First Page: Useful information and equations:

**Law I** \( \Delta U = q + w \)

\[ U = U(T, V) \]

\[
dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV
\]

**Law II** \( S = S(T, V) \)

\[
ds = \frac{q_{rev}}{T} dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV
\]

Comb I, II: \( dU = T dS - P dV \)

\[ H = U + PV; \quad A = U - TS \]

\[ G = H - TS; \quad dG = -SDT + VdP \]

Thermodynamic Equation of State

\[
\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P
\]

\[
\left( \frac{\partial S}{\partial T} \right)_P = C_p / T; \quad \left( \frac{\partial S}{\partial V} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P
\]

\[ \mu_A = \mu_A^0 + RT \ln \frac{P_A}{P_o} \]

Dalton's Law

\[ P_A = x_A P; \quad P = \sum A P_A; \quad G = \sum n_i \mu_i \]

\[ \Delta G_{mix} = RT \sum n_i \ln \left( \frac{P_i}{P_o} \right) \]

**Calculus Identities:**

\[ \Delta Z = \int \left( \frac{\partial Z}{\partial x} \right)_y dx \]

\[
\left( \frac{dx}{dy} \right)_z \left( \frac{dx}{dz} \right)_y = -1
\]

\[ d(yz) = z \frac{d(y)}{dx} + y \frac{d(z)}{dx} \]

\[
\frac{dx}{dz} = \frac{dy}{dz} \frac{dx}{dy}; \quad \left( \frac{\partial x}{\partial z} \right)_a = \left( \frac{\partial y}{\partial z} \right)_a \left( \frac{\partial x}{\partial y} \right)_a
\]

Thermal expansion and compression coefficient

\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \]

vdW Gas EoS: \( P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \)

**Reaction Info**

\[ \Delta H_{rxn}^o = \sum_i v_i \Delta H_f^o (i) \]

\[ \Delta S_{rxn}^o = \sum_i v_i \Delta S_f^o (i) \]

\[ dn_i = n_i - n_i^{init} = v_i dX \]

\[ \Delta C_{P,rxn} = \sum_i v_i C_{P,m} (i) \]

\[ \Delta H_{rxn}^o = \Delta H_{rxn}^o dX \]

\[ \Delta G_{rxn} = \Delta G_{rxn}^o + RT \ln Q_p = RT \ln \frac{Q_p}{K_p} \]

\[ Q_p = \prod_{i=1}^N \left( \frac{P_i}{P_o} \right)^{v_i} \]

\[ K_p = \left( \frac{P}{P_o} \right)^{\Delta v} = \left( \frac{c_a RT}{P_o} \right)^{\Delta v} \]

Van’t Hoff Eqn:

\[ \ln \left( \frac{K_p (T_2)}{K_p (T_1)} \right) = - \frac{\Delta H_{rxn}^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

Gas Constant:

\[ R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \]

\[ R = 0.082 \text{ atm L}^{-1} \text{ mol}^{-1} \text{ K}^{-1} \]

\[ R \cdot 300K = 2.5kJ \text{ mol}^{-1} \]

\[ 1 \text{ atm} \approx 1 \text{ bar} = 10^5 \text{ Pa} \]

\[ T(K) = T(C) + 273 \]

Show your work throughout; clearly show what equations you are using, and always show units for computed quantities.
Use this page for additional space if you need it. Be sure to write out clearly the equation you are using, in a compact form if possible, before substituting in numbers to obtain a numerical result. You will not need a calculator for this exam.
Name ______________________________

ID____________

Q1) A high diver of mass m dives from a platform $h$ meters high into a pool of water.

a) What is the energy change of the diver? (3pts)
\[ \Delta E = -mgh \], he loses the potential energy by diving

b) What is the entropy change of the pool after the splashing stops, but before the heat can leave the pool. [Leave this as an algebraic expression] (5pts)

\[ \Delta S = \frac{q_{\text{rev}}}{T} \] We must assume that the energy of the diver becomes heat for the pool.

