Homework #5

Chapter 10

Spontaneity, Entropy and Free Energy

7. The larger the positional probability or energy probability (the more available microstates) the larger the entropy

   1. Entropy increases from solid to liquid to gas corresponding to an increase in positional probability.
   2. Entropy increases when you dissolve a solid in liquid corresponding to an increase in positional probability.
   3. The higher the temperature the greater the entropy because the wider the range of possible velocities (increase in energy probability).
   4. The larger the volume the larger the positional probability and the greater the entropy for gases.
   5. The larger the pressure the smaller the positional probability and the lower the entropy.

   a) (l) → (g), ΔS=+, (1)
   b) (l) → (s), ΔS=-, (1)
   c) As the gas is compressed the number of available microstates decreases, ΔS=-, (4 and 5)
   d) ΔS=+, (3)
   e) (s) → (aq), ΔS=+, (2)

12. a) Spontaneous Process: A process that occurs without energy from external sources.
   b) Entropy: A value that shows the positional and energy microstates available in a system. The great the entropy the more microstate available.
   c) Positional Probability: A type of probability that depends on the number of arrangements in space.
   d) System: That part of the universe on which attention is to be focused.
   e) Surroundings: Everything in the universe surrounding the thermodynamic system.
   f) Universe: The system and the surroundings.

19. a) As you increase the volume of a gas there are more possible locations for the particle to occupy; or the positional probability of the system has increased.
   b) As you increase the temperature of a gas the positional probability remains the same because the number of locations that the particle can occupy is the same. Although the positional probability is the same, increasing the temperature increases the entropy because, there is a wider range of possible velocities (energy states) for any given gas particle thereby, increasing the energy probability.
   c) As the pressure of a gas is increased the particles are forced closer together, decreasing the possible positions of particles. This corresponds to a decrease in positional probability.

23. Case 1

Even though this question says to calculate the energy (ΔE), they want you to calculate heat (q) for the first two parts and change in internal energy for the last part (ΔE).

The first part of the problem wants you to calculate the heat a constant V.

$$q = nC_V\Delta T$$

$$C_V = 44.60\,\frac{J}{mol\cdot K}$$

$$\Delta T = 73.4℃ - 25.0℃ = 48.4℃ = 48.4K$$

$$n = 1.00\,kg\left(\frac{1000\,g}{1\,kg}\right)\left(\frac{1\,mol\,C_2H_6}{30.08\,g\,C_2H_6}\right) = 33.2\,mol\,C_2H_6$$

$$q = nC_V\Delta T = (33.2\,mol)\left(44.60\,\frac{J}{mol\cdot K}\right)(48.4K) = 71{,}700\,J = 71.7\,kJ$$

Case 2

The second part of the problem wants you to calculate the heat at constant P. You can assume that C_2H_6 is an ideal gas and that C_P and C_V are related by. $C_P=C_V+R$

$$q = nC_P\Delta T$$

$$C_P = C_V + R = 44.60\,\frac{J}{mol\cdot K} + 8.3145\,\frac{J}{mol\cdot K} = 52.91\,\frac{J}{mol\cdot K}$$

$$q = nC_P\Delta T = (33.2\,mol)\left(52.91\,\frac{J}{mol\cdot K}\right)(48.4\,K) = 8.50\times10^4\,J = 85.0\,kJ$$

The third part of the problem wants you to calculate the internal energy (ΔE) for case 1.

$$\Delta E = q + w$$

Since we are at constant volume w=0

$$\Delta E = q = 71.7\,kJ$$

The forth part of the problem wants you to calculate the internal energy (ΔE) for case 2.

$$\Delta E = q + w = q - P\Delta V$$

Since we can assume that C_2H_6 is an ideal gas

$$P\Delta V = nR\Delta T$$

$$\Delta E = q - nR\Delta T = 85.0\,kJ - (33.2\,mol)\left(0.0083145\,\frac{J}{mol\cdot K}\right)(48.4K) = 71.6\,kJ$$

25. In order for the cold box to warm up, energy must be transferred between the warmer box and the colder box until the two are at the same temperature. Since the volume of the box is constant, q_{He}=-q_{N_2}

$$q = nC_V\Delta T$$

$$q_{He} = -q_{N_2}$$

$$n_{He}C_{V_{He}}\left(T_f - T_{i_{He}}\right) = -n_{N_2}C_{V_{N_2}}\left(T_f - T_{i_{N_2}}\right)$$

$$(0.400\,mol)\left(12.5\,\frac{J}{mol\cdot K}\right)\left(T_f - 293K\right) = -(0.600\,mol)\left(20.7\,\frac{J}{mol\cdot K}\right)\left(T_f - 373K\right)$$

$$(0.403\,)\left(T_f - 293K\right) = -T_f - 373K$$

$$T_f = 350.\,K$$

27. Work

The gas expands into an evacuated bulb which is a vacuum therefore P_{ext} = 0.

$$w = -P_{ext}\Delta V = 0$$

Heat

For isothermal ideal gas changes ΔE=0, therefore, since ΔE=q+w and w = 0

$$q = 0$$

q_{rev}

For this part of the problem instead of considering the system to be expanding into an evacuated bulb the process must be carried out reversible. To do this an infinite number of small expansions must be allowed to happen in which every step is at equilibrium.

Note: Reversible processes give the maximum possible work that a system can perform.

$$q_{rev} = nRTln\left(\frac{V_2}{V_1}\right)$$

Calculate the temperature. You must use the initial conditions because we do not know the final pressure.

$$PV = nRT$$

$$T = \frac{PV}{nR} = \frac{(5.0\ atm)(1.0\ L)}{(1\ mol)\left(0.08206\ \frac{L\cdot atm}{mol\cdot K}\right)} = 61\ K$$

$$q_{rev} = nRTln\left(\frac{V_2}{V_1}\right) = (1.0\ mol)\left(8.3145\ \frac{J}{mol\cdot K}\right)(61K)ln\left(\frac{2.0\ L}{1.0\ L}\right) = 350\ J$$

Note: If the system is expanded reversible ΔE is still 0, which is consistent with the first part of the problem, because $w_{rev} = -nRTln\left(\frac{V_2}{V_1}\right) = -350\ J$

28. a) For isothermal expansion/contraction

$$w_{rev} = -nRTln\left(\frac{V_2}{V_1}\right) = -(1.00\ mol)\left(8.3145\ \frac{J}{mol\cdot K}\right)(298K)ln\left(\frac{20.0\ L}{10.0\ L}\right) = -1{,}720\ J$$

The change in internal energy (ΔE) of a system is 0 for isothermal expansion/contraction of an ideal gas therefore the q=-w

$$q_{rev} = 1{,}720\ J$$

b) When they say that the pressure changes instantaneously from 2.46 atm to 1.23 atm they are telling you that the external pressure during the expansion is 1.23 atm

$$w = -P_{ex}\Delta V = -(1.23\ atm)(20.0\ L - 10.0\ L) = -12.3\ L\cdot atm\left(\frac{101.325\ J}{1\ L\cdot atm}\right) = -1{,}250\ J$$

The expansion is still isothermal therefore q=-w

$$q = 1{,}250\ J$$

31. The question wants you to calculate ΔH_{vap} they give you ΔS of the process. To calculate ΔS of the process you will need to break the process into three steps

A(l) (75° C= 348K) → A(l) (125° C=398K)→A(g) (125° C=398K)→ A(g) (155° C =398K)

Where ΔS_{tot} will equal the sum of the ΔS for each step

$$\Delta S_{tot} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

Calculate ΔS_1

$$\Delta S_1 = C_P ln\left(\frac{T_2}{T_1}\right) = \left(75.0\ \frac{J}{mol\cdot K}\right) ln\left(\frac{398K}{348K}\right) = 10.1\ \frac{J}{mol\cdot K}$$

Calculate ΔS_2

Phase Change therefore T is constant. The problem indicates that P is also constant.

$$\Delta S_2 = \frac{q}{T} = \frac{\Delta H_{vap}}{T} = \frac{\Delta H_{vap}}{398\ K}$$

