QUESTION 1 [12 pts]
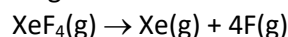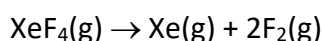
a) [**3**] What is the bond dissociation enthalpy for Xe-F, knowing that the enthalpy of formation of $XeF_4(g)$ is -252.0 kJ mol^{-1} and that the bond dissociation energy of $F_2(g)$ is 158.0 kJ mol^{-1}.

Using $Xe(g) + 2F_2(g) \rightarrow XeF_4(g)$ $\Delta_f H° = $ -252.0 kJ mol^{-1}
$F_2(g) \rightarrow 2F(g)$ BDE = 158.0 kJ mol^{-1}
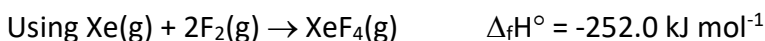
To get the BDE of Xe – F you need:
$XeF_4(g) \rightarrow Xe(g) + 4F(g)$
(note that this is for breaking four Xe-F bonds)
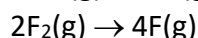
$XeF_4(g) \rightarrow Xe(g) + 2F_2(g)$ $\Delta_f H° = $ 252.0 kJ mol^{-1}
$2F_2(g) \rightarrow 4F(g)$ BDE = 2 x158.0 kJ mol^{-1}
_____
$XeF_4(g) \rightarrow Xe(g) + 4F(g)$ 568.0 kJ mol^{-1}

BDE for Xe-F is 568.0 kJ mol^{-1}/4 = 142.0 kJ mol^{-1}
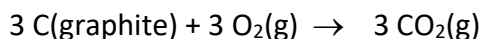
b) [**4**] Using the enthalpy of combustion values provided in Table 1. Calculate the enthalpy of formation of 32 g of $C_3H_8(g)$ (M.W. of C_3H_8 = 44.096 g mol^{-1}). Note that the combustion product for the substances listed in Table 1 are $H_2O(l)$ and $CO_2(g)$ when applicable. HINT: Ensure to balance the reactions before proceeding.
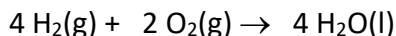
Table 1

Unbalanced Reactions	Enthalpy of combustion
$C_3H_8(g) + $ $O_2(g) \rightarrow$ $CO_2(g) + $ $H_2O(l)$	-2219.9 kJ/mol
$C(graphite) + $ $O_2(g) \rightarrow$ $CO_2(g)$	-393.5 kJ/mol
$H_2(g) + $ $O_2(g) \rightarrow$ $H_2O(l)$	-285.8 kJ/mol

$3\ CO_2(g) + $ $4\ H_2O(l) \rightarrow$ $C_3H_8(g) + $ $5\ O_2(g)$ 2219.9 kJ/mol
   $3\ C(graphite) + 3\ O_2(g) \rightarrow$ $3\ CO_2(g)$ 3 (-393.5 kJ/mol)
      $4\ H_2(g) + $ $2\ O_2(g) \rightarrow$ $4\ H_2O(l)$ 4 (-285.8 kJ/mol)
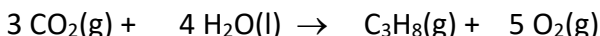
$4\ H_2(g) + $ $3\ C(graphite) \rightarrow C_3H_8(g)$ -103.8 kJ/mol

Number of moles of C_3H_8 = 32 g/44.096 g mol^{-1} = 0.7257 mol
Enthalpy for 32 g: 0.7257 mol x -103.8 kJ/mol = -75.33 kJ

c) [**5**] Magnesium chloride is soluble in water according to the reaction $MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$ and the heat of solution is -160.0 kJ mol^{-1}. Assuming that no heat is transferred to the surroundings, calculate the final temperature when 17.2 g of $MgCl_2$ are dissolved in 300.0 g of water (at 298 K). Molar mass of $MgCl_2$ is 95.21 g mol^{-1}; specific heat capacity of water is 4.184 J $K^{-1} g^{-1}$

The system is isolated:

