

CT101 - Assignment 1 (Answers)

Q1

Ans. (a) $\Delta U = \Delta H = 0$ (ideal gas, isothermal)

$$\begin{aligned} w &= -nRT \ln\left(\frac{V_f}{V_i}\right) \\ &= - (1.00) \text{ mol} \times (8.314) \text{ J K}^{-1} \text{ mol}^{-1} \times 273 \text{ K} \ln\left(\frac{44.8}{22.4}\right) \\ &= -1.57 \text{ kJ} \end{aligned}$$

$$q = \Delta U - w = 0 + 1.57 = +1.57 \text{ kJ}$$

(b) $\Delta U = \Delta H = 0$

$$w = -P_{\text{ext}} \Delta V \quad \Delta V = 22.4 \text{ L}$$

$$\begin{aligned} P_{\text{ext}} = P_f &= \frac{nRT}{V_f} = \frac{1.00 \times 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}{44.8 \text{ L}} \\ &= 0.500 \text{ atm} \end{aligned}$$

$$\begin{aligned} w &= -0.5 \text{ atm} \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}}\right) \times 22.4 \text{ L} \times \left(\frac{1 \text{ m}^3}{10^3 \text{ L}}\right) \\ &= -1.13 \times 10^3 \text{ Pa m}^3 = -1.13 \times 10^3 \text{ J} = -1.13 \text{ kJ} \end{aligned}$$

$$q = \Delta U - w = +1.13 \text{ kJ}$$

(c) $\Delta U = \Delta H = 0$

$$w = 0 \quad [\text{free expansion}]$$

$$q = \Delta U - w = 0$$

02

Ans. (a) $q = 0$ (adiabatic)

$$(b) w = -P_{ext} \Delta V = - (1.01 \times 10^5 \text{ Pa}) \times (20 \times 10 \text{ cm}^3) \times \left(\frac{10^{-6} \text{ m}^3}{\text{cm}^3} \right) \\ = -20 \text{ J}$$

$$(c) \Delta U = q + w = -20 \text{ J}$$

$$(d) \Delta U = n C_{v,m} \Delta T$$

$$\Delta T = \frac{\Delta U}{n C_{v,m}} = \frac{-20 \text{ J}}{(2 \text{ mol}) \times (28.8 \text{ J K}^{-1} \text{ mol}^{-1})} = -0.347 \text{ K}$$

$$(e) dU = T ds - P dv \Rightarrow ds = \frac{dU}{T} + \frac{P}{T} dv$$

$$\Rightarrow ds = \frac{n C_{v,m} dT}{T} + \frac{nR}{v} dv \quad (\text{perfect gas})$$

$$\Rightarrow \Delta S = n C_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta T = -0.347 \Rightarrow T_f = T_i - 0.347 = (298.15 \text{ K}) - (0.347 \text{ K}) \\ = 297.8 \text{ K}$$

$$V_i = \frac{nRT}{P_i} = \frac{(2.0 \text{ mol}) (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{10 \text{ atm}} \\ = 4.893 \text{ L}$$

$$V_f = V_i + \Delta V = 5.09 \text{ L}$$

$$\Rightarrow \Delta S = (2.0 \text{ mol}) \times (28.8 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{297.8}{298.15} \right) \\ + 2.0 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \ln \left(\frac{5.09}{4.893} \right)$$

$$\boxed{\Delta S = 0.6 \text{ J K}^{-1}}$$

Q3

Ans. (a) $\Delta S_{\text{gas}} = nR \ln \frac{V_f}{V_i} = \left(\frac{14 \text{ gm}}{28.02 \text{ gm mol}^{-1}} \right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln 2$
 $= 2.9 \text{ J K}^{-1}$

$\Delta S_{\text{sur}} = -2.9 \text{ J K}^{-1}$ [reversible process]

$\Delta S_{\text{total}} = 0$

(b) $\Delta S_{\text{gas}} = 2.9 \text{ J K}^{-1}$ [S is a state function]

$\Delta S_{\text{sur}} = 0$ [No change in the surroundings]