Calculate ΔS_2

$$\Delta S_1 = C_P ln\left(\frac{T_2}{T_1}\right) = \left(29.0\ \frac{J}{mol\cdot K}\right) ln\left(\frac{428K}{398K}\right) = 2.11\ \frac{J}{mol\cdot K}$$

$$\Delta S_{tot} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$75.0\,\frac{J}{mol\cdot K} = 10.1\,\frac{J}{mol\cdot K} + \frac{\Delta H_{vap}}{398K} + 2.11\,\frac{J}{mol\cdot K}$$

$$\Delta H_{vap} = 2.50\times 10^4\,\frac{J}{mol} = 25.0\,\frac{kJ}{mol}$$

32. In order to calculate q, w, ΔE, ΔH, and ΔS you will have to break down the change into steps.
ice (-30.0°C=243K)→ice(0.0°C=273K)→water(0.0°C=273K)→water(100.0°C=373K)→steam(100.0°C=373K)→ steam(140.0°C=413K)

Calculate the moles of H_2O

$$18.02\ g\ H_2O\left(\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}\right)1.000\ mol\ H_2O$$

Calculate q

$$q_1 = nC\Delta T = (1.00\ mol)\left(37.5\,\frac{J}{mol\cdot K}\right)(273\text{K}-243\text{K}) = 1{,}130\ J = 1.13\ kJ$$

$$q_2 = n\Delta H_{fus} = (1.00\ mol)\left(6.01\,\frac{kJ}{mol}\right) = 6.01\ kJ$$

$$q_3 = nC\Delta T = (1.00\ mol)\left(75.3\,\frac{J}{mol\cdot K}\right)(373\text{K}-273\text{K}) = 7{,}530\ J = 7.53\ kJ$$

$$q_4 = n\Delta H_{vap} = (1.00\ mol)\left(40.7\,\frac{kJ}{mol}\right) = 40.7\ kJ$$

$$q_5 = nC_P\Delta T = (1.00\ mol)\left(36.4\,\frac{J}{mol\cdot K}\right)(413\text{K}-373\text{K}) = 1{,}460\ J = 1.46\ kJ$$

Calculate q_{tot}:

$$q_{tot} = q_1 + q_2 + q_3 = 1.13\ kJ + 6.01\ kJ + 7.53\ kJ + 40.7\ \text{kJ} + 1.46\ k = 56.8\ kJ$$

Calculate w.

The only time the volume will change is when the liquid turns to a gas and when the gas is heated. Therefore w_1, w_2, and w_3 = 0

$w_4 = -P_{ex}\Delta V$

Assume that the initial volume is 0 because the volume occupied by the gas is >> (much greater) than the volume occupied by the liquid

Calculate the final volume (use the ideal gas law)

$$V_f = \frac{nRT}{P} = \frac{(1.000\ mol)\left(0.08206\,\frac{L\cdot atm}{mol\cdot K}\right)(373.2K)}{1.00\ atm} = 30.6\ L$$

$$w_4 = -P_{ext}(V_f - V_i) = -(1.00\ atm)(30.6\ L - 0\ L) = -30.6\ L\cdot atm\left(\frac{101.325\ J}{1\ L\cdot atm}\right)$$
$$= -3.10\times 10^3\ J$$

Calculate w_5, the work that goes into expanding the gas. In the gas phase we can assume that it behaves like an ideal gas therefore,

$$w_5 = -P_{ext}\Delta V = -nR\Delta T$$
$$= -(1.000\ mol)\left(8.3145\,\frac{J}{mol\cdot K}\right)(413.15K - 373.15K) = -333\ J$$

$$w_{tot} = w_4 + w_5 = -3.10\ kJ + -0.333\ kJ = -3.43\ kJ$$

Calculate ΔE

$$\Delta E = q + w = 56.8\ kJ + -3.43\ kJ = 53.4\ kJ$$

Calculate ΔH

$\Delta H = q = 56.8\ kJ$ Since the system is at constant pressure ΔH=q

Calculate ΔS (need to break it up into steps):

$$\Delta S_1 = nCln\left(\frac{T_2}{T_1}\right) = (1.000\ mol)\left(37.5\,\frac{J}{mol\cdot K}\right)ln\left(\frac{273.2K}{243.2K}\right) = 4.36\,\frac{J}{K}$$

$$\Delta S_2 = n\frac{\Delta H}{T} = (1.000\ mol)\frac{6.01\,\frac{kJ}{mol}}{273.2\ K} = 0.0220\,\frac{kJ}{K} = 22.0\ \frac{J}{K}$$

$$\Delta S_3 = nCln\left(\frac{T_2}{T_1}\right) = (1.000\ mol)\left(74.3\ \frac{J}{mol\cdot K}\right) ln\left(\frac{373.2K}{273.2K}\right) = 23.5\ \frac{J}{K}$$
$$\Delta S_4 = n\frac{\Delta H}{T} = (1.000\ mol)\frac{40.7\ \frac{kJ}{mol}}{373.2\ K} = 0.109\ \frac{kJ}{K} = 109\ \frac{J}{K}$$
$$\Delta S_5 = nC_P ln\left(\frac{T_2}{T_1}\right) = (1.000\ mol)\left(36.4\ \frac{J}{mol\cdot K}\right) ln\left(\frac{413.2K}{373.2K}\right) = 3.71\ \frac{J}{K}$$
$$\Delta S_{tot} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 = 4.26\ \frac{J}{K} + 22.0\ \frac{J}{K} + 23.5\ \frac{J}{K} + 109\ \frac{J}{K} + 3.71\ \frac{J}{K} = 162\ \frac{J}{K}$$

33. Need to find entropy change

$$\Delta S = nC_P ln\left(\frac{T_2}{T_1}\right)$$

In order to calculate the entropy change you need to figure out the final temperature of the system. The heat gained by the cold system must equal the heat lost from the hot system.

$$q_{cold} = -q_{hot}$$
$$q = -nC_P\Delta T = nC_P(T_2 - T_1)$$
$$n_C C_P\left(T_2 - T_{1_C}\right) = -n_H C_P\left(T_2 - T_{1_H}\right)$$
$$(3.00\ mol)(T_2 - 273K) = -(1.00\ mol)(T_2 - 373K)$$
$$3T_2 - 819K = -T_2 + 373K$$
$$T_2 = 298\ K$$

Calculate ΔS_{tot}

$$\Delta S_{tot} = \Delta S_{cold} + \Delta S_{warm} = n_C C_P ln\left(\frac{T_2}{T_{1_C}}\right) + n_H C_P ln\left(\frac{T_2}{T_{1_H}}\right)$$
$$\Delta S_{tot} = (3.00\ mol)\left(75.3\ \frac{J}{mol\cdot K}\right) ln\left(\frac{298K}{273K}\right) + (1.00\ mol)\left(75.3\ \frac{J}{mol\cdot K}\right) ln\left(\frac{298K}{373K}\right) = 2.9\ \frac{J}{K}$$

41. a) $\Delta S_{surr} = -\frac{\Delta H}{T}$

$$T = 25°C = 25 + 273.15 = 298K$$
$$\Delta S_{surr} = -\frac{-2221\ kJ}{298K} = 7.45\ \frac{kJ}{K} = 7{,}450\ \frac{J}{K}$$

b) $\Delta S_{surr} = -\frac{\Delta H}{T}$

$$T = 25°C = 25 + 273.15 = 298K$$
$$\Delta S_{surr} = -\frac{112\ kJ}{298K} = -0.376\ \frac{kJ}{K} = -376\ \frac{J}{K}$$

42. The more possible microstates available the greater the entropy.

1. Entropy increases from solid to liquid to gas corresponding to an increase in positional probability
2. The larger the molecule the greater the positional probability
3. If there are the same number of atoms in the molecules/elements; then the one more electrons has the greater the positional probability
4. For the same atom but different structures the positional probability is greater in the more disordered structure

a) graphite (4)

b) $C_2H_5OH(g)$ (1)

c) $CO_2(g)$ (1)
d) $N_2O(g)$ (2)
e) $HCl(g)$ (3)

43. The larger the positional probability (the more available microstates) the larger the entropy
   1. Entropy increases from solid to liquid to gas corresponding to an increase in positional probability
   2. Entropy increases when you dissolve a solid in liquid corresponding to an increase in positional probability

a) negative
b) (s) → (aq) positive
c) (g) → (l) negative
d) (g)→(s) negative
e) (g)→(aq) negative
f) (s) →(aq) positive

