Exam 2022 solution – Thermodynamique

PROBLÈME I CALUCLATE PH (9P)

1. In water: (1p)

   - Before adding NaOH, pH = 7.

   - After adding NaOH, $C_M(\text{NaOH}) = 0.005$ M, pH = 11.7.

2. In HCl solution 0.02 M:

   - Before adding NaOH, pH = 1.7. (1p)

   - After adding NaOH,

   $\text{NaOH(l)} + \text{HCl(l)} \longrightarrow \text{NaCl(l)} + \text{H}_2\text{O}$

   $C_M(\text{HCl}) = 0.005$ M, pH = 2.3. (1p)

3. In H_2SO_4 solution 0.02M:

   - Before adding NaOH:

   $\text{HSO}_4{}^-\text{(l)} \rightleftharpoons \text{H}^+\text{(l)} + \text{SO}_4{}^{2-}\text{(l)}$

   x is the amount of $SO_4{}^{2-}$ dissociated in the equilibrium, we have:

   $$\frac{x(0.02+x)}{0.02-x} = 10^{-2} \rightarrow x = 0.0056(M) \quad \text{(1p)}$$

   C_M (H^+) = 0.0256 M, pH = 1.6 (1p)

   - After adding NaOH,

   $\text{NaOH(l)} + \text{H}_2\text{SO}_4\text{(l)} \longrightarrow \text{NaHSO}_4\text{(l)} + \text{H}_2\text{O}$

   $C_M(\text{NaHSO}_4) = 0.005$ M, $C_M(\text{H}_2\text{SO}_4) = 0.005$ M

   x is the amount of $SO_4{}^{2-}$ dissociated in this equilibrium, we have:

   $$\frac{x(0.005+x)}{0.01-x} = 10^{-2} \rightarrow x = 0.005(M) \quad \text{(1p)}$$

   C_M (H^+) = 0.01 M, pH = 2.00 (1p)

4. In buffer solution:

   - Before adding NaOH,

   $$\text{pH} = \text{pK}_a + \log\frac{[\text{Ac}^-]}{[\text{HAc}]} = 4.76 \quad \text{(1p)}$$

- After adding NaOH, $C_M(\text{HAc}) = 0.005$ M, $C_M(\text{Ac}^-) = 0.015$ M

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Ac}^-]}{[\text{HAc}]} = 5.24 \qquad \text{(1p)}$$

PROBLÈME II CARNOT CYCLE (22P)

1. Figure for the Carnot cycle: (3p, 1 per graph)

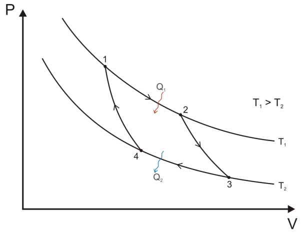

FIG. 1. p-V diagram

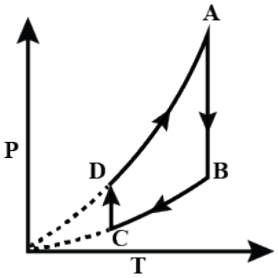

FIG. 2. p-T diagram

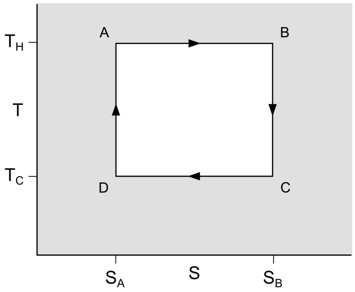

FIG. 3. T-S diagram

2. All p,V,T value (3p, 1/4 per value)

	p(atm)	V(l)	T(K)
A	10	4.92	600
B	1	49.2	600
C	0.18	139.2	300
D	1.8	13.92	300

3. (10p, 1/2 per value)