\[ q_{\text{rev}} = mgh \]

c) What assumptions do you need to make to estimate the entropy change of the water? (6pts)

We must assume that all of the diver’s kinetic energy is converted into heat in the pool, that the process can be approximated as a reversible transfer of heat, and that the temperature of the water does not change significantly. There are several other good assumptions that can be

d) Assuming reasonable values for the temperature of the water, the height of the diving board, and the mass of the diver, estimate the entropy change of the pool in J/K. Given that an Olympic-size swimming pool contains 2.5E6 L of water, do you think the change in entropy per mole of water would be significant? (6pts)

Very small change, not significant.

\[ \Delta S = \frac{q_{\text{rev}}}{T} = \frac{10,000}{300} = 30 \text{ J/K} \approx 2.16 \times 10^{-7} \text{ J/mol K} \]

\[ q_{\text{rev}} = mgh = 50 \times 10 \times 20 = 10,000 \text{ J} \]

\[ C_v = 2.5 \cdot 10^5 \cdot 10^3 \cdot 4 = \frac{q}{\Delta T} \]

\[ \Delta T = 10^{-6} \text{ K} \]

Students do not need to estimate the temperature change or calculate the entropy change per mole.
Q2) The combustion of glucose (HCOH) \textsubscript{sugar} is exothermic and has a free energy change for the reaction: \[ \frac{1}{6} \text{(HCOH)} \textsubscript{6} + O_2 \rightleftharpoons CO_2 + H_2O \text{ of } \Delta G_{\text{rxn}}^0 = -500 \text{kJ} / \text{mol} \]

a) Is the reaction spontaneous as written? (Explain) (4pts)

Yes, The free energy change as $\Delta G_{\text{rxn}}^0$ is negative so the reaction will proceed in the direction as written, which is toward products.

b) Photosynthesis is the process of part a) in the reverse direction. Is photosynthesis spontaneous? If not, what allows photosynthesis to occur? Does this make sense in terms of the Second Law of Thermodynamics. (8pts)

No, of itself the chemical reaction to make sugar is not spontaneous. Photosynthesis occurs because the energy of light is acting like a reactant or an additional term to the free energy. Assuming the light can be coupled to this reaction then the light can make the system run in the other direction. The tree is not an isolated system. The tree plus the sun is the relevant thermodynamic system.

c) Since plants are green, we can infer that red and blue light are used to make sugar. The energy of one mole of blue plus one mole of red light (as photons) is $E = N_A \ h (\nu_{\text{red}} + \nu_{\text{blue}}) = 400 \text{kJ} / \text{mole}$. How many pairs of photons (at minimum) are needed to make a single glucose molecule? (4pts)

Need about $6 \cdot \frac{500}{400} = 8$ photons to make a single glucose molecule or 8 moles of photons to make one mole of glucose.

d) Does the energy inequality $\Delta G \leq w_{\text{extra}}$ apply to the process of photosynthesis or does this process violate this criterion of spontaneity of thermodynamics? Explain. (4pts)

As stated above, when the system includes the light, the energy is added to the free energy (as a large negative number) and makes the $\Delta G_{\text{rxn}}$ negative again so that it could do productive work.
Q3) The final oxidation of CO to CO₂ must be completed in a furnace running at \(T = 600K\). The reaction energy is known at \(T = 300K\). For the reaction:

\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO}_2, \quad \Delta G^0_{\text{rxn}} = -250 \quad \text{and} \quad \Delta H^0_{\text{rxn}} = -300 \text{ kJ/mole}.
\]

(approximately)

a) Assuming that the enthalpy does not change between these two temperatures, what is \(\Delta G^0_{\text{rxn}}\) @ 600K? (5pts)

