

CH 331
Physical Chemistry

Mid-term Examination

Given:

$$g = 9.81 \text{ m/s}^2$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ atm} = 1.0133 \times 10^5 \text{ Nm}^{-2} = 760 \text{ Torr}$$

$$P = P_0 \exp\{-Mgh/RT\}$$

$$P_2 = P_1 + \frac{\Delta_{trs}H_m}{\Delta_{trs}V_m} \ln\left(\frac{T_2}{T_1}\right) \quad , \quad \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{trs}H_m}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_m}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta S = -R \sum_{i=1}^N x_i \ln x_i \text{ where } N \text{ is the number of components}$$

$$\Pi = cRT \quad , \quad \rho = mgh \quad , \quad P = \rho gh \quad , \quad DT_{fus} = K_f m \quad , \quad K_f = \frac{RT_{fus}^2 M}{1000 \Delta H_{fus}}$$

Please answer all questions.

1. A. Assuming that an ideal gas has a density of $4 \times 10^{-2} \text{ g/cm}^3$ at 10 atm and 400 K calculate its molar mass (5 points):

Solution: The density expression $\rho = MP/RT$ rearranges to $M = \rho RT/P$
 $M = (40.0 \text{ kg/m}^3) (8.31 \text{ J/mol-K})(400 \text{ K}) / (10.133 \times 10^5 \text{ Nm}^{-2})$
 $= 0.131 \text{ kg/mol} = 131 \text{ g/mol}$

M (g/mol) = _____

- B. Calculate the root-mean-square velocity of argon gas at 400 K (3 points).

Solution: $\text{sqrt}(\langle v^2 \rangle) = \text{sqrt}(3RT/M) = \text{sqrt}(3(8.31 \text{ J/mol-K})(400 \text{ K}) / 0.0399 \text{ kg/mol})$
 $= 500 \text{ m/s}$

- C. Calculate the molar heat capacity at constant volume of argon gas at 400 K (2 points).

Solution: $C_v = 3/2R = (1.5)(8.31 \text{ J/mol-K})$
 $= 12.465 \text{ J/mol-K}$

2. Calculate the depth at which you would measure a pressure of 1764 bars in the ocean at 10 °C assume that water has a density of $1.0 \times 10^3 \text{ gL}^{-1}$ (5 points).

Solution:

$$P = \rho gh \text{ rearranges to } h = P/\rho g = (1764 \text{ bars})(10^5 \text{ Pa/bar})/(1.0 \times 10^3 \text{ kg/m}^3)(9.8 \text{ m/s}^2) \\ = 18000 \text{ m}$$

$$h(\text{meters}) = \underline{\hspace{2cm}}$$

3. Determine the mole fractions x_1 and x_2 of two gases, which will give the maximum entropy of mixing.
- Write down the formula for the entropy of mixing (5 points)
 - Take the derivative with respect to x_1 (keep in mind that $x_2 = 1 - x_1$) (7 points)
 - Solve for x_1 (3 points)

An alternative method is to plot the function and empirically determine the minimum (5 points).

Solution:

$$\Delta S = -R(x_1 \ln(x_1) + x_2 \ln(x_2))$$

$$= -R(x_1 \ln(x_1) + (1 - x_1) \ln(1 - x_1))$$

$$\frac{\partial \Delta S}{\partial x_1} = -R(1 + \ln(x_1) - 1 - \ln(1 - x_1)) = 0$$

$$\ln\left(\frac{x_1}{1 - x_1}\right) = 0$$

$$\frac{x_1}{1 - x_1} = 1$$

$$x_1 = \frac{1}{2} \text{ and therefore } x_2 = \frac{1}{2}$$

4. An ideal gas is initially at 10.0 atm and 300 K. Its volume is initially 10 L and the gas is compressed to 0.1 L under the following conditions (15 points):

- $P_{\text{external}} = 10,000.0 \text{ atm}$
- $P_{\text{external}} = \text{constant}$ (single-step)
- $P_{\text{external}} = P_{\text{gas}}$ (reversible compression)

For each of the above conditions calculate q , and w , for the gas.

$q(\text{J})$ $w(\text{J})$

(1.) _____ _____

(2.) _____ _____

(3.) _____ _____

Solution: The initial and final temperature is the same for all three expansions. Note that this means that they are also isothermal (if we look at the initial and final states) although only process

3 is at constant temperature throughout the expansion. Since U is a state function $\Delta U = 0$ for all three processes.

Using the first law $\Delta U = q + w \rightarrow q = -w$. Therefore, if we calculate the work we will also be able to find the heat ($q = -w$).

Process 1 is clearly irreversible $w = -P_{\text{external}}\Delta V$ and since $P_{\text{external}} = 10,000.0$ we have $w = -(10,000.0 \text{ atm})(0.1 \text{ L} - 10.0 \text{ L}) = 99,000 \text{ L-atm} = 10^7 \text{ J}$
(Note: the sign is positive since this is a compression)

Process 2 is $w = -P_{\text{external}}\Delta V = -(1000.0 \text{ atm})(0.1 \text{ L} - 10.0 \text{ L}) = 99,000 \text{ L-atm} = 10^6 \text{ J}$.
Therefore, $q = -10^5 \text{ J}$.