Process 1 (Isothermal):

$$w = -nRT\ln\left(\frac{V_B}{V_A}\right) = -nRT\ln\left(\frac{p_A}{p_B}\right)$$

$$w = -1.00\,\mathrm{mol}\cdot 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}\cdot 600\,\mathrm{K}\cdot\ln\left(\frac{10.00\,\mathrm{atm}}{1.00\,\mathrm{atm}}\right) = -11\,486\,\mathrm{J}$$

$$q = -w = 11\,486\,\mathrm{J}$$

$$\Delta U = \Delta H = 0$$

Process 2 (Adiabatic):

$$q = 0$$

$$w = \Delta U = nC_{V,m}\Delta T$$

$$w = \Delta U = 1.00\,\mathrm{mol}\cdot\frac{3}{2}\cdot 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}\cdot(300\mathrm{K} - 600\mathrm{K}) = -3741\,\mathrm{J}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T$$

$$\Delta H = -3741\,\mathrm{J} + 1.00\,\mathrm{mol} \cdot 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \cdot (-300\,\mathrm{K}) = -6235\,\mathrm{J}$$

Process 3 (Isothermal):

Because this is the Carnot cycle, the heat of this process can be calculated from the Carnot efficiency formula:

$$\epsilon = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{300\,\mathrm{K}}{600\,\mathrm{K}} = 0.50 = 1 + \frac{q_1}{q_3}$$

$$q_3 = -0.50 \cdot q_1 = -0.50 \cdot 11\,486\,\mathrm{J} = -5743\,\mathrm{J}$$

$$w = -q_3 = 5743\,\mathrm{J}$$

$$\Delta U = \Delta H = 0$$

Process 4 (Adiabatic): With in a cycle, the total chance in state functions are zero because the cycle returns to the original state. Therefore:

$$\Delta U = 3741\,\mathrm{J}$$

$$\Delta H = 6235\,\mathrm{J}$$

$$q = 0$$

$$w = \Delta U = 3741\,\mathrm{J}$$

The total heat exchanged is: $q_{cycle} = 11486$ J $-$ 5743 J $=$ 5743 J

The total work exchanged is: $w_{cycle} = -11486$ J $+$ 5743 J $= -5743$ J

$$\Delta U_{cycle} = \Delta H_{cycle} = 0$$

	q (J)	w (J)	ΔU (J)	ΔH (J)
Process 1	11486	-11486	0	0
Process 2	0	-3741	-3741	-6235
Process 3	-5743	5743	0	0
Process 4	0	3741	3741	6235
Cycle	5743	-5743	0	0

4. (3p, 1 per value)

Since all the processes considered are reversible, we have:

Process 1 (Isothermal):

$$\Delta S = \frac{q}{T} = \frac{11\,486\,\mathrm{J}}{600\,\mathrm{K}} = 19.14\,\mathrm{J\,K^{-1}}$$

Process 2 (Adiabatic):

$$\Delta S = 0$$

Efficiency of the cycle is:

$$\epsilon = 0.5$$

5. Efficiency of the fridge (3p, 1 per value)

$$\epsilon_{fridge} = \frac{270}{400 - 270} = 2.08$$

Heat extracted from the cold source:

$$q_c = w_{cycle} \cdot \epsilon_{fridge} = 11\,928\,\mathrm{J}$$

Heat received from the heat souece:

$$q_h = q_c + w_{cycle} = 17\,671\,\mathrm{J}$$

PROBLÈME III VAPORIZING WATER (17P)

1. Using Clapeyron - Clausius Eq:

   $$\ln\frac{p_1}{p_2}=\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \qquad \text{(1p)}$$

   $\mathrm{p_1 = 1\ atm, T_1 = 373\ K,\ p_2 = 0.5\ atm}$

   We have $T_2 = 355.2$ K (1p)

2. - The reaction is not spontaneous at all temperature. (1p)

   - Reason: The reaction is endothermic. (1p)

3. Using Kirchhoff's equation:

   $$\left(\frac{\partial\Delta H}{\partial T}\right)_p = \Delta C_p \qquad \text{(1p)}$$

   $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$ with C_p is independent of temperature

   At T = 150^{o}C, or 423 K

   $\Delta H = 40690 + (423 - 373)(35 - 75) = 38690$ J (2p)

   At T = 273 K

   $\Delta H = 40690 + (273 - 373)(35 - 75) = 44690$ J (2p)

