endothermic – Most likely, however, the  $\Delta G$  reaction equation is not longer valid!

b)

In equilibrium:  $\Delta G = \Delta G^0 + \ln[K_p] = 0$ ;

with  $K_p = \left( \frac{p_{\text{ZnS}} \times p_{\text{H}_2}}{p_{\text{Zn}} \times p_{\text{H}_2\text{S}}} \right)$  and  $K_p = \left( \frac{p_{\text{CdS}} \times p_{\text{H}_2}}{p_{\text{Cd}} \times p_{\text{H}_2\text{S}}} \right)$ , for reaction 1 and 2, respectively.

$$\Rightarrow \frac{p_{\text{ZnS}} \times p_{\text{H}_2}}{p_{\text{Zn}} \times p_{\text{H}_2\text{S}}} = \frac{p_{\text{H}_2}}{p_{\text{Zn}} \times p_{\text{H}_2\text{S}}} = \exp\left[\frac{-\Delta G^0}{R \times T}\right] = \exp\left[\frac{152588 \text{ [J/mol]}}{8.31 \text{ [J / mol K]} \times 953\text{K}}\right] = \exp[19.26] = 2.33 \times 10^8$$

$$\text{and } \frac{p_{\text{CdS}} \times p_{\text{H}_2}}{p_{\text{Cd}} \times p_{\text{H}_2\text{S}}} = \frac{p_{\text{H}_2}}{p_{\text{Cd}} \times p_{\text{H}_2\text{S}}} = \exp\left[\frac{-\Delta G^0}{R \times T}\right] = \exp\left[\frac{73256 \text{ [J/mol]}}{8.31 \text{ [J / mol K]} \times 873\text{K}}\right] = \exp[10.10] = 2.43 \times 10^4.$$

$$\Rightarrow \log(p_{\text{Zn}}) = -\frac{7070}{T} + 9.41 = -\frac{7070}{953} + 9.41 = 1.991 \Rightarrow p_{\text{Zn}} = 98.02$$

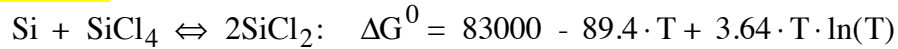
$$\Rightarrow \frac{p_{\text{H}_2\text{S}}}{p_{\text{H}_2}} = \left[ \frac{1}{2.33 \cdot 10^8 \cdot 98.02} \right] = 4.37 \cdot 10^{-11}$$

Similarly for reaction 2,

$$\Rightarrow \log(p_{\text{Cd}}) = -\frac{5940}{T} + 9.02 = -\frac{5940}{873} + 9.02 = 2.21 \Rightarrow p_{\text{Cd}} = 164.39$$

$$\Rightarrow \frac{p_{\text{H}_2\text{S}}}{p_{\text{H}_2}} = \left[ \frac{1}{2 \cdot 43 \cdot 10^4 \cdot 164.39} \right] = 2.57 \cdot 10^{-7}$$

## 2. Si deposition via



$$\begin{aligned} \text{source @ } 900^\circ\text{C}: \Delta G^0 &= 83000 - 89.4 \cdot 1173\text{K} + 3.64 \cdot 1173\text{K} \cdot \ln(1173\text{K}) \\ &= 8309 \text{ [Cal / mol]} = 34746 \text{ [J / mol]} \end{aligned}$$

$$\begin{aligned} \text{substrate @ } 750^\circ\text{C}: \Delta G^0 &= 83000 - 89.4 \cdot 1023\text{K} + 3.64 \cdot 1023\text{K} \cdot \ln(1023\text{K}) \\ &= 17351 \text{ [Cal / mol]} = 72558 \text{ [J / mol]} \end{aligned}$$

