

Ch 19 Free Energy and Thermodynamics

Exercises

27) a + c spontaneous 28) a + c non spontaneous; Not impossible - add work

35) a) $\Delta S(+)$ gas produced b) $\Delta S(-)$ 2 mol gas \rightarrow 1 mol c) $\Delta S(-)$ sto g d) $\Delta S(-)$ 4 \rightarrow 2 gas

37) a) $\Delta S_{sys}(+)$ 6 \rightarrow 7 gas because ΔH is $(-)$ $\Delta S_{surr}(+)$ reaction is spontaneous at all temperatures

b) $\Delta S_{sys}(-)$ 2 moles of diff gases to 2 mol of 1 gas $\Delta H(+)$ and $\Delta S_{surr}(-)$ non spont at all T

c) $\Delta S_{sys}(-)$ 3 \rightarrow 2 $\Delta H(+)$ and $\Delta S_{surr}(-)$ non spont at all T

d) $\Delta S_{sys}(+)$ 9 \rightarrow 10 $\Delta H(-)$ and $\Delta S_{surr}(+)$ spont at all T

39) a) $\Delta S_{surr} = \frac{-\Delta H_{sys}}{T} = \frac{-(-385,000 \text{ J})}{298 \text{ K}} = 1290 \text{ J/K}$

b) $\Delta S_{surr} = \frac{-(-385,000 \text{ J})}{77 \text{ K}} = 5.00 \times 10^3 \text{ J/K}$ d) $\Delta S_{surr} = \frac{-(114,000 \text{ J})}{77 \text{ K}} = -1480 \text{ J/K}$

c) $\Delta S_{surr} = \frac{-(114,000 \text{ J})}{298 \text{ K}} = -383 \text{ J/K}$

41) a) $\Delta S_{surr} = \frac{-(115,000 \text{ J})}{298 \text{ K}} = -385.9 \text{ J/K}$ $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = -263 \text{ J/K} - 385.9 \text{ J/K} = -649 \text{ J/K}$ Non

43) a) $\Delta G = \Delta H - T\Delta S = 115 \text{ KJ} - ((298 \text{ K})(-0.263 \text{ KJ/K})) = 193 \text{ KJ}$ Non spont

41) b) $\Delta S_{surr} = \frac{-(-115,000 \text{ J})}{298 \text{ K}} = 385.9 \text{ J/K}$ $\Delta S_{univ} = +263 \text{ J/K} + 385.9 \text{ J/K} = 649 \text{ J/K}$

43) b) $\Delta G = -115 \text{ KJ} - ((298 \text{ K})(0.263 \text{ KJ/K})) = -193 \text{ KJ}$ Spont

45) $\Delta G = \Delta H - T\Delta S = -2217 \text{ KJ} - ((298 \text{ K})(0.1011 \text{ KJ/K})) = -2247 \text{ KJ}$ Spont

49) Molar entropy \uparrow with $\uparrow T$ KE + molecular motion \uparrow Substance has access to $\uparrow \#$ of energy levels

50) 3rd Law states entropy of perfect crystal at $0 \text{ K} = 0$ for enthalpy we defined a standard state to define zero for the scale. Not necessary for entropy. Since there is an abs. zero for the entropy scale

51) a) $\text{CO}_2 > \text{CO}$ \rightarrow higher molar mass/complexity d) $\text{SiH}_4 > \text{CH}_4$ greater mass/complex

b) $\text{CH}_3\text{OH(g)} > \text{(l)}$ gas

e) $\text{CH}_3\text{CH}_2\text{CH}_3 > \text{NO}_2$ " "

c) $\text{CO}_2\text{(s)} > \text{Ar(g)}$ higher mass/complex

f) $\text{NaBr(g)} > \text{(s)}$ more entropy

53) a) $\text{He} < \text{Ne} < \text{SO}_2 < \text{NH}_3 < \text{CH}_3\text{CH}_2\text{OH}$ all gas \uparrow MM and complexity

b) $\text{H}_2\text{O}(s) < (l) < (g)$ c) $\text{CH}_4 < \text{CF}_4 < \text{CCl}_4$ \uparrow MM

55) a) $\Delta S^\circ = P-R$ $[229.2 \text{ J/K}] - [(219.3) + (30.7)] = -120.8 \text{ J/K}$ #moles gas \downarrow

b) $\Delta S^\circ = (197.7 + 130.7) - (5.7 \text{ J/K} + 188.8 \text{ J/K}) = 133.9$ moles of gas \uparrow

d) $\Delta S^\circ = [2(70.0) + 2(248.2)] - [2(205.8) + 3(205.2)] = -390.8 \text{ J/K}$ #gas \downarrow

59) $\Delta H^\circ = [2(-393.5) + 4(-241.8)] - [2(-238.6) + 3(0)] = -1277 \text{ KJ}$

$\Delta S^\circ = [2(213.8) + 4(188.8)] - [2(126.8) + 3(205.2)] = 313.6 \text{ J/K}$

$\Delta G = -1277 \text{ KJ} - (298 \text{ K})(0.316 \text{ KJ/K}) = -1370. \text{ KJ}$ spont

61) a) $\Delta S^\circ = [2(240.1) - (304.4)] = 0.1758 \text{ KJ}$

$\Delta H^\circ = [2(33.2) - (9.16)] = 57.2 \text{ KJ}$ $\Delta G = 57.2 - ((298 \text{ K})(0.1758 \text{ KJ/K})) = 4.9 \text{ KJ}$

