

- 28 The equilibrium constant (K_p) for the reaction $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ is 4.40 at 2000 K.

(a) Calculate the ΔG° for the reaction

$$\Delta G^\circ = -RT \ln K_p$$

$$\Delta G^\circ = -(8.314 \text{ J/mol}\cdot\text{K})(2000 \text{ K}) \ln(4.40) = -2.46 \times 10^4 \text{ J/mol} = -24.6 \text{ kJ/mol}$$

(b) Calculate ΔG for the reaction when the partial pressures are P of $\text{H}_2 = 0.25 \text{ atm}$, P of $\text{CO}_2 = 0.78 \text{ atm}$, P of $\text{H}_2\text{O} = 0.66 \text{ atm}$ and P of $\text{CO} = 1.20 \text{ atm}$

$$\Delta G = \Delta G^\circ + RT \ln Q_p, \text{ where } Q_p = \frac{P_{\text{H}_2\text{O}} \cdot P_{\text{CO}}}{P_{\text{H}_2} \cdot P_{\text{CO}_2}} = \frac{(0.66)(1.20)}{(0.25)(0.78)} = 4.1$$

$$\Delta G = -2.46 \times 10^4 \text{ J/mol} + (8.314 \text{ J/mol}\cdot\text{K})(2000 \text{ K}) \ln(4.1)$$

$$\Delta G = (-2.46 \times 10^4 \text{ J/mol}) + (2.35 \times 10^4 \text{ J/mol})$$

$$\Delta G = -1.10 \times 10^3 \text{ J/mol} = -1.10 \text{ kJ/mol}$$

(note: get -1.33 kJ/mol if calculate straight through w/no rounding until end)

- 38 Calculate ΔG for the reaction, $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$ at 25°C

In each part of this problem we can use the following equation to calculate ΔG .

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln [\text{H}^+][\text{OH}^-]$$

However, one needs to know ΔG° , to solve for ΔG . Thus, one needs to use $\Delta G^\circ = -RT \ln K$
The given reaction is the ionization of water. Thus, its equilibrium constant is K_w

Thus, $\Delta G^\circ = -RT \ln K_w$

$$\Delta G^\circ = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(1.0 \times 10^{-14}) = 8.0 \times 10^4 \text{ J/mol}$$

(a) $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$, $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$

In this case, the given concentrations are equilibrium concentrations at 25°C . Since the reaction is at equilibrium, $\Delta G = 0$. This is advantageous, because it allows us to calculate ΔG° . Also recall that at equilibrium, $Q = K$. We can write:

$$\Delta G^\circ = -RT \ln K_w$$

$$\Delta G^\circ = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(1.0 \times 10^{-14}) = 8.0 \times 10^4 \text{ J/mol}$$

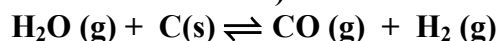
(b) $[\text{H}^+] = 1.0 \times 10^{-3} \text{ M}$, $[\text{OH}^-] = 1.0 \times 10^{-4} \text{ M}$

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln [\text{H}^+][\text{OH}^-]$$

$$\Delta G = (8.0 \times 10^4 \text{ J/mol}) + (8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln[(1.0 \times 10^{-3})(1.0 \times 10^{-4})]$$

$$= 4.0 \times 10^4 \text{ J/mol}$$

- 52 Water gas, a mixture of H_2 and CO , is a fuel made by reacting steam with red-hot coke (a by-product of coal distillation):



From the data in appendix 3, estimate the temperature at which the reaction begins to favor the formation of products.

Assuming that both ΔH° and ΔS° are temperature independent, we can calculate both ΔH° and ΔS° :

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{CO}) + \Delta H_f^\circ(\text{H}_2) - [\Delta H_f^\circ(\text{H}_2\text{O}) + \Delta H_f^\circ(\text{C})] \\ &= (1)(-110.5 \text{ kJ/mol}) + (1)(0) - [(1)(-241.8 \text{ kJ/mol}) + (1)(0)] = 131.3 \text{ kJ/mol} \\ \Delta S^\circ &= S^\circ(\text{CO}) + S^\circ(\text{H}_2) - [S^\circ(\text{H}_2\text{O}) + S^\circ(\text{C})] \\ &= [(1)(197.9 \text{ J/K}\cdot\text{mol}) + (1)(131.0 \text{ J/K}\cdot\text{mol})] - [(1)(188.7 \text{ J/K}\cdot\text{mol}) + (1)(5.69 \text{ J/K}\cdot\text{mol})] \\ &= 134.5 \text{ J/K}\cdot\text{mol}\end{aligned}$$

It is obvious from the given conditions that the reaction must take place at a fairly high temperature (in order to have red-hot coke).

$$\text{Set } \Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{131.3 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{134.5 \text{ J/K}\cdot\text{mol}} = 976 \text{ K} = 703^\circ\text{C}$$

The temperature must be greater than 703°C for the reaction to be spontaneous.

54 Crystallization of sodium acetate from a supersaturated solution occurs spontaneously (see p. 488). What can you deduce about the signs of ΔS and ΔH ?

For a reaction to be spontaneous at constant temperature and pressure, $\Delta G < 0$. The process of crystallization proceeds with more order (less disorder), so $\Delta S < 0$. We also know that

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

Since ΔG must be negative, and since the entropy term will be positive ($-T\Delta S$, where ΔS is negative), then ΔH must be negative ($\Delta H < 0$). The reaction will be exothermic.

56 A certain reaction is spontaneous at 72°C . If the enthalpy change for the reaction is 19 kJ/mol , what is the minimum value of ΔS for the reaction?

For the reaction to be spontaneous, ΔG must be negative.