44. Entropy increases as you go from a solid → liquid → gas therefore:
(number of moles of gas in products)-(number of moles of gas reactants)=x if:
X is positive ΔS is +
X is negative ΔS is –
X is 0 unable to predict

$$\Delta S^\circ_{rxn} = \sum S^\circ_{prod} - \sum S^\circ_{reac}$$

a) ΔS is negative
From appendix 4

Compound	S° $\left(\frac{J}{mol\cdot K}\right)$
$H_2S(g)$	206
$SO_2(g)$	248
$S_{rhombic}(s)$	32
$H_2O(g)$	189

$$\Delta S^\circ_{rxn} = n_S S^\circ_S + n_{H_2O} S^\circ_{H_2O} - n_{H_2S} S^\circ_{H_2S} - n_{SO_2} S^\circ_{SO_2}$$
$$\Delta S^\circ_{rxn} = (3)\left(32\,\frac{J}{mol\cdot K}\right) + (2)\left(189\,\frac{J}{mol\cdot K}\right) - (2)\left(206\,\frac{J}{mol\cdot K}\right) - (1)\left(248\,\frac{J}{mol\cdot K}\right)$$
$$= -186\,\frac{J}{mol\cdot K}$$

b) ΔS is positive
From appendix 4

Compound	S° $\left(\frac{J}{mol\cdot K}\right)$
$SO_3(g)$	257
$SO_2(g)$	248
$O_2(g)$	205

$$\Delta S^\circ_{rxn} = n_{SO_2} S^\circ_{SO_2} + n_{O_2} S^\circ_{O_2} - n_{SO_3} S^\circ_{SO_3}$$
$$\Delta S^\circ_{rxn} = (2)\left(248\,\frac{J}{mol\cdot K}\right) + (1)\left(205\,\frac{J}{mol\cdot K}\right) - (2)\left(257\,\frac{J}{mol\cdot K}\right) = 187\,\frac{J}{mol\cdot K}$$

c) ΔS is unable to predict

From appendix 4

Compound	$S^\circ\left(\frac{J}{mol \cdot K}\right)$
$Fe_2O_3(s)$	90
$H_2(g)$	131
$Fe(s)$	27
$H_2O(g)$	189

$$\Delta S^\circ_{rxn} = n_{Fe}S^\circ_{Fe} + n_{H_2O}S^\circ_{H_2O} - n_{Fe_2O_3}S^\circ_{Fe_2O_3} - n_{H_2}S^\circ_{H_2}$$

$$\Delta S^\circ_{rxn} = (2)\left(27\,\frac{J}{mol \cdot K}\right) + (3)\left(189\,\frac{J}{mol \cdot K}\right) - (1)\left(90\,\frac{J}{mol \cdot K}\right) - (3)\left(131\,\frac{J}{mol \cdot K}\right)$$

$$= 138\,\frac{J}{mol \cdot K}$$

48. The definition of boiling is the temperature in which the liquid and gas are at equilibrium.

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

At equilibrium ΔG=0 therefore:

$$\Delta S = \frac{\Delta H}{T}$$

$$T = 35℃ = 35 + 273.15 = 308K$$

$$\Delta S = \frac{27.5\,\frac{kJ}{mol}}{308K} = 0.0893\,\frac{kJ}{mol \cdot K} = 89.3\,\frac{J}{mol \cdot K}$$

49. The definition of boiling is the temperature in which the liquid and gas are at equilibrium.

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

At equilibrium ΔG=0 therefore:

$$\Delta S = \frac{\Delta H}{T}$$

$$92.92\,\frac{J}{mol \cdot K} = \frac{58{,}510\,\frac{J}{mol}}{T}$$

$$T = 629.7K$$

50. Since the system is at a constant pressure:

$$\Delta S_{sys} = \frac{q}{T} = \frac{n\Delta H}{T} = \frac{(1.00\,mol)\left(38.7\,\frac{kJ}{mol \cdot K}\right)}{351K} = 0.110\,\frac{kJ}{K} = 110\,\frac{J}{K}$$

Since the system is at equilibrium:

$$\Delta S_{surr} = -\Delta S_{sys} = -110\,\frac{J}{K}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur} = 110.\frac{J}{K} + -110.\frac{J}{K} = 0$$

51. a) In order to determine if something is spontaneous you must look at the sign of ΔG. $\Delta H°$ and $\Delta S°$ are relatively temperature independent use $\Delta G° = \Delta H° - T\Delta S°$ to find $\Delta G°$.

$$\Delta G° = \Delta H° - T\Delta S° = 5.65\,\frac{kJ}{mol} - (200.\,K)\left(0.0289\,\frac{kJ}{mol \cdot K}\right) = -0.13\,\frac{kJ}{mol}$$

Since ΔG is negative, the reaction will be spontaneous

b) At the melting point $NH_3(l)$ is in equilibrium with $NH_3(s)$ and ΔG=0

We can assume that we are at constant pressure therefore q=ΔH

$$0 = \Delta H° - T\Delta S°$$
$$\Delta H° = T\Delta S°$$
$$5.65\,\frac{kJ}{mol} = T\left(0.0289\,\frac{kJ}{mol{\cdot}K}\right)$$
$$T = 196K$$

54. $\Delta H^{\circ}_{rxn} = \sum \Delta H^{\circ}_{f}(prod) - \sum H^{\circ}_{f}(reac)$

$$\Delta S^{\circ}_{rxn} = \sum S^{\circ}_{prod} - \sum S^{\circ}_{reac}$$
$$\Delta G^{\circ}_{rxn} = \sum \Delta G^{\circ}_{f}(prod) - \sum G^{\circ}_{f}(reac)$$

a) From appendix 4

Compound	$\Delta H_f°\left(\frac{kJ}{mol}\right)$	$S°\left(\frac{J}{mol{\cdot}K}\right)$	$\Delta G_f°\left(\frac{kJ}{mol}\right)$
$CH_4(g)$	-75	186	-51
$O_2(g)$	0	205	0
$CO_2(g)$	-393.5	214	-394
$H_2O(g)$	-242	189	-229

$$\Delta H^{\circ}_{rxn} = n_{CO_2}\Delta H^{\circ}_{f}(CO_2) + n_{H_2O}\Delta H^{\circ}_{f}(H_2O) - n_{CH_4}\Delta H^{\circ}_{f}(CH_4) - n_{O_2}\Delta H^{\circ}_{f}(O_2)$$
$$\Delta H^{\circ}_{rxn} = (1)\left(-393.5\,\frac{kJ}{mol}\right) + (2)\left(-242\,\frac{kJ}{mol}\right) - (1)\left(-75\,\frac{kJ}{mol}\right) - (2)\left(0\,\frac{kJ}{mol}\right)$$
$$= -803\,\frac{kJ}{mol}$$
$$\Delta S^{\circ}_{rxn} = n_{CO_2}S^{\circ}_{CO_2} + n_{H_2O}S^{\circ}_{H_2O} - n_{CH_4}S^{\circ}_{CH_4} - n_{O_2}S^{\circ}_{O_2}$$
$$\Delta S^{\circ}_{rxn} = (1)\left(214\,\frac{J}{mol{\cdot}K}\right) + (2)\left(189\,\frac{J}{mol{\cdot}K}\right) - (1)\left(186\,\frac{J}{mol{\cdot}K}\right) - (2)\left(205\,\frac{J}{mol{\cdot}K}\right)$$
$$= -4\,\frac{J}{mol{\cdot}K}$$
$$\Delta G^{\circ}_{rxn} = n_{CO_2}\Delta G^{\circ}_{f}(CO_2) + n_{H_2O}\Delta G^{\circ}_{f}(H_2O) - n_{CH_4}\Delta G^{\circ}_{f}(CH_4) - n_{O_2}\Delta G^{\circ}_{f}(O_2)$$
$$\Delta G^{\circ}_{rxn} = (1)\left(-394\,\frac{kJ}{mol}\right) + (2)\left(-229\,\frac{kJ}{mol}\right) - (1)\left(-51\,\frac{kJ}{mol}\right) - (2)\left(0\,\frac{kJ}{mol}\right)$$
$$= -801\,\frac{kJ}{mol}$$

b) From appendix 4

Compound	$\Delta H_f°\left(\frac{kJ}{mol}\right)$	$S°\left(\frac{J}{mol{\cdot}K}\right)$	$\Delta G_f°\left(\frac{kJ}{mol}\right)$
$CO_2(g)$	-393.5	214	-394
$H_2O(l)$	-286	70	-237
$C_6H_{12}O_6(s)$	-1275	212	-911
$O_2(g)$	0	205	0