$\Delta S_{\text{total}} = 2.9 \text{ J K}^{-1}$ [Irreversible process]

(c) $\Delta S_{\text{gas}} = 0$ [q_{rev} = 0]

$\Delta S_{\text{sur}} = 0$ [no heat transferred]

$\Delta S_{\text{total}} = 0$

Q4

Ans. (a) $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b} = \frac{29.4 \times 10^3 \text{ J mol}^{-1}}{334.8 \text{ K}} = 87.8 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta S_{\text{sur}} = -87.8 \text{ J K}^{-1} \text{ mol}^{-1}$ [reversible]

Q5

$$S(p, T) \Rightarrow ds = \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT$$

$$\textcircled{1} \left(\frac{\partial S}{\partial T}\right)_p : ds = \frac{dq_p}{T} = \frac{C_p dT}{T} \quad (\text{const pressure})$$

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

$$\textcircled{2} \left(\frac{\partial S}{\partial p}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_p \quad (\text{Maxwell relation})$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \alpha V$$

$$\Rightarrow ds = \frac{C_p}{T} dT - \alpha V dp$$

$$\boxed{T ds = C_p dT - \alpha TV dp}$$

Q6

$$dG = -SdT + Vdp \quad (\text{Fundamental Eq.})$$

$$dG = Vdp \quad (\text{const temperature})$$

$$\Rightarrow \Delta G = nRT \ln\left(\frac{P_f}{P_i}\right)$$

$$\Rightarrow \Delta G = nRT \ln\left(\frac{V_i}{V_f}\right)$$

$$= (3.0 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \ln\left(\frac{36}{60}\right)$$

$$= -3.8 \text{ J}$$

Q7

Ans. Clausius - Clapeyron Eqⁿ:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$(a) \quad \ln\left(\frac{40}{10}\right) = \frac{\Delta H_{\text{vap}}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{359 \text{ K}} - \frac{1}{392.5 \text{ K}} \right)$$

$$1.386 = \Delta H_{\text{vap}} \times (2.86 \times 10^{-5} \text{ J}^{-1} \text{ mol})$$

$$\Delta H_{\text{vap}} = 48.5 \text{ kJ mol}^{-1}$$

(b) The normal boiling point corresponds to a vapour pressure of 760 Torr.

$$\ln\left(\frac{760}{40}\right) = \frac{48.5 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{392.5 \text{ K}} - \frac{1}{T_b} \right)$$

$$2.944 = 14.86 - \frac{5831 \text{ K}}{T_b} \Rightarrow T_b = 489 \text{ K}$$

$$(c) \quad \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b} = 99 \text{ J K}^{-1} \text{ mol}^{-1}$$

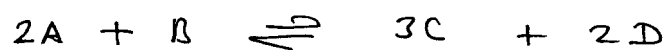
Q8 At the triple point, the v.p of liquid & solid are equal

$$\Rightarrow 10.5916 - \frac{1871.2 \text{ K}}{T_3} = 8.3186 - \frac{1425.7 \text{ K}}{T_3}$$

$$\boxed{T_3 = 196.0 \text{ K}}$$

$$\log(P_3/\text{Torr}) = \frac{-1871.2 \text{ K}}{196.0 \text{ K}} + 10.5916 \Rightarrow \boxed{P_3 = 11.1 \text{ Torr}}$$

Q9



	A	B	C	D	total
Initial no. of moles	1.00	2.00	0	1.00	4.0
Change in the no. of moles	-0.60	-0.30	0.90	0.60	
Eq ^m amounts	0.40	1.70	0.90	1.60	4.60
mole fractions	0.087	0.370	0.196	0.348	1.00

$$K_x = \frac{(0.196)^3 \times (0.348)^2}{(0.087)^2 \times (0.370)} = 0.33$$

(a) $P_j = x_j P$ $P = 1 \text{ bar}$ $P^\circ = 1 \text{ bar}$

$$K_p = \left(\frac{P}{P^\circ}\right)^{-2} K_x = 0.33$$

(b) $\Delta G^\circ = -RT \ln K_p = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (\ln 0.33)$

$$= 2.8 \times 10^3 \text{ J mol}^{-1}$$

Q10

Ans.