We determine the final (external) pressure using $P_2V_2 = P_1V_1$. Here it is 1000.0 atm.

Process 3 is reversible and isothermal so that $w = -nRT \ln(V_2/V_1)$. We need n.
 $n = PV/RT = (10 \text{ atm})(10.0 \text{ L})/(0.08206 \text{ L-atm/mol-K})(300 \text{ K}) = 4.06 \text{ moles}$.
 $w = -nRT \ln(V_2/V_1) = -(4.06 \text{ mol})(8.31 \text{ J/mol-K})(300 \text{ K}) \ln(0.1/10.0) = 46,611 \text{ J}$
Therefore, $q = -46,611 \text{ J}$

	q(J)	w(J)	ΔU (J)
(1.)	___-10 ⁷ ___	___10 ⁷ ___	___0___
(2.)	___-10 ⁶ ___	___10 ⁶ ___	___0___
(3.)	___-46,611___	___46,611___	___0___

5. A. The thermodynamic efficiency of a steam turbine is 0.6 and the operating is at 800 K. Please calculate the exhaust temperature (3 points).

Solution:

$$\eta = (T_{\text{hot}} - T_{\text{cold}})/T_{\text{hot}} = 1 - T_{\text{cold}}/T_{\text{hot}}$$

$$T_{\text{cold}}/T_{\text{hot}} = 1 - \eta$$

$$T_{\text{cold}} = T_{\text{hot}}(1 - \eta) = 800(1 - 0.6) = 320 \text{ K}$$

- B. How much work would be derived for every kJ of heat expelled into the environment by this engine (2 points)?

Solution: $\eta = |w|/q \rightarrow |w| = \eta q = 0.6 \times 1 \text{ kJ} = 0.6 \text{ kJ}$

6. The standard enthalpy of the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$ is -92.2 kJ/mol of ammonia and the third law entropies of H_2 , N_2 , and NH_3 at 298 K are given in the table below. Assuming that the entropy and enthalpy are independent of temperature calculate the Gibbs free energy at 230 K. The enthalpy of vaporization of ammonia is $\Delta_{\text{vap}}H^\circ = 23.3 \text{ kJ/mol}$ and $T_b = 239.7 \text{ K}$. (20 points).

Substance	C_p (J/mol-K)	S° (J/mol-K)
$\text{NH}_3(\text{aq})$	75.3	111.3

NH ₃ (g)	35.4	192.4
H ₂ (g)	27.3	130.6
N ₂ (g)	29.1	191.6

Solution: *** Still nor worked out for 230 K.***

Note that the problem states that ΔH° and ΔS° are independent of temperature. Thus, you need only calculate

$$\Delta S^\circ(298 \text{ K}) = 2S^\circ(\text{NH}_3, \text{g}) - 3S^\circ(\text{H}_2, \text{g}) - S^\circ(\text{N}_2, \text{g}) = 2(192.4) - 3(130.6) - 191.6 = -198.6 \text{ J/mol-K}$$

and then plug this value and $\Delta H^\circ(298 \text{ K})$ into the free energy expression to receive full credit.

$$\Delta G^\circ(240 \text{ K}) = \Delta H^\circ(240 \text{ K}) - T\Delta S^\circ(240 \text{ K}) = -92,200 - 240(-198.6) = -44,536 \text{ J/mol}$$

However, many of you worked out the full temperature dependence. Although this was not necessary you received full credit if this was done correctly.

The temperature dependence of the enthalpy is:

$$\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \Delta C_{p,\text{liq}}(T_2 - T_1)$$

$$\Delta S^\circ(T_2) = \Delta S^\circ(T_1) + \Delta C_{p,\text{liq}} \ln(T_2/T_1)$$

There is no phase change over the specified temperature range so:

$$\Delta C_{p,\text{liq}} = 2 C_p(\text{NH}_3, \text{g}) - 3 C_p(\text{H}_2, \text{g}) - C_p(\text{N}_2, \text{g}) = 2(35.4) - 3(27.3) - 29.1 = -40.2 \text{ J/mol-K}$$

The entropy change is:

$$\Delta S^\circ(298 \text{ K}) = 2S^\circ(\text{NH}_3, \text{g}) - 3S^\circ(\text{H}_2, \text{g}) - S^\circ(\text{N}_2, \text{g}) = 2(192.4) - 3(130.6) - 191.6 = -198.6 \text{ J/mol-K}$$

$$\Delta H^\circ(240 \text{ K}) = -92,200 + (-40.2)(240 - 298) = -89,870 \text{ J/mol-K} = -89.87 \text{ J/mol-K}$$

$$\Delta S^\circ(240 \text{ K}) = -198.6 + (-40.2)\ln(240/298) = -189.9 \text{ J/mol-K}$$

$$\Delta G^\circ(240 \text{ K}) = \Delta H^\circ(240 \text{ K}) - T\Delta S^\circ(240 \text{ K}) = -89,870 - 240(-189.9) = -44,293 \text{ J/mol}$$