$$\Delta H^{\circ}_{rxn} = n_{C_6H_{12}O_6}\Delta H^{\circ}_{f}(C_6H_{12}O_6) + n_{O_2}\Delta H^{\circ}_{f}(O_2) - n_{CO_2}\Delta H^{\circ}_{f}(CO_2) - n_{H_2O}\Delta H^{\circ}_{f}(H_2O)$$
$$\Delta H^{\circ}_{rxn} = (1)\left(-1{,}275\,\frac{kJ}{mol}\right) + (6)\left(0\,\frac{kJ}{mol}\right) - (6)\left(-393.5\,\frac{kJ}{mol}\right) - (6)\left(-286\,\frac{kJ}{mol}\right)$$
$$= 2{,}802\,\frac{kJ}{mol}$$
$$\Delta S^{\circ}_{rxn} = n_{C_6H_{12}O_6}S^{\circ}_{C_6H_{12}O_6} + n_{O_2}S^{\circ}_{O_2} - n_{CO_2}S^{\circ}_{CO_2} - n_{H_2O}S^{\circ}_{H_2O}$$
$$\Delta S^{\circ}_{rxn} = (1)\left(212\,\frac{J}{mol{\cdot}K}\right) + (6)\left(205\,\frac{J}{mol{\cdot}K}\right) - (6)\left(214\,\frac{J}{mol{\cdot}K}\right) - (6)\left(70\,\frac{J}{mol{\cdot}K}\right)$$
$$= -262\,\frac{J}{mol{\cdot}K}$$
$$\Delta G^{\circ}_{rxn} = n_{C_6H_{12}O_6}\Delta G^{\circ}_{f}(C_6H_{12}O_6) + n_{O_2}\Delta G^{\circ}_{f}(O_2) - n_{CO_2}\Delta G^{\circ}_{f}(CO_2) - n_{H_2O}\Delta G^{\circ}_{f}(H_2O)$$

$$\Delta G^{\circ}_{rxn} = (1)\left(-911\,\frac{kJ}{mol}\right) + (6)\left(0\,\frac{kJ}{mol}\right) - (6)\left(-394\,\frac{kJ}{mol}\right) - (6)\left(-237\,\frac{kJ}{mol}\right)$$
$$= 2{,}875\,\frac{kJ}{mol}$$

c) From appendix 4

Compound	$\Delta H_f^{\circ}\left(\frac{kJ}{mol}\right)$	$S^{\circ}\left(\frac{J}{mol\cdot K}\right)$	$\Delta G_f^{\circ}\left(\frac{kJ}{mol}\right)$
P_4O_{10}(s)	-2984	229	-2698
H_2O(l)	-286	70	-237
H_3PO_4(s)	-1279	110	-1119

$$\Delta H^{\circ}_{rxn} = n_{H_3PO_4}\Delta H^{\circ}_f(H_3PO_4) - n_{P_4O_{10}}\Delta H^{\circ}_f(P_4O_{10}) - n_{H_2O}\Delta H^{\circ}_f(H_2O)$$
$$\Delta H^{\circ}_{rxn} = (4)\left(-1{,}279\,\frac{kJ}{mol}\right) - (1)\left(-2{,}984\,\frac{kJ}{mol}\right) - (6)\left(-286\,\frac{kJ}{mol}\right) = -416\,\frac{kJ}{mol}$$
$$\Delta S^{\circ}_{rxn} = n_{H_3PO_4}S^{\circ}_{H_3PO_4} - n_{P_4O_{10}}S^{\circ}_{P_4O_{10}} - n_{H_2O}S^{\circ}_{H_2O}$$
$$\Delta S^{\circ}_{rxn} = (4)\left(110\,\frac{J}{mol\cdot K}\right) + (1)\left(229\,\frac{J}{mol\cdot K}\right) - (6)\left(70\,\frac{J}{mol\cdot K}\right) = -209\,\frac{J}{mol\cdot K}$$
$$\Delta G^{\circ}_{rxn} = n_{H_3PO_4}\Delta G^{\circ}_f(H_3PO_4) - n_{P_4O_{10}}\Delta G^{\circ}_f(P_4O_{10}) - n_{H_2O}\Delta G^{\circ}_f(H_2O)$$
$$\Delta G^{\circ}_{rxn} = (4)\left(-1{,}119\,\frac{kJ}{mol}\right) - (1)\left(-2{,}698\,\frac{kJ}{mol}\right) - (6)\left(-237\,\frac{kJ}{mol}\right) = -356\,\frac{kJ}{mol}$$

d) From appendix 4

Compound	$\Delta H_f^{\circ}\left(\frac{kJ}{mol}\right)$	$S^{\circ}\left(\frac{J}{mol\cdot K}\right)$	$\Delta G_f^{\circ}\left(\frac{kJ}{mol}\right)$
HCl(g)	-92	187	-95
NH_3(g)	-46	193	-17
NH_4Cl(s)	-314	96	-203

$$\Delta H^{\circ}_{rxn} = n_{NH_4Cl}\Delta H^{\circ}_f(NH_4Cl) - n_{HCl}\Delta H^{\circ}_f(HCl) - n_{NH_3}\Delta H^{\circ}_f(NH_3)$$
$$\Delta H^{\circ}_{rxn} = (1)\left(-314\,\frac{kJ}{mol}\right) - (1)\left(-92\,\frac{kJ}{mol}\right) - (1)\left(-46\,\frac{kJ}{mol}\right) = -176\,\frac{kJ}{mol}$$
$$\Delta S^{\circ}_{rxn} = n_{NH_4Cl}S^{\circ}_{NH_4Cl} - n_{HCl}S^{\circ}_{HCl} - n_{NH_3}S^{\circ}_{NH_3}$$
$$\Delta S^{\circ}_{rxn} = (1)\left(96\,\frac{J}{mol\cdot K}\right) - (1)\left(187\,\frac{J}{mol\cdot K}\right) - (1)\left(193\,\frac{J}{mol\cdot K}\right) = -284\,\frac{J}{mol\cdot K}$$
$$\Delta G^{\circ}_{rxn} = n_{NH_4Cl}\Delta G^{\circ}_f(NH_4Cl) - n_{HCl}\Delta G^{\circ}_f(HCl) - n_{NH_3}\Delta G^{\circ}_f(NH_3)$$
$$\Delta G^{\circ}_{rxn} = (1)\left(-203\,\frac{kJ}{mol}\right) - (1)\left(-95\,\frac{kJ}{mol}\right) - (1)\left(-17\,\frac{kJ}{mol}\right) = -91\,\frac{kJ}{mol}$$

56. The values of ΔH and ΔS do not change much with temperature, because the enthalpies and entropies of both reactants and products are affected by the temperature rise and the difference between them hardly changes. However, $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ therefore, has a stronger temperature dependence. When calculating ΔG° at temperature other than 25° C, ΔH° and ΔS° are assumed to be temperature independent (which is not always the best assumption).

57. $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

$$\Delta G^{\circ} = -58.03\,kJ - (-298K)\left(-0.1766\,\frac{kJ}{K}\right) = -5.40\,kJ$$

ΔG° will equal 0 when ΔH°=TΔS°

$$-58.03\,kJ = T\left(-0.1766\,\frac{kJ}{K}\right)$$
$$T = 328.6K$$

Above this temperature ΔG° will be positive and below this temperature ΔG° will be negative.

59. a) $\Delta G^\circ_{rxn} = \sum \Delta G^\circ_f(prod) - \sum G^\circ_f(reac)$

$\Delta G^\circ_{rxn} = n_{PCl_3}\Delta G^\circ_f(PCl_3) + n_{O_2}\Delta G^\circ_f(O_2) - n_{POCl_3}\Delta G^\circ_f(POCl_3)$

$\Delta G^\circ_{rxn} = (2)\left(-270\,\frac{kJ}{mol}\right) + (1)\left(0\,\frac{kJ}{mol}\right) - (2)\left(-502\,\frac{kJ}{mol}\right) = 464\,\frac{kJ}{mol}$

b) ΔG is +, therefore, the reaction is not spontaneous.

c) Calculate ΔH° at original temperature.

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

$464\,\frac{kJ}{mol} = \Delta H^\circ - (298K)\left(0.179\,\frac{kJ}{mol\cdot K}\right)$

$\Delta H^\circ = 517\frac{kJ}{mol}$

Assume ΔH˚ and ΔS˚ are temperature independent. In order to be spontaneous ΔG˚ must be greater than whatever the temperature is when ΔG˚ is 0.

