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) → 2 KClO\(_3\) (s) + O\(_2\) (g)
   b) N\(_2\) (g) → 2 N (g)
   c) 2 Na (s) + 2 H\(_2\)O (l) → 2 NaOH (aq) + H\(_2\) (g)
   d) 2 LiOH (aq) + CO\(_2\) (g) → Li\(_2\)CO\(_3\) (aq) + H\(_2\)O (l)

4. Calculate the standard molar entropy change for each of the following reactions at 25 °C.
   a) Ca (s) + 2 H\(_2\)O (l) → Ca(OH)\(_2\) (aq) + 2 H\(_2\) (g)
   b) Na\(_2\)CO\(_3\) (aq) + 2 HCl (aq) → 2 NaCl (aq) + H\(_2\)O (l) + CO\(_2\) (g)

5. What is the value of \(\Delta G_f^\circ\) for BaCO\(_3\) (s), if \(\Delta G_{rxn}^\circ = +218.1\) kJ for the reaction
   \[\text{BaCO}_3\ (s) \rightarrow \text{BaO}\ (s) + \text{CO}_2\ (g)\]
6. For the combustion of butane gas, \( C_4H_{10} (g) + \frac{13}{2} O_2 (g) \rightarrow 4 CO_2 (g) + 5 H_2O (g) \)
   Calculate \( \Delta G^\circ \) by two different methods.

7. Consider the decomposition of calcium carbonate: \( CaCO_3 (s) \rightarrow CaO (s) + CO_2 (g) \)
   Calculate the pressure in atm of \( CO_2 \) in an equilibrium process
   (a) at 25 °C
   b) at 800 °C. Assume that \( \Delta H^\circ = 177.8 \text{ k} \) and \( \Delta S^\circ = 160.5 \text{ J/K} \)

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 \( 2 Fe^{3+} (aq) + Hg_2^{2+} (aq) \rightarrow 2 Fe^{2+} (aq) + 2 Hg^{2+} (aq) \)
   is \( K_c = 9.1 \times 10^{-6} \) at 298 K.
   a) What is the \( \Delta G^\circ \) at this temperature
   b) Calculate \( \Delta G \) 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 \( CO (g) + 2 H_2 (g) \rightarrow CH_3OH (l) \).
    a) Demonstrate that this reaction is thermodynamically feasible.
    b) Is it favored at low or at high temperature?
    c) Calculate \( \Delta G^\circ \) at 100 °C for this reaction.
1. **First Law** (Law of Conservation of Energy) \[ \Delta U = q + w \]

2. **Second Law** - The total entropy of a system and its surroundings increases for a spontaneous process.

3. **Third Law** - Perfectly crystalline substances at 0 K have zero entropy.

4. a) \( \text{CO}_2 \) vapor at 0°C. (Gases are more random)

b) Sugar dissolved in a cup of tea

c) Beaker containing a mixture H2O and alcohol.

5. a) \( 2 \text{KClO}_4(s) \rightarrow 2 \text{KClO}_3(s) + 3\text{O}_2(g) \) \( \Delta S > 0 \)

   More gaseous products than reactants.

b) \( \text{N}_2(g) \rightarrow 2 \text{N}(g) \) \( \Delta S > 0 \)

   More particles.

c) \( 2 \text{Na}_2\text{O}_3 + 2\text{H}_2\text{O}(s) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g) \) \( \Delta S > 0 \)

   More gaseous products... (aq) solutions more random.

d) \( 2\text{LiOH}(ag) + \text{CO}_2(g) \rightarrow \text{Li}_2\text{CO}_3(ag) + \text{H}_2\text{O}(g) \) \( \Delta S < 0 \)

   Less gaseous products than reactants.

4. a) \( \text{CaO}_3 + 2\text{H}_2\text{O}(g) \rightarrow \text{Ca}(	ext{OH})_2 + 2\text{H}_2\text{O}(g) \)

\[ \Delta S^o_{\text{work}} = 41.6 \text{ J/K} \]

\[ \Delta S^o = \left[ 2(130.6) + (-55.2) + 2(-10.54) \right] \text{ J/K} - \left[ 41.6 + 2(69.94) \right] \text{ J/K} \]

\[ \Delta S^o = 3.44 \text{ J/K} \]
\[ \text{Na}_2 \text{CO}_3 (aq) + 2 \text{HCl (aq)} \rightarrow 2 \text{NaCl (aq)} + \text{H}_2 \text{O (l)} + \text{CO}_2 (g) \]
\[ \Delta S_\text{mol}^{\circ} = -53.1 \quad \frac{J}{mol K} \quad 2(60.2) \quad 2(55.10) \quad 2(60.2) \quad 2(55.10) \quad 69.940 \quad 213.7 \]
\[ \Delta S^{\circ} = \left[ 2(60.2) + 2(55.10) + (69.940) + (213.7) \right] - \left[ (53.1) + 2(60.2) + 2(55.10) \right] \]
\[ \Delta S^{\circ} = 334.7 \quad \frac{J}{K} \]

5. \[ \text{BaCO}_3 (s) \rightarrow \text{BaO(s)} + \text{CO}_2 (g) \]
\[ \Delta G^\circ_f = (?) \quad -520.4 \text{ kJ/mol} \quad -394.4 \text{ kJ/mol} \]

\[ \Delta G^\circ_{\text{Rxn}} = \Delta G^\circ_f (\text{BaO}) + \Delta G^\circ_f (\text{CO}_2) - \Delta G^\circ_f (\text{BaCO}_3) \]
\[ (218.1 \text{ kJ}) = (-520.4 \text{ kJ}) + (-394.4 \text{ kJ}) - \Delta G^\circ_f (\text{BaCO}_3) \]

\[ \Delta G^\circ_f (\text{BaCO}_3) = -1132.9 \text{ kJ} \]

