

## Thermodynamics of Materials 3.00

### Example Problems for Week 9

#### Example Problem 9.1

For the reaction  $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{CO}_2(g)$

- Write down a general expression for the partial pressure of oxygen,  $P_{\text{O}_2}$ , at equilibrium using the concept of the equilibrium constant and its relation to the free energy of reaction,  $\Delta\bar{G}_{rxn}$ .
- For a fixed  $P_{\text{CO}_2}/P_{\text{CO}}$  ratio make plots that show the relation between  $P_{\text{O}_2}$  and  $P_{\text{T}}$  and  $P_{\text{O}_2}$  and  $T$ .
- For a general reaction beginning with  $n_{\text{CO}}^0$ ,  $n_{\text{O}_2}^0$ , and  $n_{\text{CO}_2}^0$  moles of the substances write down an expression for the reaction constant in terms of the final number of moles of  $\text{O}_2$ ,  $x$ .

#### Solution 9.1

a) The reaction constant can be written for the reaction in terms of the partial pressures and the total pressure at equilibrium assuming that this is a closed system.

$$K = \frac{(P_{\text{CO}_2}/P_{\text{T}})}{(P_{\text{CO}}/P_{\text{T}})(P_{\text{O}_2}/P_{\text{T}})^{\frac{1}{2}}}$$

$$K = \frac{P_{\text{CO}_2} P_{\text{T}}^{\frac{1}{2}}}{P_{\text{CO}} P_{\text{O}_2}^{\frac{1}{2}}}$$

also there is a relation between the equilibrium reaction constant and  $\Delta\bar{G}_{rxn}$ .

$$K = \exp\left(\frac{-\Delta\bar{G}_{rxn}}{RT}\right)$$

$$\frac{P_{\text{CO}_2} P_{\text{T}}^{\frac{1}{2}}}{P_{\text{CO}} P_{\text{O}_2}^{\frac{1}{2}}} = \exp\left(\frac{-\Delta\bar{G}_{rxn}}{RT}\right)$$

Rearranging we get:

$$P_{\text{O}_2} = \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}}\right)^2 P_{\text{T}} \exp\left(\frac{2\Delta\bar{G}_{rxn}}{RT}\right)$$

b) We can observe the linear relation between  $P_{\text{O}_2}$  and  $P_{\text{T}}$  from the above with slope  $m$  and intercept  $b$  given below.

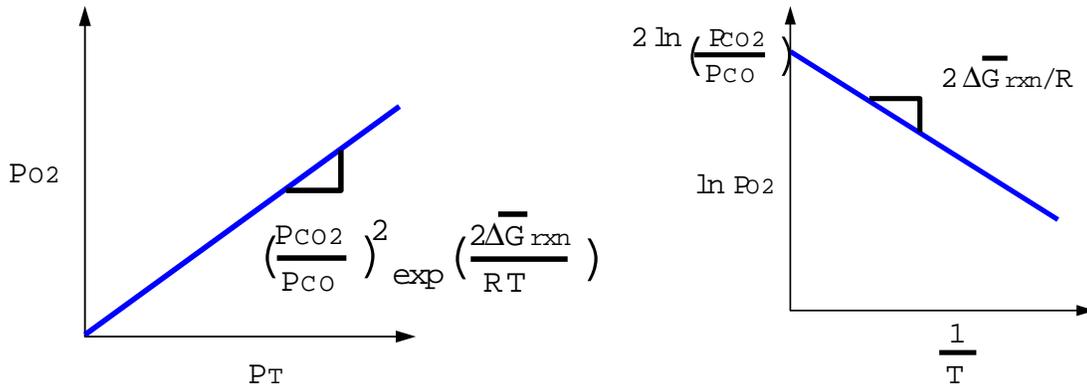
$$m = \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}}\right)^2 \exp\left(\frac{2\Delta\bar{G}_{rxn}}{RT}\right)$$

$$b = 0$$

Taking the natural log of both sides of the above we can see the relation between  $\ln P_{O_2}$  and  $\frac{1}{T}$ .

$$\ln P_{O_2} = 2 \ln \frac{P_{CO_2}}{P_{CO}} + \frac{2\Delta\bar{G}_{rxn}}{R} \frac{1}{T}$$

In this form the slope is  $\frac{2\Delta\bar{G}_{rxn}}{R}$  and the intercept  $2 \ln \frac{P_{CO_2}}{P_{CO}}$ . The slope is negative as  $\Delta\bar{G}_{rxn} < 0$ .



c) Assuming that the gases act as an ideal gas mixture we can write the equilibrium reaction constant in terms of the mole fractions of each gas. But first we have to find out the equilibrium amounts of each substance. The following table shows the knowns to begin with.

reaction	CO	$\frac{1}{2}O_2$	$\rightleftharpoons$	CO <sub>2</sub>
initial	$n_{CO}^0$	$n_{O_2}^0$		$n_{CO_2}^0$
change	.	.		.
equilibrium	.	$x$		.