Heat from the dissolution = Heat absorbed by the water

Number of moles of $MgCl_2$ = 17.2 g / 95.21 g mol^{-1} = 0.1807 mol

Heat from the dissolution = 0.1807 mol x -160.0 kJ mol^{-1} = - 28.905 kJ

Heat absorbed by the water = 28.905 kJ = mass of water x C_{water} ΔT

28905 J = 300.0 g x 4.184 J $K^{-1} g^{-1}$ (T_f -298.0 K) solve for T_f

28905 J = 1255.2 J K^{-1} T_f – 374049.6 J

T_f = 321.0 K

QUESTION 2 [13 pts]

During photosynthesis, glucose is formed from carbon dioxide and water:

$6 CO_2$ (g) + $6 H_2O$ (l) → $C_6H_{12}O_6$ (s) + $6 O_2$ (g)
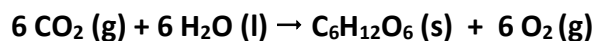
At **298 K**, for one mole of the reaction,

Table 2

Substance	$C_{p,m}$ (J K^{-1}mol^{-1})
CO_2(g)	37.1
H_2O(l)	75.3
$C_6H_{12}O_6$ (s)	219.2
O_2 (g)	29.4

$\Delta_r S° = -262.4\ J\ K^{-1}\ mol^{-1}$ and $\Delta_r H° = 2803\ kJ\ mol^{-1}$

a) **[3]** Calculate the entropy change in the surroundings, $\Delta S°_{surr}$, and the universe, $\Delta S°_{tot}$ at 298 K.

$$\Delta S°_{surr} = \frac{-\Delta_r H°}{T} = \frac{-2803\ kJ\ mol^{-1}}{298\ K} = -9.406 \times 10^3 J K^{-1}\ mol^{-1}$$

$$\Delta S°_{tot} = \Delta_r S° + \Delta S°_{surr} = -262.4\ J\ K^{-1}\ mol^{-1} - 9406 J\ K^{-1}\ mol^{-1} = -9668\ J\ K^{-1}\ mol^{-1}$$

b) **[5]** Calculate $\Delta_r S°$ and $\Delta_r H°$ at 400 K for the reaction shown above. **HINT**: To account for the temperature dependence of entropy and enthalpy, you need to use the values of $C_{p,m}$ provided in the table above (Table 2).

$\Delta C_{p,m}$ = 6 × 29.4 J K^{-1}mol^{-1} + 219.2 J K^{-1}mol^{-1} - 6 × 37.1 J K^{-1}mol^{-1} - 6 × 75.3 J K^{-1}mol^{-1} = **- 278.8 J K^{-1}mol^{-1}**

$$\Delta_r H°(400\ K) = \Delta_r H°(298\ K) + \Delta Cp, m\Delta T = 2803000\ Jmol^{-1} + (-278.8 J\ K^{-1}\ mol^{-1})(400\ K - 298\ K)$$
$$= 2775\ kJ\ mol^{-1}$$

$$\Delta S°(400\ K) = \Delta S°(298\ K) + \int_{298}^{400} \Delta C_P \frac{dT}{T}$$

$$\Delta S°(400\ K) = -262.4\ J\ K^{-1}\ mol^{-1} + (-278.8 J\ K^{-1}\ mol^{-1}) ln\frac{400}{298} = -344.5\ J\ K^{-1}\ mol^{-1}$$

QUESTION 2 [13 pts] cont'd

c) [**2**] Calculate the entropy change in the surroundings, $\Delta S°_{surr}$, and the universe, $\Delta S°_{tot}$ at **400 K** for the reaction shown above.

$$\Delta S°_{surr} = \frac{-\Delta_r H°(400\ K)}{T} = \frac{-\ 2775\ kJ\ mol^{-1}}{400\ K} = -6.94 \times 10^3 JK^{-1}\ mol^{-1}$$

$$\Delta S°_{tot} = \Delta_r S° + \Delta S°_{surr} = -344.5\ J\ K^{-1}\ mol^{-1} - 6940\ JK^{-1}\ mol^{-1} = -7285\ J\ K^{-1}\ mol^{-1}$$

d) [**3**] Based on your results in part a) and part c), comment on the following points and **explain** your reasoning:
   i)   Is the reaction spontaneous at 298 K?
   ii)   Is the reaction spontaneous at 400 K?
   iii) Has the increase in temperature from 298 K to 400 K lead to the reaction being more spontaneous (less non-spontaneous) or less spontaneous (more non-spontaneous) ?