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

$0\,\frac{kJ}{mol} = 517\,\frac{kJ}{mol} - T\left(0.179\,\frac{kJ}{mol\cdot K}\right)$

$T = 2{,}890K$

60. $\Delta S^\circ_{rxn} = \sum S^\circ_{prod} - \sum S^\circ_{reac}$

$\Delta H^\circ_{rxn} = \sum \Delta H^\circ_f(prod) - \sum H^\circ_f(reac)$

From appendix 4

Compound	S°$\left(\frac{J}{mol\cdot K}\right)$	ΔH$_f$°$\left(\frac{kJ}{mol}\right)$
C_2H_4(g)	219	52
H_2O(g)	189	-242
CH_3CH_2OH(l)	161	-278
C_2H_6(g)	229.5	-84.7
H_2(g)	131	0

Reaction 1:

$\Delta S^\circ_{rxn} = n_{CH_3CH_2OH}S^\circ_{CH_3CH_2OH} - n_{C_2H_4}S^\circ_{C_2H_4} - n_{H_2O}S^\circ_{H_2O}$

$\Delta S^\circ_{rxn} = (1)\left(161\,\frac{J}{mol\cdot K}\right) - (1)\left(219\,\frac{J}{mol\cdot K}\right) - (1)\left(189\,\frac{J}{mol\cdot K}\right) = -274\,\frac{J}{mol\cdot K}$

$\Delta H^\circ_{rxn} = n_{CH_3CH_2OH}\Delta H^\circ_f(CH_3CH_2OH) - n_{C_2H_4}\Delta H^\circ_f(C_2H_4) - n_{H_2O}\Delta H^\circ_f(H_2O)$

$\Delta H^\circ_{rxn} = (1)\left(-278\,\frac{kJ}{mol}\right) - (1)\left(52\,\frac{kJ}{mol}\right) - (1)\left(-242\,\frac{kJ}{mol}\right) = -88\,\frac{kJ}{mol}$

Reaction 2:

$\Delta S^\circ_{rxn} = n_{CH_3CH_2OH}S^\circ_{CH_3CH_2OH} + n_{H_2}S^\circ_{H_2} - n_{C_2H_6}S^\circ_{C_2H_6} - n_{H_2O}S^\circ_{H_2O}$

$\Delta S^\circ_{rxn} = (1)\left(161\,\frac{J}{mol\cdot K}\right) + (1)\left(131\,\frac{J}{mol\cdot K}\right) - (1)\left(229.5\,\frac{J}{mol\cdot K}\right) - (1)\left(189\,\frac{J}{mol\cdot K}\right)$
$= -127\,\frac{J}{mol\cdot K}$

$\Delta H^\circ_{rxn} = n_{CH_3CH_2OH}\Delta H^\circ_f(CH_3CH_2OH) + n_{H_2}\Delta H^\circ_f(H_2) - n_{C_2H_6}\Delta H^\circ_f(C_2H_6)$
$- n_{H_2O}\Delta H^\circ_f(H_2O)$

$\Delta H^\circ_{rxn} = (1)\left(-278\,\frac{kJ}{mol}\right) + (1)\left(0\,\frac{kJ}{mol}\right) - (1)\left(-84.7\,\frac{kJ}{mol}\right) - (1)\left(-242\,\frac{kJ}{mol}\right)$
$= 49\,\frac{kJ}{mol}$

Reactions are spontaneous when ΔG is -. $\Delta G = \Delta H - T\Delta S$, therefore, reaction 2 can never be spontaneous because ΔG will always be +. Therefore, reaction 1 is more thermodynamically feasible because at low temperatures it will be spontaneous.

61. $\Delta H^\circ_{rxn} = \sum \Delta H^\circ_f(prod) - \sum H^\circ_f(reac)$

$$\Delta G^\circ_{rxn} = \sum \Delta G^\circ_f(prod) - \sum G^\circ_f(reac)$$

$$\Delta S^\circ_{rxn} = \sum S^\circ_{prod} - \sum S^\circ_{reac}$$

From Appendix 4

Compound	ΔH$_f$° $\left(\frac{kJ}{mol}\right)$	ΔG$_f$° $\left(\frac{kJ}{mol}\right)$	ΔS° $\left(\frac{J}{mol\cdot K}\right)$
CH_4(g)	-75	-51	186
CO_2(g)	-393.5	-394	214
CH_3CO_2H(l)	-484	-389	160
CH_3OH(g)	-201	-163	240
CO(g)	-110.5	-137	198

Reaction 1:

$$\Delta H^\circ_{rxn} = n_{CH_3CO_2H}\Delta H^\circ_f(CH_3CO_2H) - n_{CH_4}\Delta H^\circ_f(CH_4) - n_{CO_2}\Delta H^\circ_f(CO_2)$$

$$\Delta H^\circ_{rxn} = (1)\left(-484\,\frac{kJ}{mol}\right) - (1)\left(-75\,\frac{kJ}{mol}\right) - (1)\left(-393.5\,\frac{kJ}{mol}\right) = -16\,\frac{kJ}{mol}$$

$$\Delta G^\circ_{rxn} = n_{CH_3CO_2H}\Delta G^\circ_f(CH_3CO_2H) - n_{CH_4}\Delta G^\circ_f(CH_4) - n_{CO_2}\Delta G^\circ_f(CO_2)$$

$$\Delta G^\circ_{rxn} = (1)\left(-389\,\frac{kJ}{mol}\right) - (1)\left(-51\,\frac{kJ}{mol}\right) - (1)\left(-394\,\frac{kJ}{mol}\right) = 56\,\frac{kJ}{mol}$$

$$\Delta S^\circ_{rxn} = n_{CH_3CO_2H}S^\circ_{CH_3CO_2H} - n_{CH_4}S^\circ_{CH_4} - n_{CO_2}S^\circ_{CO_2}$$

$$\Delta S^\circ_{rxn} = (1)\left(160\,\frac{J}{mol\cdot K}\right) - (1)\left(186\,\frac{J}{mol\cdot K}\right) - (1)\left(214\,\frac{J}{mol\cdot K}\right) = -240.\,\frac{J}{mol\cdot K}$$

Reaction 2:

$$\Delta H^\circ_{rxn} = n_{CH_3CO_2H}\Delta H^\circ_f(CH_3CO_2H) - n_{CH_3OH}\Delta H^\circ_f(CH_3OH) - n_{CO}\Delta H^\circ_f(CO)$$

$$\Delta H^\circ_{rxn} = (1)\left(-484\,\frac{kJ}{mol}\right) - (1)\left(-201\,\frac{kJ}{mol}\right) - (1)\left(-110.5\,\frac{kJ}{mol}\right) = -173\,\frac{kJ}{mol}$$

$$\Delta G^\circ_{rxn} = n_{CH_3CO_2H}\Delta G^\circ_f(CH_3CO_2H) - n_{CH_3OH}\Delta G^\circ_f(CH_3OH) - n_{CO}\Delta G^\circ_f(CO)$$

$$\Delta G^\circ_{rxn} = (1)\left(-389\,\frac{kJ}{mol}\right) - (1)\left(-163\,\frac{kJ}{mol}\right) - (1)\left(-137\,\frac{kJ}{mol}\right) = -89\,\frac{kJ}{mol}$$

$$\Delta S^\circ_{rxn} = n_{CH_3CO_2H}S^\circ_{CH_3CO_2H} - n_{CH_3OH}S^\circ_{CH_3OH} - n_{CO}S^\circ_{CO}$$

$$\Delta S^\circ_{rxn} = (1)\left(160\,\frac{J}{mol\cdot K}\right) - (1)\left(240\,\frac{J}{mol\cdot K}\right) - (1)\left(198\,\frac{J}{mol\cdot K}\right) = -278\,\frac{J}{mol\cdot K}$$

For a commercial process you want the reaction to be spontaneous. Both reactions will be spontaneous at temperatures below $T = \frac{\Delta H}{\Delta S}$. For reaction 1 this temperature is 67K and for reaction 2 this temperature is 622K. Raising the temperature of a reaction will raise the reaction rate. Therefore, reaction 2 is preferable because it will still be spontaneous at high temperatures.

62.