This is just a reminder of the derivation

\[
\frac{\Delta G^0_{\text{rxn}}}{T} = \frac{1}{T} \Delta H^0_{\text{rxn}} - \Delta S^0_{\text{rxn}}
\]

\[
\Delta \left( \frac{\Delta G^0_{\text{rxn}}}{T} \right) = \int \frac{\partial \left( \frac{\Delta G^0_{\text{rxn}}}{T} \right)}{\partial \frac{1}{T}} \frac{d}{d\frac{1}{T}} = \int \frac{\Delta H^0_{\text{rxn}}}{T^2} = \Delta H^0_{\text{rxn}} \left( \frac{1}{T} - \frac{1}{T_o} \right)
\]

\[
\frac{\Delta G^0_{\text{rxn}}(T)}{T} - \frac{\Delta G^0_{\text{rxn}}(T_o)}{T_o} = \Delta H^0_{\text{rxn}} \left( \frac{1}{T} - \frac{1}{T_o} \right)
\]

\[
\Delta G^0_{\text{rxn}}(T) = T \frac{\Delta G^0_{\text{rxn}}(T_o)}{T_o} + \Delta H^0_{\text{rxn}} \left( 1 - \frac{T}{T_o} \right)
\]

This is the same as the van’t Hoff equation on the front page

\[
\Delta G^0_{\text{rxn}}(T) = 2(-250) + (-300)(1 - 2) = -200\text{kJ/mole}
\]

b) We need to know at what temperature this reaction will no longer be spontaneous. Is the reaction spontaneous at these two temperatures? (5pts)

Yes, \(\Delta G^0_{\text{rxn}}(T) < 0\) at these two temperatures, so still spontaneous.

c) By what criterion would you determine that the reaction is no longer spontaneous? \(\Delta G^0_{\text{rxn}}(T) = 0\) is the point where the reaction changes from possible to not possible. (5pts)

d) Using the criterion of part c), determine at what temperature the reaction will no longer be spontaneous. (5pts)

\[
0 = \Delta G^0_{\text{rxn}}(T) = \frac{T}{T_o} \Delta G^0_{\text{rxn}}(T_o) + \Delta H^0_{\text{rxn}} \left( 1 - \frac{T}{T_o} \right)
\]

\[
\frac{T}{T_o} \Delta G^0_{\text{rxn}}(T_o) = \Delta H^0_{\text{rxn}} \left( \frac{T}{T_o} - 1 \right)
\]

\[
\frac{T}{T_o} \left( \Delta G^0_{\text{rxn}}(T_o) - \Delta H^0_{\text{rxn}} \right) = -\Delta H^0_{\text{rxn}}
\]

\[
\frac{T}{T_o} \left( \Delta H^0_{\text{rxn}} - \Delta G^0_{\text{rxn}}(T_o) \right) = \frac{-300}{-50} = 6
\]

\[
T = 1800K
\]
Q4) Consider an equilibrium system of ammonia, nitrogen, and hydrogen, written two different ways:

\[ A: \ \frac{3}{2} H_2 + \frac{1}{2} N_2 \rightleftharpoons NH_3 \quad B: \ 2NH_3 \rightleftharpoons 3H_2 + N_2 \]

\[
K_p(A) \quad K_p(B) \\
\Delta G_{\text{rxn}}^\circ(A) \quad \Delta G_{\text{rxn}}^\circ(B)
\]

Each reaction has its own equilibrium constant and standard free energy

a) What is the relationship between \( K_p(A) \) and \( K_p(B) \)? \((4 \text{ pts})\)

\[
\rho_i = \frac{P_{eq}(i)}{P_o} \quad K_p(A) = \frac{P_{NH3}^{\frac{3}{2}}}{P_{H2}^{\frac{1}{2}}P_{N2}^{\frac{1}{2}}} \quad \text{and} \quad K_p(B) = \frac{P_{H2}^{\frac{3}{2}}P_{N2}^{\frac{1}{2}}}{P_{NH3}^{3}}
\]

\[
(K_p(A))^2 = \frac{P_{NH3}^{2}}{P_{H2}^{3}P_{N2}^{1}} = (K_p(B))^{-1} \quad K_p(B) = \frac{1}{(K_p(A))^2}
\]

