Chem132A: Midterm 1 Solutions

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1 Definitions

Intensive/Extensive

For each of the following indicate if it is an **Intensive** or **Extensive** property.

Volume	Extensive
Mass	Extensive
Entropy	Extensive
Density	Intensive
Internal Energy	Extensive
Pressure	Intensive
Temperature	Intensive
Gibbs Free energy	Extensive
Helmholtz Free Energy	Extensive
C_P	Extensive

State functions

Indicate whether the indicated properties are state functions or not.

Temperature	Yes
Gibbs Free energy	Yes
Work	No
Heat	No
Entropy	Yes

2 Phase Diagram

Consider the phase diagram shown above.

Is the difference in molar volumes $[V_m(\text{liquid}) - V_m(\text{solid})]$ positive or negative? State clearly how you arrive at your answer. A simple 'positive' or 'negative' without any explanation will receive no credit.

We are asked about the molar volume, so it may be useful to recall the definition.

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial \mu}{\partial P}\right)_T = V_m \tag{1}$$

Specifically we are interested in the solid to liquid molar volume transition, so we need to focus on the solid to liquid phase line.

The slope for this transition is positive which suggests the molar volume difference between the liquid and solid state $(V_m(\text{liquid}) - V_m(\text{solid}))$ must be positive.

3   Free Energy Calculations

Reversible Work

Consider a reversible, constant temperature process. Starting from the definition of the Helmholtz Free Energy, show that the Helmholtz Free Energy is equal to the reversible work for the process.

$$
\begin{aligned}
A &= U - TS \\
dA &= dU - d(TS) \\
dA_r &= dU_r - TdS_r \\
dA_r &= dU_r - T\frac{\delta q_r}{T} \\
dA_r &= dU_r - \delta q_r \\
dA_r &= \delta q_r + \delta w_r - \delta q_r \\
dA_r &= \delta w_r
\end{aligned} \tag{2}
$$

Maximum Work for Propane Combustion

Consider the reaction associated with the combustion of propane:

$$
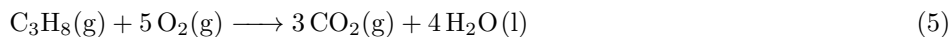\mathrm{C_3H_8(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)} \tag{3}
$$
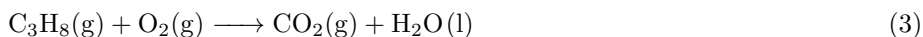
Assuming propane is an ideal gas and a constant temperature of 298K, compute the maximum work that can be obtained from the combustion of propane:

Given at 298K:

$$
\Delta G^0_{\mathrm{rxn}} = -2108\,\frac{\mathrm{kJ}}{\mathrm{mol}} \quad R = 8.314\,\frac{\mathrm{J}}{\mathrm{mol\text{-}K}} \tag{4}
$$

Balance the equation!

$$
\mathrm{C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)} \tag{5}
$$

$$
\begin{aligned}
\Delta A^0_{\mathrm{rxn}} &= \Delta U^0_{\mathrm{rxn}} - T\Delta S^0_{\mathrm{rxn}} \\
\Delta A^0_{\mathrm{rxn}} &= \Delta H^0_{\mathrm{rxn}} - \Delta(PV) - T\Delta S^0_{\mathrm{rxn}} \\
\Delta A^0_{\mathrm{rxn}} &= \Delta G^0_{\mathrm{rxn}} - \Delta(PV) \\
\Delta A^0_{\mathrm{rxn}} &= \Delta G^0_{\mathrm{rxn}} - \Delta n_g RT \\
\Delta A^0_{\mathrm{rxn}} &= (-2108) - (-3)(0.008314)(298) = -2101\,\frac{\mathrm{kJ}}{\mathrm{mol}} = w_{\max}
\end{aligned} \tag{6}
$$

4 First and Second Law

4.1 State Functions

Consider the following diagram for one mole of a gas. For this system, all processes are done reversibly and the Internal Energy of the gas is only a function of temperature.

Figure 2: Point 1: (P_1, V_1, T_1), Point 2: (P_2, V_2, T_1), Point 3: (P_1, V_2, T_3).
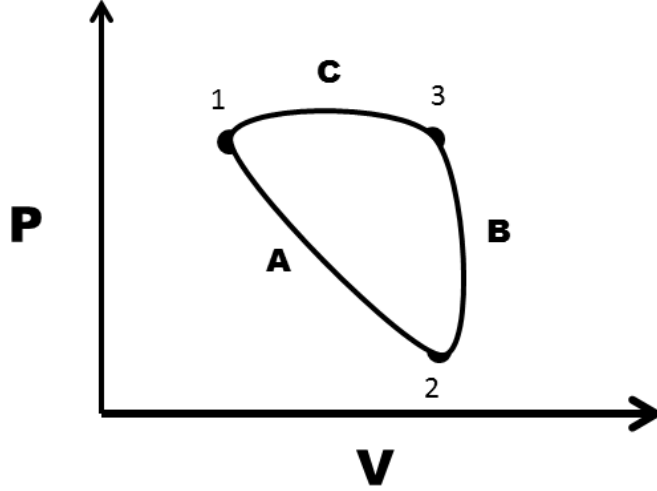
Only consider PV work for this problem. Calculate the change in Internal Energy (ΔU), the change in Entropy (ΔS), the Heat (q), and the work (w) associated with pathways A,B, and C.