$\frac{1}{2}(12CO_2(g) + 6H_2O(l) \rightarrow 2C_6H_6(l) + 15O_2(g))$	$\Delta G_a = -\frac{1}{2}\Delta G_1 = 3200.$ kJ
$6(C(s) + O_2(g) \rightarrow CO_2(g))$	$\Delta G_b = 6\Delta G_2 = -2364$kJ
$3(H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l))$	$\Delta G_c = 3\Delta G_3 = -711$ kJ
$6C(s) + 3H_2(g) \rightarrow C_6H_6(l)$	$\Delta G = \Delta G_a + \Delta G_b + \Delta G_c = 3200.$kJ + -2364kJ + -711kJ= 125kJ

64. a) Since there are more moles of gas on the reactants side than the products side , ΔS is negative. You should know that it is spontaneous for $2O \rightarrow O_2$, therefore, ΔG is negative. In order for this to happen ΔH must be negative.

b) $\Delta G = \Delta H - T\Delta S$ ΔG is spontaneous when ΔG is negative, therefore, since ΔS is positive we want TΔS to be as small as possible, i.e. the reaction becomes more spontaneous at low temperatures.

68. From appendix 4

Compound	$\Delta G_f^\circ\left(\frac{kJ}{mol}\right)$
$SO_2(g)$	-300
$O_2(g)$	0
$SO_3(g)$	-371

$$\Delta G^\circ_{rxn} = \sum \Delta G_f^\circ(prod) - \sum \Delta G_f^\circ(reac)$$
$$\Delta G^\circ_{rxn} = n_{SO_3}\Delta G_f^\circ(SO_3) - n_{SO_2}\Delta G_f^\circ(SO_2) - n_{O_2}\Delta G_f^\circ(O_2)$$
$$\Delta G^\circ_{rxn} = (2)\left(-371\,\frac{kJ}{mol}\right) - (2)\left(-300.\frac{kJ}{mol}\right) - (1)\left(0\,\frac{kJ}{mol}\right) = -142\,\frac{kJ}{mol}$$
$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RTln(Q) = \Delta G^\circ_{rxn} + RTln\left(\frac{{P_{SO_3}}^2}{{P_{SO_2}}^2 P_{O_2}}\right)$$
$$\Delta G_{rxn} = -142\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298.K)ln\left(\frac{10.0^2}{(10.0^2)(10.0)}\right) = -148\,\frac{kJ}{mol}$$

69. From Appendix 4

Compound	$\Delta G^\circ\ \left(\frac{kJ}{mol}\right)$
$NO_2(g)$	52
$N_2O_4(g)$	98

$$\Delta G^\circ_{rxn} = \sum \Delta G_f^\circ(prod) - \sum \Delta G_f^\circ(reac)$$
$$\Delta G^\circ_{rxn} = n_{N_2O_4}\Delta G_f^\circ(N_2O_4) - n_{NO_2}\Delta G_f^\circ(NO_2)$$
$$\Delta G^\circ_{rxn} = (1)\left(98\,\frac{kJ}{mol}\right) - (2)\left(52\,\frac{kJ}{mol}\right) = -6\,\frac{kJ}{mol}$$
$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RTln(Q) = \Delta G^\circ_{rxn} + RTln\left(\frac{P_{N_2O_4}}{{P_{NO_2}}^2}\right)$$

a) When all of the pressures are 1.0 (this is standard condition and therefore) ΔG=ΔG˚=-6kJ
ΔG < 1, therefore, the forward reaction will proceed to reach equilibrium.

b) $\Delta G_{rxn} = -6\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln\left(\frac{0.5}{0.21^2}\right) = 0\,\frac{J}{mol}$
If you plug these numbers into your calculator, you get 0.016 $\frac{J}{mol}$ but if you take into account significant figures you get 0 $\frac{J}{mol}$ (this is due to the fact that to -6 $\frac{J}{mol}$ is only significant to the ones place.)
ΔG=0, therefore, the system is at equilibrium.

c) $\Delta G_{rxn} = -6\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln\left(\frac{1.6}{0.29^2}\right) = 1\,\frac{kJ}{mol}$
ΔG>1, therefore, the reverse reaction will proceed to reach equilibrium.

70. $\Delta G_{rxn} = \Delta G^\circ_{rxn} + RTln(Q)$

$$Q = \frac{P_{H_2O}^2}{P_{H_2S}^2 P_{SO_2}} = \frac{(0.030)^2}{(0.00010)^2(0.010)} = 9.0 \times 10^6$$

* Sulfur is left off because it is a solid

$$\Delta G^\circ_{rxn} = \sum \Delta G^\circ_f(prod) - \sum \Delta G^\circ_f(reac)$$

From appendix 4

Compound	$\Delta G_f^\circ\ \left(\frac{kJ}{mol}\right)$
$H_2S(g)$	-34
$SO_2(g)$	-300.
S(s)	0.
$H_2O(g)$	-229

$$\Delta G^\circ_{rxn} = n_S \Delta G^\circ_f(S) + n_{H_2O}\Delta G^\circ_f(H_2O) - n_{H_2S}\Delta G^\circ_f(H_2S) - n_{SO_2}\Delta G^\circ_f(SO_2)$$

$$\Delta G^\circ_{rxn} = (3)\left(0\,\frac{kJ}{mol}\right) + (2)\left(-229\,\frac{kJ}{mol}\right) - (2)\left(34\,\frac{kJ}{mol}\right) - (1)\left(-300.\,\frac{kJ}{mol}\right) = -90\,\frac{kJ}{mol}$$

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RTln(Q) = -90\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln(9.0\times 10^6) = -50.\,\frac{kJ}{mol}$$

71. $\Delta S^\circ_{rxn} = \sum S^\circ_{prod} - \sum S^\circ_{reac}$

$$\Delta H^\circ_{rxn} = \sum \Delta H^\circ_f(prod) - \sum \Delta H^\circ_f(reac)$$

$$\Delta G^\circ_{rxn} = \sum \Delta G^\circ_f(prod) - \sum \Delta G^\circ_f(reac)$$

From appendix 4

Compound	$S^\circ\left(\frac{J}{mol\cdot K}\right)$	$\Delta H_f^\circ\left(\frac{kJ}{mol}\right)$	$\Delta G_f^\circ\left(\frac{kJ}{mol}\right)$
$N_2(g)$	192	0	0
$H_2(g)$	131	0	0
$NH_3(g)$	193	-46	-17

$$\Delta S^\circ_{rxn} = n_{NH_3}S^\circ_{NH_3} - n_{N_2}S^\circ_{N_2} - n_{H_2}S^\circ_{H_2}$$

$$\Delta S^\circ_{rxn} = (2)\left(193\,\frac{J}{mol\cdot K}\right) - (1)\left(192\,\frac{J}{mol\cdot K}\right) - (3)\left(131\,\frac{J}{mol\cdot K}\right) = -199\,\frac{J}{mol\cdot K}$$

$$\Delta H^\circ_{rxn} = n_{NH_3}\Delta H^\circ_f(NH_3) - n_{N_2}\Delta H^\circ_f(N_2) - n_{H_2}\Delta H^\circ_f(H_2)$$

$$\Delta H^\circ_{rxn} = (2)\left(-46\,\frac{kJ}{mol}\right) - (1)\left(0\,\frac{kJ}{mol}\right) - (1)\left(0\,\frac{kJ}{mol}\right) = -92\,\frac{kJ}{mol}$$

$$\Delta G^\circ_{rxn} = n_{NH_3}\Delta G^\circ_f(NH_3) - n_{N_2}\Delta G^\circ_f(N_2) - n_{H_2}\Delta G^\circ_f(H_2)$$

$$\Delta G^\circ_{rxn} = (2)\left(-17\,\frac{kJ}{mol}\right) - (1)\left(0\,\frac{kJ}{mol}\right) - (1)\left(0\,\frac{kJ}{mol}\right) = -34\,\frac{kJ}{mol}$$

$$\Delta G^\circ_{rxn} = -RTln(K)$$

$$-34\,\frac{kJ}{mol} = -\left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln(K)$$

$$K = 9.1\times 10^5$$

a) $\Delta G = \Delta G^\circ_{298} + RTln(Q)$

$$Q = \frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}} = \frac{(50.)^2}{(200.)(200.)^3} = 1.6\times 10^{-6}$$

$$\Delta G = -34\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln(1.6\times 10^6) = -67\,\frac{kJ}{mol}$$

