Key begins on page 3.

1. What are the three laws of thermodynamics?

2. Which substance has the higher entropy in each of the following pairs?
   a) A sample of Dry Ice (solid CO_2) at –78 °C or CO_2 vapor at 0 °C

   b) Sugar, as a solid or dissolved in a cup of tea

   c) Two 100 mL beakers, one containing 1 mol of pure water and the other containing 1 mol of pure alcohol, or a beaker containing a mixture of water and alcohol

3. Without consulting the thermodynamic tables, predict whether the entropy change is positive or negative for each of the following reactions. Give reasons for your predictions.
   a) $2\ KClO_4\ (s) \rightarrow 2\ KClO_3\ (s) + O_2\ (g)$

   b) $N_2\ (g) \rightarrow 2\ N\ (g)$

   c) $2\ Na\ (s) + 2\ H_2O\ (l) \rightarrow 2\ NaOH\ (aq) + H_2\ (g)$

   d) $2\ LiOH\ (aq) + CO_2\ (g) \rightarrow Li_2CO_3\ (aq) + H_2O\ (l)$

4. Calculate the standard molar entropy change for each of the following reactions at 25 °C.

   a) $Ca\ (s) + 2\ H_2O\ (l) \rightarrow Ca(OH)_2\ (aq) + 2\ H_2\ (g)$

   b) $Na_2CO_3\ (aq) + 2\ HCl\ (aq) \rightarrow 2\ NaCl\ (aq) + H_2O\ (l) + CO_2\ (g)$

5. What is the value of ΔG_f^o for $BaCO_3$ (s), if $\Delta G^o_{rxn} = +218.1$ kJ for the reaction

$$BaCO_3\ (s) \rightarrow BaO\ (s) + CO_2\ (g)$$

6. For the combustion of butane gas, C_4H_{10} (g) + 13/2 O_2 (g) → 4 CO_2 (g) + 5 H_2O (g)
Calculate ΔG^o by two different methods.

7. Consider the decomposition of calcium carbonate: $CaCO_3$ (s) → CaO (s) + CO_2 (g)
Calculate the pressure in atm of CO_2 in an equilibrium process
(a) at 25 °C

b) at 800 °C. Assume that ΔH^o = 177.8 k and ΔS^o = 160.5 J/K

8. In what form is the portion of reaction enthalpy given off that cannot do work? What happens to a portion of the useful energy as it does work?

9. The equilibrium constant for the reaction $2\ Fe^{3+}$ (aq) + Hg_2^{2+} (aq) → $2\ Fe^{2+}$ (aq) + $2\ Hg^{2+}$ (aq) is $K_c = 9.1 \times 10^{-6}$ at 298 K.
a) What is the ΔG^o at this temperature

b) Calculate ΔG when $[Fe^{3+}] = 0.20\ M$, $[Hg_2^{2+}] = 0.010\ M$, $[Fe^{2+}] = 0.010\ M$, and $[Hg^{2+}] = 0.025\ M$. In which direction will the reaction proceed to achieve equilibrium?

10. Methanol, on of the most important industrial feedstocks, is made by several catalyzed reactions, on of which is CO (g) + 2 H_2 (g) → CH_3OH (l).
a) Demonstrate that this reaction is thermodynamically feasible.

b) Is it favored at low or at high temperature?

c) Calculate ΔG^o at 100 °C for this reaction.

① FIRST LAW (LAW OF CONSERVATION OF ENERGY) $\Delta U = q + w$

SECOND LAW - THE TOTAL ENTROPY OF A SYSTEM AND ITS SURROUNDINGS INCREASES FOR A SPONTANEOUS PROCESS.

THIRD LAW - PERFECTLY CRYSTALLINE SUBSTANCES AT 0 K HAVE ZERO ENTROPY.

② a) CO_2 VAPOR AT 0°C. (GASES ARE MORE RANDOM)

b) SUGAR DISSOLVED IN A CUP OF TEA

c) BEAKER CONTAINING A MIXTURE H_2O AND ALCOHOL.

③ a) $2KClO_{4(s)} \longrightarrow 2KClO_{3(s)} + 3O_{2(g)} \quad \Delta S > 0$

MORE GASEOUS PRODUCTS THAN REACTANTS.

b) $N_{2(g)} \longrightarrow 2N_{(g)} \quad \Delta S > 0$

MORE PARTICLES

c) $2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)} \quad \Delta S > 0$

MORE GASEOUS PRODUCTS ... (aq) SOLUTIONS MORE RANDOM.

d) $2LiOH_{(aq)} + CO_{2(g)} \longrightarrow Li_2CO_{3(aq)} + H_2O_{(l)} \quad \Delta S < 0$

LESS GASEOUS PRODUCTS THAN REACTANTS.