7. A. What is the total pressure above a solution of ethanol ($x_{\text{ethanol}} = 0.2$) and methanol as it begins to boil? ($P_{\text{ethanol}}^* = 58 \text{ torr}$ and $P_{\text{methanol}}^* = 159 \text{ torr}$) (5 points)

Solution:

$$P_{\text{total}} = x_{\text{methanol}} P_{\text{methanol}}^* + x_{\text{ethanol}} P_{\text{ethanol}}^* \\ = 0.8(159) + 0.2(58) = 138.8 \text{ torr}$$

$$P_{\text{total}} = \underline{\hspace{10em}}$$

B. Calculate the mole fraction of ethanol in the vapor phase under the conditions above. (5 points)

Solution:

$$y_{\text{ethanol}} = x_{\text{ethanol}} P_{\text{ethanol}}^* / P_{\text{total}} \\ = 0.2(58 \text{ torr}) / 138.8 \text{ torr} = 0.0836$$

$$y_{\text{ethanol}} = \underline{\hspace{10em}}$$

8. Calculate the molar mass of a molecule whose osmotic pressure rise is 0.025 m. Assume that 1 g. of the molecule was dissolved in 1 liter.

Solution:

$$\Pi = cRT$$

$$\Pi = \rho g h$$

$$c = \rho g h / RT = (1000 \text{ kg/m}^3)(9.8 \text{ m/s}^2)(0.25 \text{ m}) / (8.31 \text{ J/mol-K})(298 \text{ K}) = 0.989 \text{ mol/m}^3$$

If 1g. was dissolved in 1 L this corresponds to dissolving 1000 g. in 1 cubic meter.

Therefore, the molar mass is $1000 \text{ g.} / 0.989 \text{ mol} = 1011 \text{ g./mol}$

9. An ice skater is able to skate across the ice because of local ice melting underneath the skates. What is the melting temperature of ice underneath a skater who has a mass of 60 kg assuming that the area of the skates is 0.1 cm^2 (20 points).

$$\begin{aligned} T_{\text{fus}} &= 273.15 \text{ K} & \Delta_{\text{fus}}H &= 6.0 \text{ kJ/mol} \\ T_{\text{vap}} &= 373.15 \text{ K} & \Delta_{\text{vap}}H &= 40.65 \text{ kJ/mol} \\ \rho_{\text{ice}} &= 0.917 \text{ gm/cm}^3 & \rho_{\text{water}} &= 1.000 \text{ gm/cm}^3 \\ \text{Triple point} & T = 273.16 \text{ K} & P &= 0.006 \text{ bar} \\ \text{Critical point} & T_c = 647.3 \text{ K} & P_c &= 218 \text{ bar} \end{aligned}$$

Solution: The data you need are $T_{\text{fus}} = 273.15 \text{ K}$ and $\Delta_{\text{fus}}H = 6.0 \text{ kJ/mol}$ added to the fact that the normal boiling point is at 1 bar of pressure (i.e. $\sim 1 \text{ atm}$). So $P_1 = 1 \text{ atm}$, $T_1 = 273 \text{ K}$ and P_2 is determined by the mass of the skater divided by the area of the skates.

$$P_2 = 60 \text{ kg}/10^{-5} \text{ m}^2 = 6 \times 10^6 \text{ kg/m}^2 = 60 \text{ bars}$$

Since the phase transition is between the liquid and the solid state you also need to calculate the change in the molar volume of the transition. Recall that the molar volume is equal to the molar mass over the molar density (i.e. since $\rho = M/V_m$ we have $V_m = M/\rho$).

$$\begin{aligned} \text{Therefore, } \Delta V_m &= V_{m,\text{liquid}} - V_{m,\text{solid}} = M/\rho_{\text{liquid}} - M/\rho_{\text{solid}} = \\ &= 0.018 \text{ kg/mol} (1/1000 \text{ kg/m}^3 - 1/917 \text{ kg/m}^3) = -1.629 \times 10^{-5} \text{ m}^3/\text{mol} \end{aligned}$$

$$P_2 = P_1 + \frac{\Delta_{\text{trs}}H_m}{\Delta_{\text{trs}}V_m} \ln\left(\frac{T_2}{T_1}\right)$$

You can rearrange the Clapeyron equation

to solve for temperature.

$$\begin{aligned} \Delta P &= \frac{\Delta_{\text{trs}}H_m}{\Delta_{\text{trs}}V_m} \ln\left(\frac{T_2}{T_1}\right) \\ T_2 &= T_1 \exp\left\{\frac{\Delta P \Delta_{\text{trs}}V_m}{\Delta_{\text{trs}}H_m}\right\} \\ &= 273.15 \exp\left\{\frac{\left(5.9 \times 10^6 \text{ kg/m}^2\right)\left(-1.629 \times 10^{-5} \text{ m}^3/\text{mol}\right)}{6000 \text{ J/mol}}\right\} \\ &= 268.8 \text{ K} \end{aligned}$$