

PHYSICAL CHEMISTRY 5200

MIDTERM EXAM

October 15, 2020

Please write neatly and clearly, and show all working. Allocate time to each question in proportion to the available credit. Keep any explanations brief and clear.

SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

$$N_A \text{ or } L = 6.022 \times 10^{23} \text{ mol}^{-1}$$

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

$$k \text{ or } k_B = R/N_A$$

$$dU = dq + dw$$

$$dS = dq_{\text{rev}}/T$$

$$dw = -p_{\text{ex}} dV$$

$$\gamma = C_p/C_v$$

$$\text{Perfect gas: } pV = nRT \quad \text{and}$$

$$C_p - C_v = nR$$

$$\text{van der Waals gas: } p = nRT/(V-b) - a(n/V)^2$$

$$\text{Adiabat: } pV^\gamma \text{ is constant}$$

$$\text{Heat engine } \varepsilon = (T_h - T_c)/T_h$$

$$H = U + pV$$

1) 40 points

(a) 1 mol of H_2 (g), the system, initially at $p = 6 \times 10^5$ Pa and $V = 4 \times 10^{-3} \text{ m}^3$, is expanded reversibly and isothermally until $p = 10^5$ Pa. C_p is 29 J K^{-1} . Calculate q , w , ΔU , ΔH and ΔS for the system.

(b) Suppose instead, from the same initial conditions, 1 mol of H_2 (g) expands until $p = 10^5$ Pa reversibly and adiabatically. Now what are q , w , ΔU , ΔH and ΔS for the system?

$$a) p_1 V_1 = p_2 V_2 \therefore V_2 = \frac{p_1}{p_2} V_1 = 6 \times 4 \times 10^{-3} \text{ m}^3 = 0.024 \text{ m}^3,$$

$$dw = -p_{\text{ext}} dV = -p dV \text{ (because reversible)}$$

$$T_1 = \frac{p_1 V_1}{nR} = 288.7 \text{ K}.$$

$$\therefore w = - \int_{V_1}^{V_2} p dV = - \int_{V_1}^{V_2} \frac{RT}{V} dV = -RT \ln \left(\frac{V_2}{V_1} \right)$$

$$= -8.314 \text{ J K}^{-1} \times 288.7 \text{ K} \times \ln 6 = -4301 \text{ J}.$$

$\Delta T = 0$ (isothermal) so $\Delta U = C_V \Delta T = 0$ and $\Delta H = C_p \Delta T = 0$

$$\Delta U = q + w \therefore q = +4301 \text{ J}. \quad \Delta S = \frac{q_{\text{rev}}}{T} = 14.9 \text{ J K}^{-1}.$$

$$b) pV^\gamma = \text{const.} \quad \gamma = C_p/C_V = \frac{C_p}{C_p - R} = \frac{29}{29 - 8.314} = 1.402.$$

$$p_1 V_1^\gamma = 26018 = p_2 V_2^\gamma \therefore V_2^\gamma = 0.002608 \therefore V_2 = 0.01436 \text{ m}^3,$$

$$T_2 = \frac{p_2 V_2}{nR} = 172.7 \text{ K}, \quad \Delta T = -116.0 \text{ K}.$$

$$\Delta U = C_V \Delta T = -2400 \text{ J}.$$

$$q = 0 = \Delta U - w \therefore w = -2400 \text{ J}.$$

$$\Delta H = C_p \Delta T = -3364 \text{ J}.$$

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = 0 \text{ because } dq_{\text{rev}} = 0.$$

2) 10 points

The melting point of toluene (the system) at 10^5 Pa is -95°C , and the enthalpy of fusion is 6.6 kJ mol^{-1} . What is ΔS for the system when 1 mol of liquid toluene freezes solid at -95°C , in J K^{-1} ? If the change happens reversibly, what is ΔS_{surr} ? If the change happens irreversibly, what can you say about ΔS_{surr} now?

$$-95^\circ\text{C} = 178\text{ K},$$

$$\Delta S_{\text{sys}} = \frac{\Delta H_{\text{rev}}}{T} = \frac{-6600\text{ J mol}^{-1}}{178\text{ K}} = -37.1\text{ J K}^{-1}\text{ mol}^{-1},$$

For a reversible change, $\Delta S_{\text{uni}} = 0 = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
 $\therefore \Delta S_{\text{surr}} = +37.1\text{ J K}^{-1}\text{ mol}^{-1}$.

For an irreversible change, $\Delta S_{\text{uni}} > 0 \therefore \Delta S_{\text{surr}} > 37.1\text{ J K}^{-1}\text{ mol}^{-1}$.

3) 10 points

Consider a system with $C_p = a + bT^2$ where a and b are constants. In terms of a and b , calculate ΔS for the system for heating from T_1 to T_2 at constant pressure p .