b) $\Delta G = \Delta G^\circ_{298} + RTln(Q)$

$$Q = \frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}} = \frac{(200.)^2}{(200.)(600.)^3} = 9.3\times 10^{-7}$$

$$\Delta G = -34\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln(9.3\times 10^{-7}) = -68\,\frac{kJ}{mol}$$

c) $\Delta G = \Delta G^\circ_{100.} + RTln(Q)$

$$\Delta G^\circ_{100.} = \Delta H - T\Delta S = -92\,\frac{kJ}{mol} - (100.K)\left(-0.199\,\frac{kJ}{mol\cdot K}\right) = -72\,\frac{kJ}{mol}$$

$$Q = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(10.)^2}{(50.)(200.)^3} = 2.5 \times 10^{-7}$$
$$\Delta G = -72\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol \cdot K}\right)(100.\,K)ln(2.5 \times 10^{-7}) = -85\,\frac{kJ}{mol}$$

d) $\Delta G = \Delta G^\circ_{700.} + RTln(Q)$

$$\Delta G^\circ_{700.} = \Delta H - T\Delta S = -92\,\frac{kJ}{mol} - (700.\,K)\left(-0.199\,\frac{kJ}{mol \cdot K}\right) = 47\,\frac{kJ}{mol}$$
$$Q = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(10.)^2}{(50.)(200.)^3} = 2.5 \times 10^{-7}$$
$$\Delta G = 47\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol \cdot K}\right)(700.\,K)ln(2.5 \times 10^{-7}) = -41\,\frac{kJ}{mol}$$

74. a) $\Delta G^\circ = -RTln(K) = -\left(0.0083145\,\frac{kJ}{mol \cdot K}\right)(298K)ln(1.00 \times 10^{-14}) = 79.9\,\frac{kJ}{mol}$

b) $\Delta G^\circ_{313\,K} = -RTln(K) = -\left(0.0083145\,\frac{kJ}{mol \cdot K}\right)(313K)ln(2.92 \times 10^{-14}) = 81.1\,\frac{kJ}{mol}$

78. a) From Appendix 4

Compound	ΔH_f° $\left(\frac{kJ}{mol}\right)$	S° $\left(\frac{J}{mol \cdot K}\right)$	ΔG_f° $\left(\frac{kJ}{mol}\right)$
$NH_3(g)$	-46	193	-17
$O_2(g)$	0	205	0
$NO(g)$	90	211	87
$H_2O(g)$	-242	189	-229
$NO_2(g)$	34	240	52
$H_2O(l)$	-286	70	-237
$HNO_3(l)$	-174	156	-81

$$\Delta H^\circ_{rxn} = \sum \Delta H^\circ_f(prod) - \sum \Delta H^\circ_f(reac)$$
$$\Delta S^\circ_{rxn} = \sum S^\circ_{prod} - \sum S^\circ_{reac}$$
$$\Delta G^\circ_{rxn} = \sum \Delta G^\circ_f(prod) - \sum \Delta G^\circ_f(reac)$$
$$\Delta G^\circ = -RTln(K)$$

Reaction 1:

$$\Delta H^\circ_{rxn} = n_{NO}\Delta H^\circ_f(NO) + n_{H_2O}\Delta H^\circ_f(H_2O) - n_{NH_3}\Delta H^\circ_f(NH_3) - n_{O_2}\Delta H^\circ_f(O_2)$$
$$\Delta H^\circ_{rxn} = (4)\left(90\,\frac{kJ}{mol}\right) + (6)\left(-242\,\frac{kJ}{mol}\right) - (4)\left(-46\,\frac{kJ}{mol}\right) - (5)\left(0\,\frac{kJ}{mol}\right) = -908\,\frac{kJ}{mol}$$
$$\Delta S^\circ_{rxn} = n_{NO}S^\circ_{NO} + n_{H_2O}S^\circ_{H_2O} - n_{NH_3}S^\circ_{NH_3} - n_{O_2}S^\circ_{O_2}$$
$$\Delta S^\circ_{rxn} = (4)\left(211\,\frac{J}{mol \cdot K}\right) + (6)\left(189\,\frac{J}{mol \cdot K}\right) - (4)\left(193\,\frac{J}{mol \cdot K}\right) - (5)\left(205\,\frac{J}{mol \cdot K}\right)$$
$$= 181\,\frac{J}{mol \cdot K}$$
$$\Delta G^\circ_{rxn} = n_{NO}\Delta G^\circ_f(NO) + n_{H_2O}\Delta G^\circ_f(H_2O) - n_{NH_3}\Delta G^\circ_f(NH_3) - n_{O_2}\Delta G^\circ_f(O_2)$$
$$\Delta G^\circ_{rxn} = (4)\left(87\,\frac{kJ}{mol}\right) + (6)\left(-229\,\frac{kJ}{mol}\right) - (4)\left(-17\,\frac{kJ}{mol}\right) - (5)\left(0\,\frac{kJ}{mol}\right) = -958\,\frac{kJ}{mol}$$
$$\Delta G = -RTln(K)$$
$$-958\,\frac{kJ}{mol} = -\left(0.0083145\,\frac{J}{mol \cdot K}\right)(298K)ln(K)$$

K is very large, most likely your calculator will say overflow

Reaction 2:

$$\Delta H^\circ_{rxn} = n_{NO_2}\Delta H^\circ_f(NO_2) - n_{NO}\Delta H^\circ_f(NO) - n_{O_2}\Delta H^\circ_f(O_2)$$

$\Delta H^\circ_{rxn} = (2)\left(34\,\frac{kJ}{mol}\right) - (2)\left(90\,\frac{kJ}{mol}\right) - (1)\left(0\,\frac{kJ}{mol}\right) = -112\,\frac{kJ}{mol}$

$\Delta S^\circ_{rxn} = n_{NO_2}S^\circ_{NO_2} - n_{NO}S^\circ_{NO} - n_{O_2}S^\circ_{O_2}$

$\Delta S^\circ_{rxn} = (2)\left(240\,\frac{J}{mol\cdot K}\right) - (2)\left(211\,\frac{J}{mol\cdot K}\right) - (1)\left(205\,\frac{J}{mol\cdot K}\right) = -147\,\frac{J}{mol\cdot K}$

$\Delta G^\circ_{rxn} = n_{NO_2}\Delta G^\circ_f(NO_2) - n_{NO}\Delta G^\circ_f(NO) - n_{O_2}\Delta G^\circ_f(O_2)$

$\Delta G^\circ_{rxn} = (2)\left(52\,\frac{kJ}{mol}\right) - (2)\left(87\,\frac{kJ}{mol}\right) - (1)\left(0\,\frac{kJ}{mol}\right) = -70\,\frac{kJ}{mol}$

$\Delta G = -RTln(K)$

$-70{,}000\,\frac{J}{mol} = -\left(8.3145\,\frac{J}{mol\cdot K}\right)(298K)ln(K)$

$K = 1.8 \times 10^{12}$

Reaction 3:

$\Delta H^\circ_{rxn} = n_{HNO_3}\Delta H^\circ_f(HNO_3) + n_{NO}\Delta H^\circ_f(NO) - n_{NO_2}\Delta H^\circ_f(NO_2) - n_{H_2O}\Delta H^\circ_f(H_2O)$

$\Delta H^\circ_{rxn} = (2)\left(-174\,\frac{kJ}{mol}\right) + (1)\left(90\,\frac{kJ}{mol}\right) - (3)\left(34\,\frac{kJ}{mol}\right) - (1)\left(-286\,\frac{kJ}{mol}\right) = -74\,\frac{kJ}{mol}$

$\Delta S^\circ_{rxn} = n_{HNO_3}S^\circ_{HNO_2} + n_{NO}S^\circ_{NO} - n_{NO_2}S^\circ_{NO_2} - n_{H_2O}S^\circ_{H_2O}$

$\Delta S^\circ_{rxn} = (2)\left(156\,\frac{J}{mol\cdot K}\right) + (1)\left(211\,\frac{J}{mol\cdot K}\right) - (3)\left(240\,\frac{J}{mol\cdot K}\right) - (1)\left(70\,\frac{J}{mol\cdot K}\right)$

$= -267\,\frac{J}{mol\cdot K}$

$\Delta G^\circ_{rxn} = n_{HNO_3}\Delta G^\circ_f(HNO_3) + n_{NO}\Delta G^\circ_f(NO) - n_{NO_2}\Delta G^\circ_f(NO_2) - n_{H_2O}\Delta G^\circ_f(H_2O)$