④ a)

$$\begin{array}{lccccc} & Ca_{(s)} + & 2H_2O_{(l)} & \longrightarrow & Ca(OH)_2 & + \quad 2H_{2(g)} \\ & & & & \swarrow \quad \searrow & \\ \Delta S^\circ \frac{J}{mol K} & 41.6 & 2(69.940) & & -55.2 \quad 2(-10.54) & 2(130.6) \end{array}$$

$$\Delta S^\circ = [2(130.6) + (-55.2) + 2(-10.54)]\ J/K - [41.6 + 2(69.940)]\ J/K$$

$$\Delta S^\circ = 3.44\ J/K$$

(4b) $Na_2CO_{3(aq)} + 2\,HCl_{(aq)} \longrightarrow 2\,NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

$\Delta S \frac{J}{mol\,K}$ $\quad -53.1 \quad 2(0) \quad 2(55.10) \quad 2(60.2) \quad 2(55.10) \quad 69.940 \quad 213.7$

$$\Delta S^\circ = \left[2(60.2) + 2(55.10) + (69.940) + (213.7)\right] - \left[(53.1) + 2(0) + 2(55.10)\right]$$

$$\Delta S^\circ = 336.7\ J/K$$

(5.) $BaCO_{3\,(s)} \longrightarrow BaO_{(s)} + CO_{2(g)}$

$\Delta G^\circ_f = \quad (?) \qquad -520.4\ kJ/mol \quad -394.4\ kJ/mol$

$$\Delta G^\circ_{RXN} = \Delta G^\circ_f(BaO) + \Delta G^\circ_f(CO_2) - \Delta G^\circ_f(BaCO_3)$$

$$(218.1\ kJ) = (-520.4\ kJ) + (-394.4\ kJ) - \Delta G^\circ_f(BaCO_3)$$

$$\Delta G^\circ_f(BaCO_3) = -1132.9\ kJ$$

(6.) METHOD I : use ΔG°_f's.

$$\Delta G^\circ_{RXN} = 4\,\Delta G^\circ_f(CO_2) + 5\,\Delta G^\circ_f(H_2O) - \Delta G^\circ_f(C_4H_{10}) - {}^{13}/_2\,\Delta G^\circ_f(O_2)$$

$$\Delta G^\circ = 4(-394.4\ kJ) + 5(-228.6\ kJ) - (-10.8\ kJ) - {}^{13}/_2(0)$$

$$\Delta G^\circ = -2703\ kJ$$

METHOD II : use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta H^\circ = 4(-393.5\ kJ) + 5(-241.8\ kJ) - (-120\ kJ) - {}^{13}/_2(0) = -2657\ kJ$$

$$\Delta S^\circ = 4(213.7\ kJ) + 5(188.72\ kJ) - (310\ kJ) - {}^{13}/_2(205\ kJ) = 155.9\ J/K$$

$$\Delta G^\circ = (-2657\ kJ) - (298\ K)\left(.1559\ \frac{kJ}{K}\right)$$

$$= -2703\ kJ$$

⑦ $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(s)}$ $\boxed{K = P_{CO_2}}$

$\boxed{\text{AT } 25^\circ\text{C.}}$

$$\Delta G^\circ = \Delta G_f^\circ(CaO) + \Delta G_f^\circ(CO_2) - \Delta G_f^\circ(CaCO_3)$$
$$= (-603.5\ kJ) + (-394.4\ kJ) - (-1128.8\ kJ)$$
$$= +130.9\ kJ$$

so,

$$\Delta G^\circ = -RT\ 2.303 \log K = -RT(2.303)\log P_{CO_2}$$

so $$\log P_{CO_2} = \frac{-\Delta G^\circ}{2.303RT} = \frac{-130.9\ kJ}{(2.303)(0.00831)(298)} = -22.9524$$

$$\underline{P_{CO_2} = 10^{-22.9524} = 1.1 \times 10^{-23}\ ATM}$$

$\boxed{\text{AT } 800^\circ\text{C}}$ $$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8\ kJ) - (1073\ K)(0.1605\ kJ/K)$$
$$= 5.58\ kJ$$

AGAIN
$$\log P_{CO_2} = \frac{-\Delta G^\circ}{2.303\ RT} = \frac{-5.58\ kJ}{(2.303)(.00831)(1073)} = -0.27173$$

$$\underline{P_{CO_2} = 10^{-0.27173} = 0.53\ ATM}$$

⑧ a) $\Delta H = \Delta G + T\Delta S$

ΔG = useful ENERGY FOR WORK

$T\Delta S$ = UNUSEABLE ENERGY FOR WORK
(GIVEN OFF AS HEAT)

b) SOME OF THE ENERGY USEFUL TO ~~DO~~ WORK DISSAPATES AS HEAT.

⑨ a) $\Delta G^\circ = -2.303\ RT \log K$

$= -2.303(.00831)(298K) \log(9.1\times10^{-6})$

$= +28.7\ kJ$

b) $\Delta G = \Delta G^\circ + 2.303\ RT \log Q$

$$Q = \frac{[Fe^{+2}]^2[Hg^{+2}]^2}{[Fe^{+3}]^2[Hg_2^{+2}]} = \frac{(0.01)^2(0.025)^2}{(0.20)^2(0.01)} = 1.6\times10^{-4}$$

so $\Delta G = (-28.7\ kJ) + (2.303)(.00831)(298)\log(1.6\times10^{-4})$

$\boxed{\Delta G = 7.0\ kJ}$

⑩ $\Delta H^\circ = (-238.6) - (-110.5) - 2(0) = -128.1\ kJ$

$\Delta S^\circ = (127) - (197.5) - 2(130.6) = -332\ J/K$

so $T\Delta S = (298)(0.332\ kJ/K) = -98.8\ kJ$

a) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-128.1kJ) - (298)(-0.332)$

$\Delta G^\circ = -29.3\ kJ$ SO IT IS SPONTANEOUS

b) SINCE ΔH IS $(-)$ AND $T\Delta S$ IS $(-)$

THE RXN IS SPONTANEOUS AT LOW TEMPS.

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

$= (-128.1\ kJ) - (373K)(-0.332\ kJ/K)$

$= -4.3\ kJ$