$$Z = g_1 + g_2 e^{-E/kT}$$

$$P_1 = \frac{n_1}{N} = \frac{g_1 e^{-0/kT}}{Z} = \frac{g_1}{Z}$$

$$P_2 = \frac{n_2}{N} = \frac{g_2 e^{-E/kT}}{Z}$$

$$\bar{E} = \sum_{i=1}^2 \epsilon_i P_i$$

$$= \frac{\epsilon g_2 e^{-E/kT}}{g_1 + g_2 e^{-E/kT}}$$

$$\bar{E} = N \bar{E} = \frac{N \epsilon g_2 e^{-E/kT}}{g_1 + g_2 e^{-E/kT}}$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{N \epsilon^2 g_1 g_2 e^{E/kT}}{kT^2 (g_1 e^{E/kT} + g_2)^2}$$

Q11

$$\frac{n_2}{N} = \frac{e^{-\epsilon_2/kT}}{Z}$$

$$\frac{n_1}{N} = \frac{e^{-\epsilon_1/kT}}{Z}$$

$$\Rightarrow \frac{n_2}{n_1} = e^{-(\epsilon_2 - \epsilon_1)/kT}$$

$$\ln \frac{n_2}{n_1} = \frac{(\epsilon_1 - \epsilon_2)}{kT} \Rightarrow T = \frac{(\epsilon_1 - \epsilon_2)}{k \ln(n_2/n_1)}$$

$$T = \frac{-8.6 \times 10^{-3} \times 1.602 \times 10^{-19} \text{ J}}{1.38 \times 10^{-23} \text{ J K}^{-1} \ln(1/3)}$$

$$\Rightarrow \boxed{T = 91.59 \text{ K}}$$

Q12

Ans

$$P_i = \frac{n_i}{N} = \frac{e^{-E_i/kT}}{Z} = \frac{e^{-E_i/kT}}{\sum e^{-E_i/kT}}$$

$$P_1 = \frac{1}{1 + 1/2 + 1/4}$$

$$P_2 = \frac{1/2}{1 + 1/2 + 1/4}$$

$$P_3 = \frac{1/4}{1 + 1/2 + 1/4}$$

$$\bar{E} = \sum E_i P_i$$

$$\bar{E} = \frac{(e^{-1} + 2e^{-2}) kT}{1 + e^{-1} + e^{-2}}$$

$$\bar{E} (\text{system}) = N \bar{E}$$

$$\bar{E} = NkT \frac{(e^{-1} + 2e^{-2})}{(1 + e^{-1} + e^{-2})}$$

$$\bar{E} = 1000 kT \quad (\text{given})$$

$$1000 kT = NkT \frac{(e^{-1} + 2e^{-2})}{(1 + e^{-1} + e^{-2})}$$

$$N = 1000 \frac{(1 + e^{-1} + e^{-2})}{(e^{-1} + 2e^{-2})} \approx 2400$$

13. The Van der Waals Equation is,

$$\left(P + \frac{an^2}{v^2}\right)(v - nb) = nRT$$

$$P = \frac{nRT}{v - nb} - \frac{an^2}{v^2}$$

The internal pressure of the gas is $\left(\frac{\partial U}{\partial v}\right)_T$

$$\left(\frac{\partial U}{\partial v}\right)_T = \frac{an^2}{v^2}$$

$$du = \frac{an^2}{v^2} \quad (\text{at constant temperature}).$$

$$\int du = \int_{v_1}^{v_2} an^2 \frac{dv}{v^2} \Rightarrow$$

$$\Rightarrow \Delta U = -an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right).$$

Using the parameters given and using the Van der Waals equation,

$$v_2 = 7.88 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$$

$$v_1 = 3.28 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}.$$

$$\Rightarrow \Delta U = 0.137 \text{ Pa m}^6 \text{ mol}^{-3} \times$$

$$\left[\frac{1}{3.28 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} - \frac{1}{7.88 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}} \right]$$
$$= -132 \text{ J}$$