b) What is the relationship between \( \Delta G_{\text{rxn}}^\circ(A) \) and \( \Delta G_{\text{rxn}}^\circ(B) \)? \((4 \text{ pts})\)

\[
\Delta G_{\text{rxn}}^\circ(B) = -2 \cdot \Delta G_{\text{rxn}}^\circ(A)
\]

c) For both A and B above, assume that we start with one mole of each species, and an external pressure such that the partial pressure of each species is 2 Atm., and consume 0.01 moles of hydrogen, at 300 K. Assume that the change is small enough that the partial pressures do not change during the reaction. Compute the two free energy changes: \( \Delta G(A) \) and \( \Delta G(B) \) for this process in terms of \( \Delta G_{\text{rxn}}^\circ(A) \) (and any other known quantities you may need). As part of your answer you should utilize the mass balance expressions. \((8 \text{ pts})\)

\[
\Delta G = \Delta G_{\text{rxn}}dX = \left(\Delta G_{\text{rxn}}^\circ + RT \ln Q_p \right)dX \quad dn_{H2} = 0.01 = \nu_{H2}\cdot dX
\]

\[
Q_p(A) = \frac{1}{2} \quad Q_p(B) = 2^2 \quad \nu_{H2}(A) = -\frac{3}{2} \quad \nu_{H2}(B) = 3
\]

\[
\Delta G(B) = \left(\Delta G_{\text{rxn}}^\circ(B) + RT \ln Q_p \right)dX(B) = \left(\Delta G_{\text{rxn}}^\circ(B) + 2RT\ln 2\right)^0.01^\frac{3}{3}
\]

\[
\Delta G(B) = \left(-2\Delta G_{\text{rxn}}^\circ(A) - 2RT \ln Q_p \right)\frac{dn_{H2}}{-2\nu_{H2}(A)} = \left(\Delta G_{\text{rxn}}^\circ(A) + RT \ln Q_p \right)\frac{dn_{H2}}{\nu_{H2}(A)} = \Delta G(A)
\]

d) Explain why the two free energy changes (in part c) are the same or different. \((4 \text{ pts})\)

The reaction energy is a construct based on how we defined the reaction but the actual free energy for a given reaction cannot depend on how we decided to write the reaction equation. Therefore \( \Delta G(A) \) and \( \Delta G(B) \) but be the same. Notice in the above derivation that the -2 cancels from the numerator and denominator.
Q5) The van’t Hoff relation:
A box is filled with a gas that will dimerize (like NO₂ that can form N₂O₄). The gas is called A and the reaction is 2A ⇌ B, where B is the dimer or A₂ molecule. The system is at equilibrium with an external pressure, \( P \), and temperature, \( T \). Through spectroscopy the mole fraction of each species can be determined at any different temperature and pressure.

a) What is the proper reaction quotient, \( Q_p \), for this reaction, written in terms of the partial pressures of the two species? (2pts)

\[
Q_p = \left( \frac{P_B}{P_a} \right)^2 \left( \frac{P_{A_2}}{P_a} \right)
\]

b) When the system is at equilibrium how can we relate \( Q_p \) and \( K_p \)? (2pts)

\[
Q_p = K_p
\]

c) What is \( \Delta G_{rxn} \) when part b) is true? (2pts)

\( \Delta G_{rxn} = 0 \)

In the following parts (d-i) assume that the reaction enthalpy \( \Delta H_{rxn}^o \) and entropy \( \Delta S_{rxn}^o \) are constant over a range of temperatures.

d) Would a plot of \( \Delta G_{rxn}^o \) as a function of T be a straight line? As part of your answers give a starting/relevant mathematical expression and a graph with axes labeled. (3pts)

\[
\Delta G_{rxn}^o = \Delta H_{rxn}^o - T \Delta S_{rxn}^o
\]

A plot of the left hand side vs T would be a straight line and the slope is \( -\Delta S_{rxn}^o \), and the intercept (at T=0) is \( \Delta H_{rxn}^o \)

e) At temperature T what would the slope of the line of the plot of data in d) be?