6. Method I: use \[ \Delta G^\circ_f \]'s.
\[ \Delta G^\circ = 4 \Delta G^\circ_f (\text{CO}_2) + 5 \Delta G^\circ_f (\text{H}_2\text{O}) - \Delta G^\circ_f (\text{CH}_4\text{O}) - \frac{13}{2} \Delta G^\circ_f (\text{O}_2) \]
\[ \Delta G^\circ = 4(-394.4 \text{ kJ}) + 5(-228.6 \text{ kJ}) - (-10.8 \text{ kJ}) - \frac{13}{2}(0) \]
\[ \Delta G^\circ = -2703 \text{ kJ} \]

Method II: use \[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]
\[ \Delta H^\circ = 4(-393.5 \text{ kJ}) + 5(-241.8 \text{ kJ}) + (-120 \text{ kJ}) - \frac{13}{2}(0) = -2657 \text{ kJ} \]
\[ \Delta S^\circ = 4(213.7 \text{ kJ}) + 5(188.7 \text{ kJ}) - (310 \text{ kJ}) - \frac{13}{2}(205 \text{ kJ}) = 155.9 \text{ J/K} \]
\[ \Delta G^\circ = (-2657 \text{ kJ}) - (298 \text{ K})(155.9 \text{ kJ/K}) \]
\[ \Delta G^\circ = -2703 \text{ kJ} \]
7. \[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \quad K = P_{CO_2} \]

\[ \text{AT 25°C} \quad \Delta G^0 = \Delta G^0(CaO) + \Delta G^0(CO_2) - \Delta G^0(CaCO_3) \]
\[ = (-403.5 \text{ kJ}) + (-399.4 \text{ kJ}) - (-1128.8 \text{ kJ}) \]
\[ = +130.9 \text{ kJ} \]

so,
\[ \Delta G^0 = -RT \log K = -RT \log P_{CO_2} \]
\[ \log P_{CO_2} = \frac{-\Delta G^0}{-RT} = \frac{-130.9 \text{ kJ}}{(2.303)(0.00831)(298)} = -22.9524 \]
\[ P_{CO_2} = 10^{-22.9524} = 1.1 \times 10^{-25} \text{ atm} \]

\[ \text{AT 800°C} \quad \Delta G^0 = \Delta H^0 - T\Delta S^0 = (177.8 \text{ kJ}) - (1073 \text{ K})(0.1605 \text{ kJ/K}) \]
\[ = 5.58 \text{ kJ} \]

AGAIN
\[ \log P_{CO_2} = \frac{-\Delta G^0}{2.303 \text{ RT}} = \frac{-5.58 \text{ kJ}}{(2.303)(0.00831)(1073)} = -0.27173 \]
\[ P_{CO_2} = 10^{-0.27173} = 0.53 \text{ atm} \]

8. a) \( \Delta H = \Delta G + T\Delta S \)
\( \Delta G = \text{useful energy for work} \)
\( T\Delta S = \text{unuseable energy for work} \)
\( \text{(given off as heat)} \)

b) \( \text{Some of the energy useful to do work dissapates as heat.} \)
9. \( a) \Delta G^0 = -2.303 \, RT \, \log K \)
   \[ = -2.303 \left( 0.00831 \right) \left( 298 \, K \right) \log \left( 9.1 \times 10^{-6} \right) \]
   \[ = +28.7 \, kJ \]

\( b) \Delta G = \Delta G^0 + 2.303 \, RT \, \log Q \)
   \[ Q = \frac{[Fe^{3+}]^2 [Hg^{2+}]^2}{[Fe^{2+}]^2 [Hg_2^{2+}]} = \frac{(0.01)^2 (0.025)^2}{(0.20)^2 (0.01)} = 1.6 \times 10^{-4} \]
   \[ \Delta G = (-28.7 \, kJ) + (2.303) \left( 0.00831 \right) \left( 298 \right) \log \left( 1.6 \times 10^{-4} \right) \]
   \[ \boxed{\Delta G = 7.0 \, kJ} \]

10. \( \Delta H^0 = (-238.6) - (-110.5) - 2(0) = -128.1 \, kJ \)
    \( \Delta S^0 = (127) - (197.5) - 2(130.6) = -332 \, J/K \)
    \[ \text{so} \quad T \Delta S = (298)(0.332 \, kJ/K) = -98.8 \, kJ \]

\( a) \Delta G^0 = \Delta H^0 - T \Delta S^0 = (-128.1 \, kJ) - (298) \times (-0.332) \)
   \[ \Delta G^0 = -29.3 \, kJ \quad \text{so it is spontaneous} \]

\( b) \text{Since} \Delta H \text{ is} (-) \text{ and } T \Delta S \text{ is} (-) \)
   \[ \text{the rxn is spontaneous at low temps.} \]

\( c) \Delta G^0 = \Delta H^0 - T \Delta S^0 \)
   \[ = (-128.1 \, kJ) - (373 \, K) \times (-0.332 \, kJ/K) \]
   \[ = -4.3 \, kJ \]