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

$$\Delta G = 19,000 \text{ J/mol} - (273 \text{ K} + 72 \text{ K})(\Delta S)$$

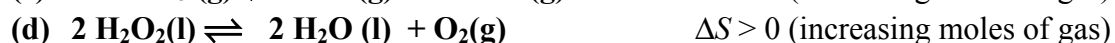
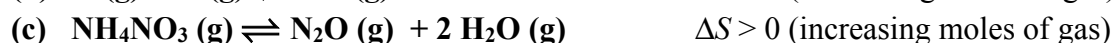
The reaction becomes spontaneous at the T at which ΔG changes from (+) to (-), or $\Delta G = 0$:

$$0 = 19,000 \text{ J/mol} - (273 \text{ K} + 72 \text{ K})(\Delta S)$$

$$\Delta S = 55 \text{ J/K}\cdot\text{mol}$$

This value of ΔS which we solved for is the value needed to produce a ΔG value of zero. The *minimum* value of ΔS that will produce a spontaneous reaction will be any value of entropy *greater than* $55 \text{ J/K}\cdot\text{mol}$.

57 Predict the whether the entropy change is positive or negative for each of these reactions:

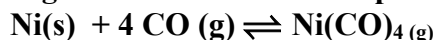


61 A certain reaction is known to have a ΔG° value of -122 kJ/mol . Will the reaction necessarily occur if the reactants are mixed together?

There is no connection between the spontaneity of a reaction predicted by ΔG and the rate at which the reaction occurs. A negative free energy change tells us that a reaction has the potential to happen, but gives no indication of the rate.

However, if a reaction occurs at a measurable rate means that the free energy difference ΔG must be negative since it is occurring spontaneously.

- 62 In the Mond process for the purification of nickel, carbon monoxide is reacted with heated nickel to produce $\text{Ni}(\text{CO})_4$, which is a gas and can therefore be separated from solid impurities:



Given the standard free energies of formation of $\text{CO}(g) = -137.3 \text{ kJ/mol}$ and $\text{Ni}(\text{CO})_4(g) = -587.4 \text{ kJ/mol}$, calculate the equilibrium constant of the reaction at 80°C . Assume that ΔG°_f is temperature independent.

Look up the standard free energies of formation in Appendix 3 of the text.

$$\begin{aligned} \Delta G^\circ &= \Delta G^\circ_f[\text{Ni}(\text{CO})_4] - [4\Delta G^\circ_f(\text{CO}) + \Delta G^\circ_f(\text{Ni})] \\ &= (1)(-587.4 \text{ kJ/mol}) - [(4)(-137.3 \text{ kJ/mol}) + (1)(0)] \\ &= -38.2 \text{ kJ/mol} = -3.82 \times 10^4 \text{ J/mol} \end{aligned}$$

Substitute ΔG° , R , and T (in K) into the following equation to solve for K_p .

$$\begin{aligned} \Delta G^\circ &= -RT \ln K_p \\ \ln K_p &= \frac{-\Delta G^\circ}{RT} = \frac{-(-3.82 \times 10^4 \text{ J/mol})}{(8.314 \text{ J/K} \cdot \text{mol})(353 \text{ K})} \text{ and } K_p = 4.5 \times 10^5 \end{aligned}$$

- 64 Calculate the pressure of O_2 (in atm) over a sample of NiO at 25°C if $\Delta G^\circ = 212 \text{ kJ/mol}$ for the reaction $\text{NiO}(s) \rightleftharpoons \text{Ni}(s) + \frac{1}{2} \text{O}_2(g)$

The equilibrium constant is related to the standard free energy change by the following equation:

$$\begin{aligned} \Delta G^\circ &= -RT \ln K_p \text{ so } 2.12 \times 10^5 \text{ J/mol} = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln K_p \\ -85.6 &= \ln K_p \text{ and } K_p = 6.7 \times 10^{-38} \end{aligned}$$

We can write the equilibrium constant expression for the reaction.

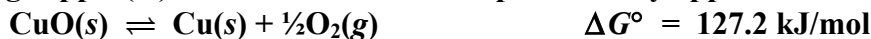
$$K_p = \sqrt{P_{\text{O}_2}} \text{ so } P_{\text{O}_2} = (K_p)^2 \text{ and } P_{\text{O}_2} = (6.7 \times 10^{-38})^2 = 4.5 \times 10^{-75} \text{ atm}$$

- 66 For a reaction with a negative ΔG° value, which of the following statements is false?

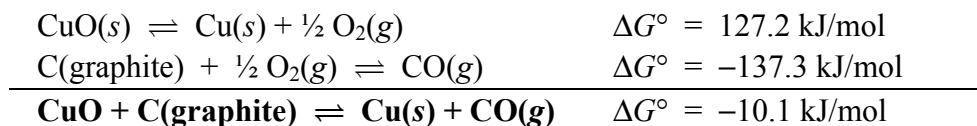
- The equilibrium constant K is greater than one.
- The reaction is spontaneous when all the reactants and products are in their standard states.
- The reaction is always exothermic.

Both (a) and (b) apply to a reaction with a negative ΔG° value. Statement (c) is not always true. An endothermic reaction that has a positive ΔS° (increase in entropy) will have a negative ΔG° value at high temperatures.

- 68 Heating copper(II)oxide at 400°C does not produce any appreciable amount of Cu :



However, if the reaction is coupled to the conversion of graphite to carbon monoxide, it becomes spontaneous. Write an equation for the coupled process and calculate the equilibrium constant for the coupled reaction.



$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-10.1 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/K} \cdot \text{mol})(673 \text{ K})} = 1.81 \text{ and } K = e^{1.81} = 6.1$$