14.

$$\mu_{J.T} = -\frac{1}{c_p} \left[\frac{\partial H}{\partial P} \right]_T \quad \text{--- ①}$$

Substituting $\left(\frac{\partial H}{\partial P} \right)_T = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left[\frac{\partial V}{\partial P} \right]_T + V$ in ①,

$$\begin{aligned} \mu_{J.T} &= -\frac{1}{c_p} \left[\left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial P} \right)_T + V \right] \\ &= -\frac{1}{c_p} \left[\left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T + V \right] \\ &= -\frac{1}{c_p} \left[\cancel{\frac{\partial U}{\partial V}} 0 + P \left(\frac{\partial V}{\partial P} \right)_T + V \right] \end{aligned}$$

$\therefore \left(\frac{\partial U}{\partial V} \right)_T$ is internal pressure.

Internal pressure for an ideal gas is zero.

$$\Rightarrow \mu_{J.T} = -\frac{1}{c_p} \left[P \left(\frac{\partial \frac{nRT}{P}}{\partial P} \right)_T + V \right]$$

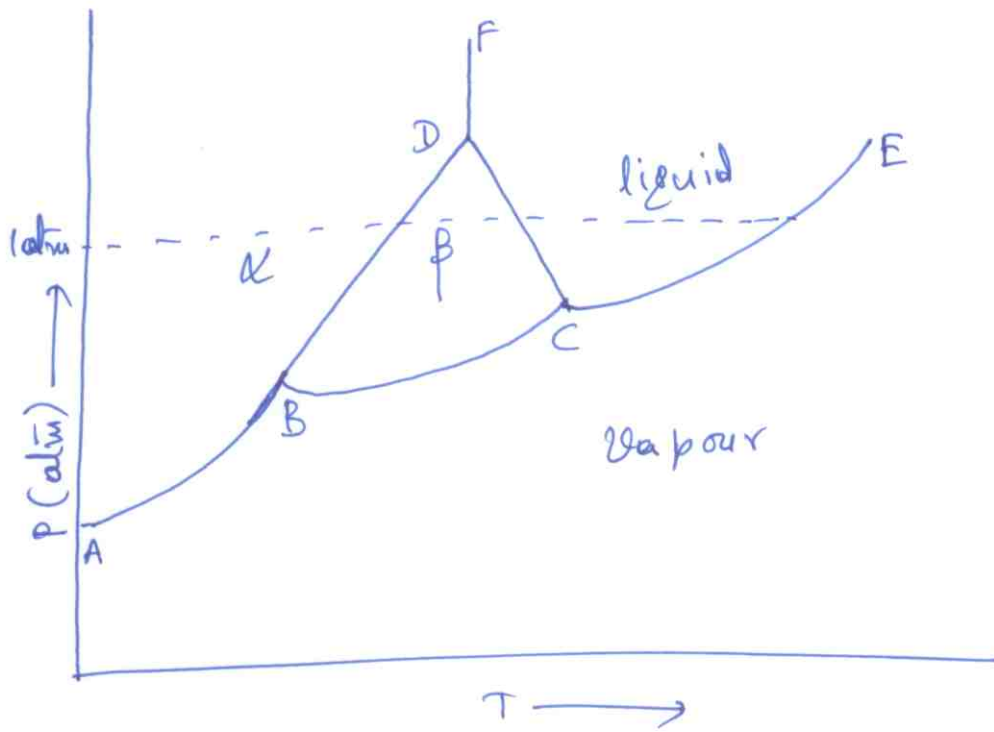
(using $PV = nRT$ equation)

$$= -\frac{1}{c_p} \left[-\frac{nRT}{P} + V \right]$$

$$= -\frac{1}{c_p} \left[-V + V \right]$$

$$\Rightarrow \mu_{J.T} = 0$$

15.



