

20. c and d; It takes an outside energy source to build a house and to launch and keep a satellite in orbit.

24. Of the three phases (solid, liquid, and gas), solids are most ordered and gases are most disordered. Thus, a, b, and f (melting, sublimation, and boiling) involve an increase in the entropy of the system since going from a solid to a liquid or a solid to a gas or a liquid to a gas increases disorder. For freezing (process c), a substance goes from the more disordered liquid state to the more ordered solid state, hence, entropy decreases. Process d (mixing) involves an increase in disorder (entropy) while separation increases order (decreases the entropy of the system). So of all the processes, a, b, d, and f result in an increase in the entropy of the system.

28. $\Delta G = \Delta H - T\Delta S$; A process is spontaneous when $\Delta G < 0$. For the following, assume ΔH and ΔS are temperature independent.

a. When ΔH and ΔS are both negative, ΔG will be negative below a certain temperature where the favorable ΔH term dominates. When $\Delta G = 0$, then $\Delta H = T\Delta S$. Solving for this temperature:

$$T = \frac{\Delta H}{\Delta S} = \frac{-18,000 \text{ J}}{-60. \text{ J/K}} = 3.0 \times 10^2 \text{ K}$$

At $T < 3.0 \times 10^2 \text{ K}$, this process will be spontaneous ($\Delta G < 0$).

b. When ΔH and ΔS are both positive, ΔG will be negative above a certain temperature where the favorable ΔS term dominates.

$$T = \frac{\Delta H}{\Delta S} = \frac{18,000 \text{ J}}{60. \text{ J/K}} = 3.0 \times 10^2 \text{ K}$$

At $T > 3.0 \times 10^2 \text{ K}$, this process will be spontaneous ($\Delta G < 0$).

c. When ΔH is positive and ΔS is negative, this process can never be spontaneous at any temperature because ΔG can never be negative.

d. When ΔH is negative and ΔS is positive, this process is spontaneous at all temperatures because ΔG will always be negative.

34. a. Decrease in disorder ($\Delta n < 0$); $\Delta S^\circ(-)$ b. Decrease in disorder ($\Delta n < 0$); $\Delta S^\circ(-)$

c. Increase in disorder; $\Delta S^\circ(+)$ d. Increase in disorder; $\Delta S^\circ(+)$

44. Because there are more product gas molecules than reactant gas molecules ($\Delta n > 0$), ΔS will be positive. From the signs of ΔH and ΔS , this reaction is spontaneous at all temperatures. It will cost money to heat the reaction mixture. Because there is no thermodynamic reason to do this, the purpose of the elevated temperature must be to increase the rate of the reaction, i.e., kinetic reasons.

52. $6 \text{ C(s)} + 6 \text{ O}_2\text{(g)} \rightarrow 6 \text{ CO}_2\text{(g)} \quad \Delta G^\circ = 6(!394 \text{ kJ})$
 $3 \text{ H}_2\text{(g)} + 3/2 \text{ O}_2\text{(g)} \rightarrow 3 \text{ H}_2\text{O(l)} \quad \Delta G^\circ = 3(!237 \text{ kJ})$
 $6 \text{ CO}_2\text{(g)} + 3 \text{ H}_2\text{O(l)} \rightarrow \text{C}_6\text{H}_6\text{(l)} + 15/2 \text{ O}_2\text{(g)} \quad \Delta G^\circ = !1/2 (!6399 \text{ kJ})$



55. $\Delta G^\circ = \sum n_p \Delta G_{f, \text{products}}^\circ - \sum n_r \Delta G_{f, \text{reactants}}^\circ$

$$\Delta G^\circ = [157.37 \text{ kJ} + (168.85 \text{ kJ}) + 3(195.30 \text{ kJ})] - [3(0) + 2(150.72 \text{ kJ})] = 1310.68 \text{ kJ}$$

For a temperature change from 25°C to ~20°C (room temperature), the magnitude of ΔG° will not change much. Therefore, ΔG° will be a negative value at room temperature (~20°C), so the reaction will be spontaneous.

68. The $\ln K$ vs. $1/T$ plot gives a straight line with slope = $-\Delta H^\circ/R$ and y-intercept = $\Delta S^\circ/R$.

$$1.352 \times 10^4 \text{ K} = \Delta H^\circ/R, \quad \Delta H^\circ = (8.3145 \text{ J/K}\cdot\text{mol})(1.352 \times 10^4 \text{ K})$$

$$\Delta H^\circ = 1.124 \times 10^5 \text{ J/mol} = 112.4 \text{ kJ/mol}$$

$$14.51 = \Delta S^\circ/R, \quad \Delta S^\circ = (14.51)(8.3145 \text{ J/K}\cdot\text{mol}) = 120.6 \text{ J/K}\cdot\text{mol}$$

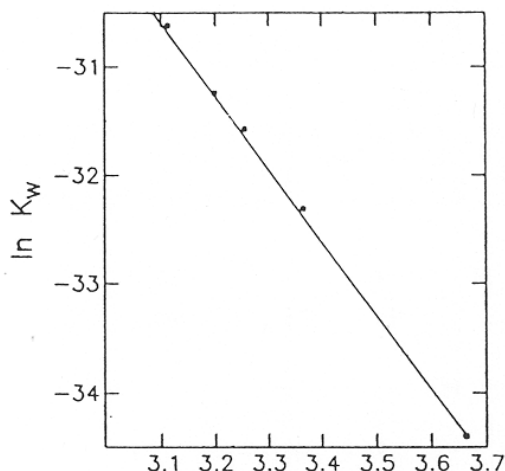
Note that the signs for ΔH° and ΔS° make sense. When a bond forms, $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$.