\( slope = -\Delta S_{rxn}^o \) (2pts)
f) What function of temperature should the $\ln(K_p)$ be plotted against in order to obtain a straight line? (Provide evidence for your assertion.) (2pts)

$$\frac{\Delta G_{\text{rxn}}^0}{T} = \frac{1}{T} \Delta H_{\text{rxn}}^0 - \Delta S_{\text{rxn}}^0$$

Therefore

$$-R \ln(K_p) = \frac{1}{T} \Delta H_{\text{rxn}}^0 - \Delta S_{\text{rxn}}^0$$

The ln(K) should be plotted as a function of (or against) $1/T$.

g) From part f), what are the slope and intercept of such a straight line? (2pts)

$$\text{Slope} = -\frac{\Delta H_{\text{rxn}}^0}{R} \quad \text{Intercept} = \frac{\Delta S_{\text{rxn}}^0}{R}$$

h) Would a plot of the $\ln(K_p)$ as a function of the temperature $T$ be a straight line? (2pts)

Explain. $\ln(K_p) = -\frac{1}{T} \frac{\Delta H_{\text{rxn}}^0}{R} + \frac{\Delta S_{\text{rxn}}^0}{R}$ so no, one cannot plot ln(Kp) as a function of T and get a straight line.

i) At temperature $T$, what would the slope of the line of part h) be? (3pts)

The slope is found from the derivative:

$$\text{Slope} = \frac{d \ln(K_p)}{dT} = \frac{d}{dT} \left( -\frac{1}{T} \frac{\Delta H_{\text{rxn}}^0}{R} + \frac{\Delta S_{\text{rxn}}^0}{R} \right) = \frac{\Delta H_{\text{rxn}}^0}{RT^2}$$

The slope takes on the sign of the enthalpy and becomes smaller in magnitude as the temperature increases, it is not a constant independent of temperature. Therefore, it cannot be a straight line.
Q6) Entropy derivatives:

a) The partial derivative \( \left( \frac{\partial S}{\partial P} \right)_V \) implies that the entropy (S) is a function of pressure and volume (2pts).

b) From \( \left( \frac{\partial S}{\partial P} \right)_V \) you can calculate the change in the entropy for a process in which the pressure is changing and the volume is held constant. (2pts)

c) From the identity: \( \left( \frac{\partial S}{\partial P} \right)_V = \left( \frac{\partial S}{\partial T} \right)_V \left( \frac{\partial T}{\partial P} \right)_V \), evaluate \( \left( \frac{\partial S}{\partial P} \right)_V \) for the van der Waals gas equation of state, in terms of P, V, T and Heat Capacities. \( C_p \) and/or \( C_v \). (8pts)

\[
\left( \frac{\partial S}{\partial P} \right)_V = \left( \frac{\partial S}{\partial T} \right)_V \left( \frac{\partial T}{\partial P} \right)_V = \frac{C_V}{T} \left( \frac{\partial P}{\partial T} \right)_V = \frac{nR}{V - nb}
\]

\[
\left( \frac{\partial S}{\partial P} \right)_V = \frac{C_v (V - nb)}{nRT}
\]

d) By evaluating the appropriate integral show how you would calculate \( \Delta S \) for the process described in part b) for the van der Waals gas. You may assume that the heat capacities are constants over the integral range. (7pts)

\[
P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \Rightarrow \frac{RT}{V_m - b} = P + \frac{a}{V_m^2}
\]

\[
\Delta S = \int_{P_a}^{p_f} \left( \frac{\partial S}{\partial P} \right)_V dP = \int_{p_a}^{p_f} \frac{C_v}{RT} dP = \frac{p_f}{p_a} \frac{C_v}{P + \frac{a}{V_m^2}} = C_v \ln \left( \frac{P_f + \frac{a}{V_m^2}}{P_a + \frac{a}{V_m^2}} \right)
\]