Pathway A

Reversible, Isothermal; therefore $\Delta T = 0$:

$$\Delta U = 0 \tag{7}$$

Since U is only a function of temperature. We can then write our first law as :

$$q_A = -w_A = \int_{V_1}^{V_2} P_{gas} dV \tag{8}$$

With this expression we can determine the Entropy of pathway A as :

$$\Delta S_A = \frac{q_{Ar}}{T} = \frac{\int_{V_1}^{V_2} P_{gas} dV}{T} \tag{9}$$

Pathway B

This pathway is Isochoric therefore $\Delta V = 0$ so :

$$w_B = 0 \tag{10}$$

The first law is then :

$$\Delta U_B = q_B = \int_{T_1}^{T_3} Cv(T) dT \tag{11}$$

The Entropy of the system can be expressed as:

$$\Delta S_B = \frac{q_B}{T} = \frac{\int_{T_1}^{T_3} Cv(T) dT}{T} \tag{12}$$

4

Pathway C

Pathway C is an Isobaric process so the First Law does not simplify:

$$\Delta U_C = q_C + w_C \tag{13}$$

The work can be written as :

$$w_C = -\int_{V_1}^{V_2} P_{gas} = -P_1 \Delta V \tag{14}$$

We then use the heat capacity to determine the Internal Energy just as before

$$\Delta U_C = \Delta U_A + \Delta U_B = \int_{T_1}^{T_3} Cv(T)dT \tag{15}$$

Then we rearrange the first law and compute the heat:

$$q_C = \int_{V_1}^{V_2} P_{gas}dV + \int_{T_1}^{T_3} Cv(T)dT \tag{16}$$

Since Entropy is a state function it can be expressed as :

$$\Delta S_C = \Delta S_A + \Delta S_B = \frac{\int_{V_1}^{V_2} P_{gas}dV + \int_{T_1}^{T_3} Cv(T)dT}{T} \tag{17}$$

5   Enthalpy of Combustion

Consider the combustion of ethanol under constant pressure conditions (1atm) and at a temperature of 370K. The balanced reaction for this combustion is shown below. Use the data provided here to calculate the $\Delta\mathrm{H_{rxn}}(370K)$.

$$\mathrm{CH_3CH_2OH\,(g) + 3\,O_2\,(g) \rightleftharpoons 2\,CO_2\,(g) + 3\,H_2O\,(l)} \tag{18}$$
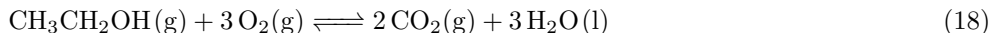
Formation of Ethanol Gas

We are only given information about the liquid state of ethanol, we need the enthalpy associated with Ethanol gas. This is done by taking the formation enthalpy of the liquid, heating the liquid to the normal boiling point, doing the phase transition to a gas, and then heating the gas to the final temperature.

$$\Delta H(\mathrm{etoh}, 370, g) = \Delta H_f(298, l) + \Delta H(l, 298 \Rightarrow 351.45) + \Delta H_{vap}(351.45) + \Delta H(g, 351.45 \Rightarrow 370)$$

$$= -277.69 + \int_{298}^{351.45} C_P(l)dT + 38.6 + \int_{351.45}^{370} C_P(g)dT$$

$$= -277.69 + 0.11146(351.45 - 290) + 38.6 + 0.06544(370 - 351.45) \tag{19}$$

$$\Delta H(\mathrm{etoh}, 370, g) = -231.919 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

Oxygen Gas

$$\Delta H(O_2, g, 370) = \Delta H_f(298, g) + \int_{298}^{370} C_P(g)dT$$

$$= 0 + 0.029355(370 - 298) \tag{20}$$

$$\Delta H(O_2, g, 370) = 2.11356$$

Carbon Dioxide Gas

$$\Delta H(CO_2, g, 370) = \Delta H_f(298, g) + \int_{298}^{370} C_P(g)dT$$

$$= -393.51 + 0.03711(370 - 298) \tag{21}$$

$$\Delta H(CO_2, g, 370) = -390.83808$$

Water Liquid

$$\Delta H(H_2O, l, 370) = \Delta H_f(298, l) + \int_{298}^{370} C_P(l)dT$$

$$= -285.83 + 0.075291(370 - 298) \tag{22}$$

$$\Delta H(H_2O, g, 370) = -280.409$$

Reaction

Now that we have calculated the heat associated with each component at the final temperature, we simple need to subtract values.

$$\Delta H_{\mathrm{rxn}}(370) = \sum_i \nu_i \Delta H_i$$

$$= 2(\Delta H(CO_2, g, 370)) + 3(\Delta H(H_2O, l, 370)) - 3(\Delta H(O_2, g, 370)) - (\Delta H(\mathrm{etoh}, 370, g))$$

$$= 2(-390.83808) + 3(-280.409) - 3(2.11356) - (-231.919) \tag{23}$$

$$\Delta H_{\mathrm{rxn}}(370) = -1397.325 \frac{\mathrm{kJ}}{\mathrm{mol}}$$