

1) For the reaction



$$\Delta H^\circ = -206.1 \text{ kJ and } \Delta S^\circ = -214.7 \text{ J/K}$$

The equilibrium constant for this reaction at **344 K** is:

A)  $1.74 \times 10^{46}$

**B)  $1.21 \times 10^{20}$**

C)  $3.46 \times 10^{42}$

D)  $8.28 \times 10^{-21}$

The equilibrium constant is related to the change in the standard Gibbs Free Energy for a reaction:

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}} = -RT \ln K_{\text{eq}}$$

Use  $\Delta H^\circ$  and  $\Delta S^\circ$  to calculate  $\Delta G^\circ$  for the reaction at **344 K**:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\dots = -206.1 \text{ kJ} - (344 \text{ K})(-0.2147 \text{ kJ/K}) = -132.24 \text{ kJ} = -1.3224\text{e}+5 \text{ J}$$

Carry extra digits here, to avoid roundoff problems when taking the antilog later.

Use  $\Delta G^\circ$  to calculate  $\ln K_{\text{eq}}$ :

$$\Delta G^\circ_{\text{rxn}} = -RT \ln K_{\text{eq}}$$

OR

$$\ln K = -(\Delta G^\circ)/RT$$

$$\dots = -(-1.3224\text{e}+5 \text{ J/mol K}) / (8.314 \text{ J/mol K})(344\text{K})$$

$$\dots = 46.239$$

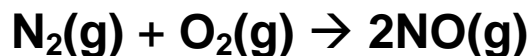
Raise to the base "e" to clear the logarithm:

$$K = e^{46.239} = 1.21\text{e}+20$$

Note that  $K_{\text{eq}}$  is greater than 1.

Products are favored at equilibrium.

2) For the reaction



$$\Delta H^\circ = 181 \text{ kJ and } \Delta S^\circ = 24.9 \text{ J/K}$$

K would be greater than 1 at temperatures: \_\_\_\_\_

A) below than  $7.27 \times 10^3 \text{ K}$

**B) above than  $7.27 \times 10^3 \text{ K}$**

C) above 273.15 K

D) below 298.15 K

The variation in  $\Delta G^\circ$  with temperature can be calculated using the following equation, assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are constant.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Since  $\Delta H^\circ$  and  $\Delta S^\circ$  are both positive, it is the negative  $-T\Delta S^\circ$  term that can cause  $\Delta G^\circ$  to become negative. Since this term is larger at higher temperatures,  **$\Delta G^\circ$  will be negative at relatively high temperatures** and positive at relatively low temperatures.

Solving for the crossover temperature at which  $\Delta G^\circ = 0$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$T = \Delta H^\circ / \Delta S^\circ =$$

$$181 \text{ kJ} / 2.49\text{e-}2 \text{ kJ K}^{-1} = 7.27\text{e+}3 \text{ K}$$

Therefore,  $\Delta G^\circ$  will be negative above **7.27e+3 K**.

Since  $\Delta G^\circ = -RT \ln K$ , when  $\Delta G^\circ < 0$ ,  $K > 1$  so the reaction will have  $K > 1$  above **7.27e+3 K**.