The partial pressure gradient  $\Delta p$  for  $\text{SiCl}_2 / \text{SiCl}_4$  at source and substrate is given by

$$\text{@ } 900^\circ\text{C}: \frac{[p_{\text{SiCl}_2}]^2}{p_{\text{SiCl}_4}} = \exp\left[\frac{-\Delta G^0}{R \cdot T}\right] = \exp\left[\frac{-34746 \text{ J/mol}}{8.31 \text{ [J / mol K]} \cdot 1173\text{K}}\right] = 2.83 \cdot 10^{-2}$$

$$\text{with } p_{\text{SiCl}_2} + p_{\text{SiCl}_4} = 1 \text{ and } [p_{\text{SiCl}_2}]^2 = \exp\left[\frac{-\Delta G^0}{R \cdot T}\right] \cdot p_{\text{SiCl}_4} = \exp\left[\frac{-\Delta G^0}{R \cdot T}\right] \cdot (1 - p_{\text{SiCl}_2})$$

$$\begin{aligned} \text{we get } [p_{\text{SiCl}_2}]^2 + 2.83 \cdot 10^{-2} \cdot p_{\text{SiCl}_2} - 2.83 \cdot 10^{-2} &= 0, \\ p_{\text{SiCl}_2} &= -0.0141 \pm \sqrt{1.988 \cdot 10^{-4} + 2.83 \cdot 10^{-2}} = 0.155 \end{aligned}$$

$$\text{@ } 750^\circ\text{C}: \frac{[p_{\text{SiCl}_2}]^2}{p_{\text{SiCl}_4}} = \exp\left[\frac{-\Delta G^0}{R \cdot T}\right] = \exp\left[\frac{-72558 \text{ J/mol}}{8.31 \text{ [J / mol K]} \cdot 1023\text{K}}\right] = 1.96 \cdot 10^{-4}$$

$$\text{with } p_{\text{SiCl}_2} + p_{\text{SiCl}_4} = 1 \text{ and } [p_{\text{SiCl}_2}]^2 = 1.96 \cdot 10^{-4} \cdot (1 - p_{\text{SiCl}_2})$$

$$\begin{aligned} \text{we get } [p_{\text{SiCl}_2}]^2 + 1.96 \cdot 10^{-4} \cdot p_{\text{SiCl}_2} - 1.96 \cdot 10^{-4} &= 0, \\ p_{\text{SiCl}_2} &= -9.8 \cdot 10^{-5} \pm \sqrt{9.604 \cdot 10^{-9} + 1.96 \cdot 10^{-4}} = 0.0139 \end{aligned}$$

The partial pressure difference  $\Delta p = 0.155 - 0.0139 = 0.1411$

The flux is given by the difference in the partial pressure between source and substrate:

$$\text{Flow} = \frac{\pi \cdot r^4}{8 \cdot \eta \cdot l} \cdot \Delta p = \frac{\pi \cdot 0.075^4 \text{ [m}^4\text{]}}{8.0 \cdot 8 \cdot 10^{-4} \text{ [Pa} \cdot \text{s]} \cdot 0.25 \text{ [m]}} \cdot 0.1411 \cdot 1.013 \cdot 10^5 \text{ [Pa]} = 8870 \text{ m}^3 \text{ s}^{-1} = 887 \cdot 10^7 \text{ [cm}^3 \cdot \text{s}^{-1}\text{]}$$

$$\text{Flux} = \text{Flow/area} = \frac{r^2 \cdot \Delta p}{8 \cdot \eta \cdot l} = \dots = 49 \cdot 6 \cdot 10^6 \text{ [cm} \cdot \text{s}^{-1}\text{]}$$

$$\text{b.) } D \cdot \frac{d^2 C}{dx^2} - v \cdot \frac{dC}{dx} - K \cdot C = 0,$$

with BC:  $C(x=0) = 1$  and  $C(x=1 \text{ m}) = 0$ ,  $D = 1000 \text{ cm}^2/\text{s}$ ,  $v = 100 \text{ cm/s}$ , and  $K=1 \text{ s}^{-1}$ ;

$$C(x) = \left( 1 - 7.56 \cdot 10^{-6} \right) \cdot \exp[-0.009 \cdot x] - 7.56 \cdot 10^{-6} \cdot \exp[0.109 \cdot x]$$