$\Delta G^\circ_{rxn} = (2)\left(-81\,\frac{kJ}{mol}\right) + (1)\left(87\,\frac{kJ}{mol}\right) - (3)\left(52\,\frac{kJ}{mol}\right) - (1)\left(-237\,\frac{kJ}{mol}\right) = 6\,\frac{kJ}{mol}$

$\Delta G = -RTln(K)$

$6{,}000\,\frac{J}{mol} = -\left(8.3145\,\frac{J}{mol\cdot K}\right)(298K)ln(K)$

$K = 0.09$

Note: The values will come out slightly different if you use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$instead of $\Delta G^\circ_{rxn} = \sum \Delta G^\circ_f(prod) - \sum \Delta G^\circ_f(reac)$. Both methods would be acceptable on a test.

b) $\Delta G^\circ_{1098} = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ_{1098} = -RTln(K)$

Reaction 1:

$\Delta G^\circ_{1098} = -908\,\frac{kJ}{mol} - (1098K)\left(0.181\,\frac{kJ}{mol\cdot K}\right) = -1{,}107\,\frac{kJ}{mol}$

$-1{,}107\,\frac{kJ}{mol} = \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(1098K)ln(K)$

$K = 4.587 \times 10^{52}$

c) There is no thermodynamic reason for the elevated temperature since ΔH° is negative and ΔS° is positive making the reaction spontaneous at all temperatures. Thus the purpose for the high temperature must be to increase the rate of the reaction.

79. $\Delta G^\circ = -RTln(K)$

$$K = \frac{P^2_{NH_3}}{P_{N_2}P^3_{F_2}} = \frac{(0.48)^2}{(0.021)(0.063)^3} = 44{,}000$$

$\Delta G^\circ = -\left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(800.\,K)ln(44{,}000) = -71.1\,\frac{kJ}{mol}$

84. a) $\Delta G^\circ = -RTln(K)$

$-30.5\,\frac{kJ}{mol} = -\left(0.0083145\,\frac{J}{mol\cdot K}\right)(298K)ln(K)$

$K = 222{,}000$

b) The question wants you to find if all of the energy was coming from the metabolism of glucose how many ATP molecules could you produce.

Calculate the energy generated when for the metabolism of glucose (ΔG)

From Appendix 4

Compound	$\Delta G(\frac{kJ}{mol})$
$C_6H_{12}O_6(s)$	-911
$O_2(g)$	0
$CO_2(g)$	-394
$H_2O(l)$	-237

$\Delta G^\circ_{rxn} = \sum \Delta G^\circ_f(prod) - \sum \Delta G^\circ_f(reac)$

$\Delta G^\circ_{rxn} = n_{CO_2}\Delta G^\circ_f(CO_2) + n_{H_2O}\Delta G^\circ_f(H_2O) - n_{C_6H_{12}O_6}\Delta G^\circ_f(C_6H_{12}O_6) - n_{O_2}\Delta G^\circ_f(O_2)$

$\Delta G^\circ_{rxn} = (6)\left(-394\,\frac{kJ}{mol}\right) + (6)\left(-237\,\frac{kJ}{mol}\right) - (1)\left(-911\,\frac{kJ}{mol}\right) - (6)\left(0\,\frac{kJ}{mol}\right)$

$= -2{,}875\,\frac{kJ}{mol}$

Therefore, when a mole of glucose is metabolized, 2,875 kJ of energy is released

Determine the amount of energy released when 1 molecule of glucose is metabolized

$$1\,molecule\ C_6H_{12}O_2\left(\frac{1\,mol\ C_6H_{12}O_2}{6.0223\times10^{23}\,molecule}\right)\left(\frac{2{,}875\,kJ}{1\,mol\ C_6H_{12}O_2}\right) = 4.774\times10^{-21}\,kJ$$

Calculate the amount of ATP that can be produced

$$4.774\times10^{-21}\,kJ\left(\frac{1\,mol\ ATP}{30.5\,kJ}\right)\left(\frac{6.0223\times10^{23}\,molecules}{1\,mol\ ATP}\right) = 94.3\,molecules$$

86. a) $\Delta G^\circ = -RTln(K)$

$14\,\frac{kJ}{mol} = -\left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln(K)$

$K = 0.0035$

b) Glutamic Acid(aq)+NH_3(aq) ⇌ Glutamine(aq)+H_2O(l) $\Delta G_a = \Delta G_1 = 14\,\frac{kJ}{mol}$

ATP(aq)+H_2O(l) ⇌ ADP(aq)+$H_2PO_4^-$(aq) $\Delta G_b = \Delta G_2 = -30.5\,\frac{kJ}{mol}$

Glutamic Acid(aq)+ATP(aq)+NH_3(aq)⇌Glutamine(aq)+ADP(aq)+$H_2PO_4^-$(aq) $\Delta G = \Delta G_a + \Delta G_b$

$\Delta G = \Delta G_a + \Delta G_b = 14\ kJ + -30.5\ kJ = -17\,\frac{kJ}{mol}$

$\Delta G^\circ = -RTln(K)$

$-17\,\frac{kJ}{mol} = -\left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln(K)$

$K = 950$

87. $\Delta G^\circ = -\Delta H^\circ - T\Delta S^\circ = -58.03\,\frac{kJ}{mol} - (298.2K)\left(-0.1766\,\frac{kJ}{mol\cdot K}\right) = -5.37\,\frac{kJ}{mol}$

$\Delta G^\circ = -RTln(K)$

$-5.37\,\frac{kJ}{mol} = -\left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298.2K)ln(K)$

$K = 8.72$

They now want you to find K at 100.0˚C. First find ΔG˚ at 100.0 ˚C.

$$\Delta G^\circ = -\Delta H^\circ - T\Delta S^\circ = -58.03\,\frac{kJ}{mol} - (373.2K)\left(-0.1766\,\frac{kJ}{mol\cdot K}\right) = 7.88\,\frac{kJ}{mol}$$

$\Delta G° = -RTln(K)$

$7.88\,\frac{kJ}{mol} = -\left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(373.2K)ln(K)$

$K = 0.0789$

109. $\Delta G° = -RTln(K) = -\left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298\,K)ln(7.2 \times 10^{-4}) = 18\,\frac{kJ}{mol}$

a) The standard state is when the concentrations are equal to 1.0 M, therefore, $\Delta G = \Delta G° = 18\,\frac{kJ}{mol}$

b) $\Delta G = \Delta G° + RTln(Q)$

$$Q = \frac{[H^+][F^-]}{[HF]} = \frac{(2.7 \times 10^{-2})(2.7 \times 10^{-2})}{(0.98)} = 7.4 \times 10^{-4}$$

$$\Delta G = 18\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln(7.4 \times 10^{-4}) = 0\,\frac{kJ}{mol}$$

c) $\Delta G = \Delta G° + RTln(Q)$

$$Q = \frac{[H^+][F^-]}{[HF]} = \frac{(1.0 \times 10^{-5})(1.0 \times 10^{-5})}{(1.0 \times 10^{-5})} = 1.0 \times 10^{-5}$$

$$\Delta G = 18\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln(1.0 \times 10^{-5}) = -11\,\frac{kJ}{mol}$$

d) $\Delta G = \Delta G° + RTln(Q)$

$$Q = \frac{[H^+][F^-]}{[HF]} = \frac{(7.2 \times 10^{-4})(0.27)}{0.27} = 7.2 \times 10^{-4}$$

$$\Delta G = 18\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln(7.2 \times 10^{-4}) = 0\,\frac{kJ}{mol}$$

e) $\Delta G = \Delta G° + RTln(Q)$

$$Q = \frac{[H^+][F^-]}{[HF]} = \frac{(1.0 \times 10^{-3})(0.67)}{0.52} = 0.0013$$

$$\Delta G = 18\,\frac{kJ}{mol} + \left(0.0083145\,\frac{kJ}{mol\cdot K}\right)(298K)ln(0.0013) = 2\,\frac{kJ}{mol}$$

If ΔG is negative, reaction will proceed to products, ΔG is positive reaction will proceed to reactants, ΔG is 0, reaction at equilibrium.

a) shifts to left (reactants)
b) no shift
c) shifts to right (products)
d) no shift
e) shifts to left (reactants)