The change in number of moles of oxygen is  $x - n_{O_2}^0$ . From this we can calculate the change in the number of moles of CO and CO<sub>2</sub> as,  $dn_{CO}^0 = 2dn_{O_2}^0$  and  $dn_{CO_2}^0 = -2dn_{O_2}^0$ , respectively. Now we can fill in the rest of the table.

reaction	CO	$\frac{1}{2}O_2$	$\rightleftharpoons$	CO <sub>2</sub>
initial	$n_{CO}^0$	$n_{O_2}^0$		$n_{CO_2}^0$
change	$2(x - n_{O_2}^0)$	$(x - n_{O_2}^0)$		$-2(x - n_{O_2}^0)$
equilibrium	$n_{CO}^0 + 2(x - n_{O_2}^0)$	$x$		$n_{CO_2}^0 - 2(x - n_{O_2}^0)$

The equilibrium constant is written as:

$$K = \frac{\frac{n_{CO_2}^0}{n_T}}{\frac{n_{CO}^0}{n_T} \left(\frac{n_{O_2}^0}{n_T}\right)^{\frac{1}{2}}}$$

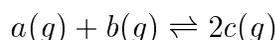
$$K = \frac{n_{CO_2}^0 n_T^{\frac{1}{2}}}{n_{CO}^0 (n_{O_2}^0)^{\frac{1}{2}}}$$

The total number of moles of gaseous substances will change during a reaction. It is important to use the total number of moles of the gaseous substances at equilibrium for the equilibrium reaction constant,  $n_T = n_{\text{CO}_2}^0 + n_{\text{CO}}^0 + x$ .

$$K = \frac{(n_{\text{CO}_2}^0 - 2(x - n_{\text{O}_2}^0))(n_{\text{CO}_2}^0 + n_{\text{CO}}^0 + x)^{\frac{1}{2}}}{(n_{\text{CO}}^0 + 2(x - n_{\text{O}_2}^0))x^{\frac{1}{2}}}$$

### Example Problem 9.2

Given the molar enthalpies at 298K,  $\bar{H}_{a,298}$ ,  $\bar{H}_{b,298}$ , and  $\bar{H}_{c,298}$ , the molar entropies at 298K,  $\bar{S}_{a,298}$ ,  $\bar{S}_{b,298}$ , and  $\bar{S}_{c,298}$ , and the heat capacities,  $\bar{C}_{p,a}$ ,  $\bar{C}_{p,b}$ , and  $\bar{C}_{p,c}$ , calculate the equilibrium reaction constant for the following reaction at an arbitrary temperature T.



**Solution 9.2** The reaction constant has the following relation to the molar gibbs free energy of the reaction,  $\Delta\bar{G}_{rxn}$ .

$$K = \exp\left(\frac{-\Delta\bar{G}_{rxn}}{RT}\right) = \left(\frac{n_c^2}{n_a n_b}\right)$$

Now we can formulate  $\Delta\bar{G}_{rxn}$ .

$$\begin{aligned} \Delta\bar{G}_{rxn} &= 2\bar{G}_c - \bar{G}_b - \bar{G}_a \\ \Delta\bar{G}_{rxn} &= 2\bar{G}_{c,298} - \bar{G}_{b,298} - \bar{G}_{a,298} + (2\Delta\bar{G}_c - \Delta\bar{G}_a - \Delta\bar{G}_b) \end{aligned}$$

Now we can use  $\bar{C}_{p,i}$  to calculate  $\Delta\bar{G}_i$ .

$$\begin{aligned} \Delta\bar{G}_{rxn} &= (2\bar{H}_{c,298} - \bar{H}_{b,298} - \bar{H}_{a,298}) \\ &\quad - 298(2\bar{S}_{c,298} - \bar{S}_{b,298} - \bar{S}_{a,298}) \\ &\quad + (2 \int_{298}^T \bar{C}_{p,c} dT - \int_{298}^T \bar{C}_{p,a} dT - \int_{298}^T \bar{C}_{p,b} dT) \\ &\quad - T(2 \int_{298}^T \frac{\bar{C}_{p,c}}{T} dT - \int_{298}^T \frac{\bar{C}_{p,a}}{T} dT - \int_{298}^T \frac{\bar{C}_{p,b}}{T} dT) \end{aligned}$$

$$\begin{aligned} \Delta\bar{G}_{rxn} &= (2\bar{H}_{c,298} - \bar{H}_{b,298} - \bar{H}_{a,298})298(2\bar{S}_{c,298} - \bar{S}_{b,298} - \bar{S}_{a,298}) \\ &\quad + \int_{298}^T (2\bar{C}_{p,c} - \bar{C}_{p,a} - \bar{C}_{p,b}) dT - T \int_{298}^T \frac{2\bar{C}_{p,c} - \bar{C}_{p,a} - \bar{C}_{p,b}}{T} dT \end{aligned}$$

The substitution is straightforward.