*Since $\underline{\Delta S°_{tot}}$ is negative at both temperatures, the reaction is **not spontaneous at both temperatures**. As the temperature increased, the $\underline{\Delta S°_{tot}}$ become less negative, which implies that it is less non-spontaneous. The reason for that is that the enthalpy of the reaction is positive, so an increase in temperature will drive the reaction more towards products.*

QUESTION 3 [12 pts]

The diagram below illustrates a reversible Carnot cycle (NOTE: it's only a schematic), where the engine operates between 200°C and 700°C. The initial volume at point A, V_A, is 3.0 L, and the volume at point B, V_B, is 10.0 L. The working substance consists of **1.5 moles** of an ideal **diatomic gas**.
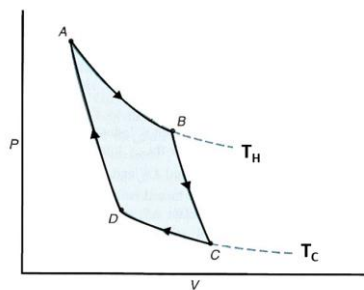
a) **[1 pts]** Calculate the thermodynamic efficiency of the cycle?

$$T_H = 973\ K \quad T_C = 473\ K \quad \varepsilon = \frac{T_H - T_C}{T_H} = \frac{973 - 473}{973} = 0.514 = \mathbf{51.4\%}$$

b) **[2 pts]** Calculate q_{AB}, the heat associated with the process A→B?

$$q_{AB} = -w_{AB} = nRT ln\frac{V_B}{V_A} = (1.5\ mol)\left(8.314\ \frac{J}{Kmol}\right)(973K) ln\frac{10L}{3L} = 14609\ J = 14.6\ kJ$$

c) **[1.5 pts]** What is the total work for the whole cycle?

$$\varepsilon = \frac{|w|}{q_{AB}} \quad |w| = \varepsilon \times q_{AB} = 0.514\ (14.6\ kJ) = 7.50\ kJ \quad \mathbf{w = - 7.50\ kJ}$$

d) **[1.5 pts]** Determine ΔS_{sys}, ΔS_{surr}, $\Delta S_{universe}$ for the process D→A?

$\Delta S_{sys} = 0$
$\Delta S_{surr} = 0$
$\Delta S_{universe} = 0$

e) **[2 pts]** For the process D→A, two factors contribute to the change in entropy – the volume change as well as the temperature change. Explain, <u>on the molecular scale</u>, **the sign** of the entropy change in the process D→A that is <u>only attributed to the volume change</u> (V_D to V_A).

*As the process is <u>a compression</u>, the volume is decreased as the gas is compressed from D to A. On the molecular scale, having a smaller volume and the same number of gas molecules will result in a **decrease in entropy** ($\Delta S_{sys} < 0$) as there are fewer possible arrangements in a smaller space.*

f) **[2 pts]** Determine V_D? Hint: use the adiabatic step to do that.

$$T_D V_D^{(\gamma-1)} = T_A V_A^{(\gamma-1)} \quad \gamma = \frac{7}{5}(diatomic)$$

$$V_D = V_A \left(\frac{T_A}{T_D}\right)^{\frac{1}{\gamma-1}} = (3\ L)\left(\frac{973}{473}\right)^{\frac{1}{\gamma-1}} = (3\ L)\left(\frac{973}{473}\right)^{\frac{1}{1.4-1}} = (3\ L)\left(\frac{973}{473}\right)^{2.5} = 18.2\ L$$

g) **[2 pts]** <u>Calculate</u> the change in entropy, ΔS, in this step (D→A) that is only attributed due to the volume change (V_D to V_A) – is the result in agreement with your explanation in part e)?

$$\Delta S = nRln\frac{V_A}{V_D} = (1.5\ mol)\left(8.314\frac{J}{Kmol}\right)ln\frac{3L}{18.2L} = -22.5\ J/K$$

*Yes, reduction in volume leads to a decrease in entropy.*

QUESTION 4 [13 pts]

(a) [**2 pts**] CO is behaving like an ideal gas. Calculate ΔG for the <u>isothermal compression</u> of 2.0 mol of CO at 300 K as the gas is compressed from an initial pressure of 1.0 bar to a final pressure of 5.0 bar.