AB: $\alpha \rightleftharpoons \text{vapour}$

BC: $\beta \rightleftharpoons \text{vapour}$

CE: $\text{liquid} \rightleftharpoons \text{vapour}$

CD: $\beta \rightleftharpoons \text{liquid}$

BD: $\alpha \rightleftharpoons \beta$

DF: $\alpha \rightleftharpoons \text{liquid}$

B: $\alpha \rightleftharpoons \beta \rightleftharpoons \text{vapour}$ (triple point)

C: $\beta \rightleftharpoons \text{liquid} \rightleftharpoons \text{vapour}$ (triple point)

D: $\alpha \rightleftharpoons \beta \rightleftharpoons \text{liquid}$

E: critical point.

16. Water is vaporized reversibly at atmospheric pressure. The heat of vaporization is 40.69 kJ/mol. (a) what is the value of ΔS for the water? (b) what is the value of ΔS for the water plus the heat reservoir at 100 °C?

$$\Delta \bar{S} = \frac{\Delta \bar{H}}{T} = \frac{40.69}{373.15} = 109.04 \text{ J/Kmol}$$

For reversible process, $\Delta S = 0$

$$\Delta S = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0.$$

17. What is the entropy of mixing of 1 mol of oxygen with 1 mole of nitrogen at 25 °C, assuming that they are ideal gases?

$$\Delta_{\text{mix}} S = -R \sum n_i \ln y_i = -n_{\text{t}} R \sum y_i \ln y_i$$

n_{t} = total no. of moles, y_i = mole fraction

$$\begin{aligned} \therefore \Delta_{\text{mix}} S &= -(2 \text{ mol}) (8.3145 \text{ J/Kmol}) \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) \\ &= 11.526 \text{ J/K} \end{aligned}$$

18. How many degrees of freedom are there for the following system;
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} (\text{s})$ in equilibrium with $\text{CuSO}_4 (\text{s})$ and $\text{H}_2\text{O} (\text{g})$



$$F = C - P + 2$$

$$C = 2, \quad P = 3$$

$$F = 2 - 3 + 2 = 1.$$

19. Determine whether (i) $\frac{dx}{y} - \frac{x}{y^2} dy$ and (ii) $xy^2 dx - x^2 y dy$ are exact differentials.

Ans :

From Maxwell relation:

$$(i) \left(\frac{\partial \left(\frac{1}{y} \right)}{\partial y} \right)_x = \left(\frac{\partial \left(-\frac{x}{y^2} \right)}{\partial x} \right)_y \Rightarrow \text{exact}$$

$$(ii) \left(\frac{\partial (xy^2)}{\partial y} \right)_x \neq \left(\frac{\partial (-x^2 y)}{\partial x} \right)_y \Rightarrow \text{inexact}$$

20. Calculate ΔS° for the reduction of Al_2O_3 by H_2 gas.

Standard entropies:

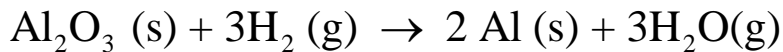
$$S^\circ(Al_2O_3, s) = 51 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S^\circ(H_2, g) = 131 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S^\circ(H_2O, g) = 189 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S^\circ(Al, s) = 28 \text{ JK}^{-1}\text{mol}^{-1}$$

Ans :



$$\Delta S^\circ = 2S^\circ_{Al} + 3S^\circ_{H_2O, g} - 3S^\circ_{H_2, g} - S^\circ_{Al_2O_3, s} = 179 \text{ JK}^{-1}\text{mol}^{-1}$$

21. What is the entropy change for the freezing of 3.33 grams of an alcohol, C_2H_5OH , at 373.2 K given that $\Delta H = -40.7 \text{ kJ/mol}$?

Ans :

$$\Delta S_{\text{freezing}} = \frac{\Delta H_f}{T_f} = \frac{-40700 \text{ Jmol}^{-1}}{373.2 \text{ K}} \times 0.0757 \text{ mol} = -8.25 \text{ JK}^{-1} \text{ for } 3.33 \text{ g of } C_2H_5OH$$