63) a) $\Delta G^\circ = \text{prod} - \text{react}$ $[2(51.3)] - [99.8] = 2.8 \text{ KJ} < \text{Non}^\circ \uparrow T$ for spont

61) c) $\Delta H^\circ = [2(0) + 3(-241.8)] - [3(0) + (-824.2)] = 98.8 \text{ KJ}$

$\Delta S^\circ = [2(27.3) + 3(188.8)] - [3(130.7) + (87.4)] = 141.5 \text{ J/K} = 0.1415 \text{ KJ/K}$

$\Delta G^\circ = 98.8 \text{ KJ} - (298)(0.1415 \text{ KJ/K}) = 56.6 \text{ KJ}$ Non $\uparrow T$

63) c) $\Delta G^\circ = [(-95.3) + (-16.4)] - [202.9] = 91.2 \text{ KJ}$ Non

61 d) $\Delta H^\circ = [2(-45.9)] - [0 + 0] = -91.8 \text{ KJ}$

$\Delta S^\circ = [2(192.8)] - [(191.6) + 3(130.7)] = -198.1 \text{ J/K}$

$\Delta G^\circ = -91.8 \text{ KJ} - (298)(-0.1981 \text{ KJ/K}) = -32.8 \text{ KJ}$ spent at room T

ΔH dominates so rxn is spontaneous as $T \uparrow$ $T\Delta S$ term \uparrow
and reaction is Non spont

63 d) $\Delta G^\circ = [2(-16.4)] - [0 + 0] = -32.8 \text{ KJ}$

65 b+c) $\Delta H^\circ = [2(33.2)] - [2(91.5) + 0] = -116.2 \text{ KJ}$

$\Delta S^\circ = [2(240.1)] - [2(210.8) + (205.2)] = -0.1466 \text{ KJ/K}$

b vs) $\Delta G^\circ = -116.2 - (715)(-0.1466) = 11.4 \text{ KJ}$ spont

$\Delta G^\circ = \text{"} - (855) \text{"} = 9.1 \text{ KJ}$ Non

69) a) $I_2(s) \rightarrow I_2(g)$ $\Delta G^\circ = [19.3] - 0 = +19.3 \text{ KJ}$ non spont

b) $\Delta G_{\text{rxn}} = \Delta G^\circ + RT \ln Q = 19.3 \text{ KJ} + \left(\frac{8.314 \text{ J}}{\text{K} \cdot \text{mol}}\right) \left(\frac{1 \text{ KJ}}{1000 \text{ J}}\right) (298 \text{ K}) \ln(0.00132)$
 i) $Q = P_{I_2}$
 $1.00 \text{ mmHg} \times \frac{1 \text{ atm}}{760} = 0.00132 \text{ atm}$ $= +2.9 \text{ KJ}$ Non

ii) $0.100 \text{ mmHg} \times \frac{1}{760} = 0.000132 \text{ atm}$ $\Delta G_{\text{rxn}} = -2.9 \text{ KJ}$ spont
(at lower P)

c) sublimates at room temp due to equilibrium betw s+g phases. Vapor pressure is low (0.31 mmHg at $25^\circ\text{C} \rightarrow 0.00041 \text{ atm}$) $\rightarrow \Delta G_{\text{rxn}} \approx 0$ small amt of iodine can be in gas phase

71) $\Delta G^\circ = [(-137.2) + 2(0)] - [-162.3] = 25.1 \text{ KJ}$ $Q = \frac{(0.125)(0.183)^2}{0.855} = 0.0004896$
 $\Delta G_{\text{rxn}} = \Delta G^\circ + RT \ln Q = 25.1 \text{ KJ} + \left(\frac{8.314 \text{ J}}{\text{K} \cdot \text{mol}}\right) \left(\frac{1 \text{ KJ}}{1000 \text{ J}}\right) (298 \text{ K}) \ln(\checkmark) \text{ NON}$
 $= 11.9 \text{ KJ}$

73) $\Delta G^\circ = [2(-394.4)] - [2(-137.2) + 0] = -514.4 \text{ KJ}$ $= (-0.5144 \text{ J})$
 a) $\Delta G^\circ_{\text{rxn}} = -RT \ln K$ $K = e^{-\frac{\Delta G^\circ_{\text{rxn}}}{RT}} = e^{\frac{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{-514.4 \text{ J}}}$
 $e^{207.6} = 1.48 \times 10^{90}$
 ΔG° is very large (-) magnitude so K is very large \uparrow

b) $\Delta G^\circ = +146.5 \text{ KJ}$ $K = e^{\frac{-0.1465}{(8.314)(298)}} = 2.09 \times 10^{-26}$ ΔG° positive large
so K very small

standard

75) a) $\Delta G^\circ = -RT \ln K = -(8.314) \left(\frac{1}{1000}\right) (298) \ln(2.26 \times 10^4) = -24.8 \text{ KJ}$

b) at equilibrium $\Delta G_{\text{rxn}} = 0$

c) $Q = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} (P_{\text{H}_2})^2} = \frac{(1.0)}{(0.010)(0.010)^2} = 1.0 \times 10^6$

$\Delta G_{\text{rxn}} = \Delta G^\circ + RT \ln Q = -24.8 + \left(\frac{8.314}{1000}\right) (298) \ln(1.0 \times 10^6)$
 $= +9.4 \text{ KJ}$

$K > 0$ so at standard we expect (-) ΔG° at Equil $\Delta G^\circ = 0$ definition
 since $Q > K$ rxn must reverse

Others?