<u>Given</u>: $dG = VdP - SdT$

$$\Delta G = G_2 - G_1 = \int_{P_1}^{P_2} \frac{nRT}{P} dP = nRT \ln\frac{P_2}{P_1} = (2.0\ mol)\left(8.314\frac{J}{Kmol}\right)(300K)\ln\frac{5\ bar}{1\ bar} = 8029\ J = \mathbf{8.0\ kJ}$$

(b) [**3 pts**] On a **G vs P graph** below, illustrate how the Gibbs Free energy would change for **CO** during the process described in part a) of the question. Explain your reasoning supporting it with a key **partial derivative expression.**
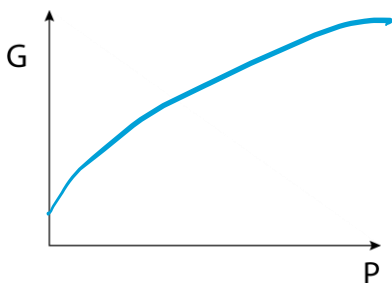
$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

- As P increases, G increases as V is a positive number
- Since V is P dependent, it will get smaller at larger P

(c) [**4 pts**] In an experiment CO reacts with oxygen producing carbon dioxide:

$CO(g) + \frac{1}{2}\ O_2(g) \rightleftharpoons CO_2(g)$. Calculate $\Delta_r G°\ and\ K\ at\ 298\ K\ and\ 1\ bar$. At equilibrium, would the reaction mixture contain mostly reactants, products, or both? Explain.

Substance	$\Delta_f G°$ (kJ / mol)
CO(g)	-137.2
CO₂(g)	-394.4

$$\Delta_R G° = \Delta_f G°\big(CO_2(g)\big) - \Delta_f G°\big(CO(g)\big) - \frac{1}{2}\Delta_f G°\big(O_2(g)\big) = \left(-394.4\frac{kJ}{mol}\right) - \left(-137.2\frac{kJ}{mol}\right) = -257.2\ kJ/mol$$

$K_p = e^{-\Delta G/RT} = e^{-(-257200/[(298\ K)(8.314\ J/Kmol)]} = 1.22\times10^{45}$

The very large value of K suggests that the equilibrium lies very close to the product side.

(d) [**4 pts**] If the $\Delta_r H°$ for the reaction in part (c) is -283 kJ/mol, **calculate $\Delta_r G°$ at 550 K** assuming that $\Delta_r H°$ is constant in the temperature interval of interest. <u>Is your calculated result consistent with prediction using Le Châtelier's principle</u> – would you have expected the equilibrium to shift more towards reactants or products upon the increase of temperature to 550 K compared to 298 K (in part c)? **Explain**.

$$\frac{\Delta_r G°\,(T_2)}{T_2} - \frac{\Delta_r G°\,(T_1)}{T_1} = \Delta H(T_1) \times \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{\Delta G(550)}{550\ K} - \frac{-257200\,\frac{J}{mol}}{298\ K} = \left(-\frac{283000 J}{mol}\right) \times \left(\frac{1}{550K} - \frac{1}{298K}\right)$$

$$\Delta_r G°\,(550) = -235382\,\frac{J}{mol} = -235.4\ kJ/mol$$

The Gibbs free energy is less negative at 550 K than at 298 K. That means that upon the increase in temperature, more reactants would be found at equilibrium than at 298 K. That is in agreement with Le Châtelier's principle as the reaction is exothermic and adding more heat to the reaction will shift the equilibrium toward the left (reactants).