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C_p \cdot dT}{T} = \frac{a + bT^2}{T} dT = \left(\frac{a}{T} + bT\right) dT$$
$$\therefore \Delta S = \int_{T_1}^{T_2} \left(\frac{a}{T} + bT\right) dT = \left[a \ln T + \frac{1}{2} bT^2 \right]_{T_1}^{T_2} = a \ln\left(\frac{T_2}{T_1}\right) + \frac{1}{2} b(T_2^2 - T_1^2)$$

4) 20 points

(a) Imagine an ideal Carnot heat engine operates between 200°C and 25°C . How much heat will be rejected at 25°C when the engine performs work $-w = 100\text{ J}$?

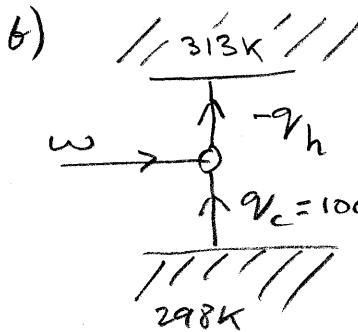
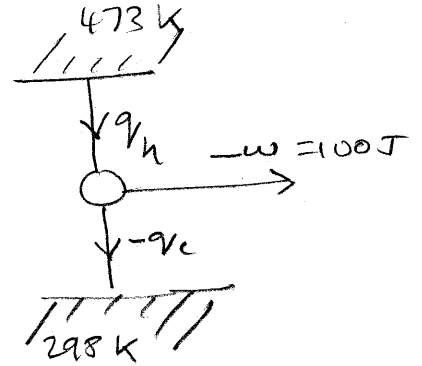
(b) An ideal Carnot heat engine operates in reverse to move heat from cold (25°C) to hot (40°C). How much work must be provided to move heat $q_c = 1000\text{ J}$ from the low temperature region?

a) $200^\circ\text{C} = 473\text{ K}$, $25^\circ\text{C} = 298\text{ K}$.

Efficiency $\frac{473-298}{473} = 0.370 = \frac{-w}{q_h}$

$\therefore q_h = \frac{-w}{0.370} = \frac{100\text{ J}}{0.370} = 270\text{ J}$

Energy conservation: $q_h = -w - q_c \therefore -q_c = 170\text{ J}$.



$\frac{-w}{q_h} = \frac{313-298}{313} = 0.0479 \therefore q_h = \frac{-w}{0.0479}$

Energy conservation $-q_h = w + q_c = \frac{w}{0.0479}$

$\therefore q_c = w \left(\frac{1}{0.0479} - 1 \right) = 19.9 w$

$\therefore w = \frac{1000\text{ J}}{19.9} = \underline{\underline{50.3\text{ J}}}$.

(and $-q_h = 1050.3\text{ J}$)

5) 20 points

(a) The Joule-Thomson coefficient is $\mu = (\partial T / \partial p)_H$, and the isothermal Joule-Thomson coefficient is $\mu_T = (\partial H / \partial p)_T$. Prove that $\mu = -\mu_T / C_p$.

(b) For a real gas at a certain T and p, attractive forces between the molecules dominate. Explain if you expect μ to be positive, zero or negative.

(c) A real gas with $\mu = 0.03 \text{ K bar}^{-1}$ flows through the throttle in a Joule-Thomson apparatus and the pressure drops by 50 bar. If the initial temperature is 300 K, what final temperature do you expect?

a) $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ and this is a constant H experiment with $dH=0$

for $H(p, T)$, $dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT = 0$

$\therefore \left(\frac{\partial H}{\partial p}\right)_T dp = -\left(\frac{\partial H}{\partial T}\right)_p dT = -C_p dT$

divide by dp
at const H

$\therefore \left(\frac{\partial H}{\partial p}\right)_T = -C_p \left(\frac{\partial T}{\partial p}\right)_H$

$\therefore \mu_T = -C_p \mu$ or $\mu = -\mu_T / C_p$.

Alternative method: use Relation 3 from partial derivative summary,

so $\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_p = -1$

$\therefore \mu \times \frac{1}{\mu_T} \times C_p = -1 \therefore \mu = -\mu_T / C_p$.

[Note Because you get the same result (of course) both ways, this proves Relation 3.]

b) As p increases it takes energy to separate the attracting molecules, so the gas cools ($\Delta U < 0$), thus for $dp > 0$, $dT > 0$ and $\mu > 0$.

c) $\frac{\Delta T}{\Delta p} \approx \left(\frac{\partial T}{\partial p}\right)_H \therefore \Delta T \approx \mu \Delta p = 0.03 \text{ K bar}^{-1} \times -50 \text{ bar} = -1.5 \text{ K}$

so $T_{\text{final}} = 300 \text{ K} - 1.5 \text{ K} = 298.5 \text{ K}$.