76. $\text{Ba}(\text{NO}_3)_2\text{(s)} \rightleftharpoons \text{Ba}^{2+}\text{(aq)} + 2 \text{NO}_3^-\text{(aq)} \quad K = K_{\text{sp}}; \quad \Delta G^\circ = 561 + 2(109) - (797) = 18 \text{ kJ}$

$$\Delta G^\circ = -RT \ln K_{\text{sp}}, \quad \ln K_{\text{sp}} = \frac{-\Delta G^\circ}{RT} = \frac{-18,000 \text{ J}}{8.3145 \text{ J/K}\cdot\text{mol} (298 \text{ K})} = -7.26, \quad K_{\text{sp}} = e^{-7.26} = 7.0 \times 10^{-4}$$

82. A graph of $\ln K$ vs. $1/T$ will yield a straight line with slope equal to $-\Delta H^\circ/R$ and y-intercept equal to $\Delta S^\circ/R$.

Temp (°C)	T(K)	1000/T (K ⁻¹)	K _w	ln K _w
0	273	3.66	1.14×10^{-15}	-34.408
25	298	3.36	1.00×10^{-14}	-32.236
35	308	3.25	2.09×10^{-14}	-31.499
40	313	3.19	2.92×10^{-14}	-31.165
50	323	3.10	5.47×10^{-14}	-30.537



The straight line equation (from a calculator) is: $\ln K = -6.91 \times 10^3 \left(\frac{1}{T} \right) + 9.09$

$$\text{Slope} = -6.91 \times 10^3 \text{ K} = \frac{-\Delta H^\circ}{R}, \quad \Delta H^\circ = (-6.91 \times 10^3 \text{ K} \times 8.3145 \text{ J/K}\cdot\text{mol}) \\ = 5.75 \times 10^4 \text{ J/mol}$$

$$\text{y-intercept} = 9.09 = \frac{\Delta S^\circ}{R}, \quad \Delta S^\circ = 9.09 \times 8.3145 \text{ J/K}\cdot\text{mol} = 75.6 \text{ J/K}\cdot\text{mol}$$

90. From Exercise 16.67, $\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$. For K at two temperatures T_1 and T_2 , the

equation can be manipulated to give (see Exercise 16.77): $\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

$$\ln \left(\frac{3.25 \times 10^{-2}}{8.84} \right) = \frac{\Delta H^\circ}{8.3145 \text{ J/K}\cdot\text{mol}} \left(\frac{1}{298 \text{ K}} - \frac{1}{348 \text{ K}} \right)$$

$$-5.61 = (5.8 \times 10^{-5} \text{ mol/J}) (\Delta H^\circ), \quad \Delta H^\circ = -9.7 \times 10^4 \text{ J/mol}$$

For K = 8.84 at $T = 25^\circ\text{C}$:

$$\ln 8.84 = \frac{-(-9.7 \times 10^4 \text{ J/mol})}{(8.3145 \text{ J/K}\cdot\text{mol})(298 \text{ K})} + \frac{\Delta S^\circ}{8.3145 \text{ J/K}\cdot\text{mol}}, \quad \frac{\Delta S^\circ}{8.3145} = 137$$

$$\Delta S^\circ = 1150 \text{ J/K}\cdot\text{mol}$$

We get the same value for ΔS° using $K = 3.25 \times 10^{-2}$ at $T = 348 \text{ K}$ data.

$\Delta G^\circ = -RT \ln K$; When $K = 1.00$, then $\Delta G^\circ = 0$ since $\ln 1.00 = 0$. Assuming ΔH° and ΔS° do not depend on temperature:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ, \quad \Delta H^\circ = T\Delta S^\circ, \quad T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-9.7 \times 10^4 \text{ J/mol}}{-310 \text{ J/K}\cdot\text{mol}} = 310 \text{ K}$$

98. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -28.0 \times 10^3 \text{ J} - 298 \text{ K}(-175 \text{ J/K}) = 24,200 \text{ J}$

$$\Delta G^\circ = -RT \ln K, \quad \ln K = \frac{-\Delta G^\circ}{RT} = \frac{-24,000 \text{ J}}{8.3145 \text{ J/K} \cdot \text{mol} \times 298 \text{ K}} = -9.767$$

$$K = e^{-9.767} = 5.73 \times 10^{-5}$$



Initial	0.125 M	0	~0
Change	-x	+x	+x
Equil.	0.125 - x	x	x

$$K_b = 5.73 \times 10^{-5} = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{x^2}{0.125 - x} \approx \frac{x^2}{0.125}, \quad x = [\text{OH}^-] = 2.68 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(2.68 \times 10^{-3}) = 2.572; \quad \text{pOH} = 14.000 - 2.572 = 11.428; \quad \text{Assumptions good}$$