4. Combustion reaction: $\mathrm{C_4H_{10}(g) + \frac{13}{2}\,O_2(g) \longrightarrow 4\,CO_2(g) + 5\,H_2O(g)}$

   $\Delta H_{comb,298K} = 5\Delta_f H^{\ominus}_{\mathrm{H_2O}} + 4\Delta_f H^{\ominus}_{\mathrm{CO_2}} - \Delta_f H^{\ominus}_{\mathrm{C_4H_{10}}} = -2656\,\mathrm{kJ\,mol^{-1}}$ (2p)

   To calculate the combustion reaction at 700 K, we use the Kirchhoff's equation:

   $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$

   $\Delta H_{comb,700K} = -2654.593\,\mathrm{kJ\,mol^{-1}}$ (2p)

5. Number of mole of water in 1L: $n = \dfrac{m}{M} = \dfrac{\rho\cdot V}{M} = 55.56$ mol (1p)

   Heat needed to boil 1mole of $\mathrm{H_2O}$ from 298 K:

   $Q = C_p\Delta T + \Delta H_{vap,373K} = 46\,315\,\mathrm{J\,mol^{-1}}$ (2p)

   Number of mole of butane required: $n_{butane} = 0.97$ mol (1p)

PROBLÈME IV DIMERIZATION REACTION OF NO_2 (18P)

1. (4p)

Let x be the volume of NO_2 after the equilibrium is reached. The volume of the product N_2O_4 is $V - \frac{x}{2}$ The total volume of the mixture is:

$$V_m = x + V - \frac{x}{2}$$

$$x = 2(V_m - V)$$

$$V - \frac{x}{2} = 2V - V_m$$

The equilibrium constant of the reaction can be calculated as follows:

$$K_p = \frac{P_{N_2O_4}}{P^2_{NO_2}} = \frac{p \cdot \dfrac{2V - V_m}{V_m}}{\left(p \cdot \dfrac{2(V_m - V)}{V_m}\right)^2} = \frac{(2V - V_m)V_m}{4(V_m - V)^2}$$

2. In the initial mixture, NO reacts fully with O_2 to give 8 mL of NO_2 at 298 K and 1 atm. The volume of NO_2 at 298 K is

$2V = 8.00\text{mL}$ (1p)

$K_p = \dfrac{(8.00 - 4.77) \cdot 4.77}{4(4.77 - 4.00)^2} = 6.50$ (1p)

3. The volume of NO_2 at 323 K is:

$2V = \dfrac{323\,\text{K}}{298\,\text{K}} \cdot 8\text{mL} = 8.67\text{mL}$ (1p)

$K_p = \dfrac{(8.67 - 5.67) \cdot 5.67}{4(5.67 - 4.335)^2} = 2.39$ (1p)

consider numerical error

4. Using the Van't Hoff equation:

$\ln\left(\dfrac{K_1}{K_2}\right) = \dfrac{\Delta H^o}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ (1p)

At $T_1 = 298$ K, $K_1 = 6.50$

At $T_2 = 323$ K, $K_2 = 2.39$

$\Delta H^o = -32\,026\,\mathrm{J\,mol^{-1}}$ (1p)

$\Delta G^0_{298\,\mathrm{K}} = -8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \cdot 298\,\mathrm{K} \cdot \ln 6.50 = -4637.5\,\mathrm{J\,mol^{-1}}$ (1p)

$\Delta S^0_{298\,\mathrm{K}} = -91.91\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (1p)

$\Delta G^0_{323\,\mathrm{K}} = -8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \cdot 323\,\mathrm{K} \cdot \ln 2.39 = -2339.8\,\mathrm{J\,mol^{-1}}$ (1p)

$\Delta S^0_{323\,\mathrm{K}} = -91.91\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (1p)

consider numerical error

5. When there is an an excess amount of O_2 in the mixture at constant pressure,

   → Partial pressure of NO_2 and N_2O_4 is reduced. (2p)

   → The equilibrium will shift to the left. (2p)

Problème V supercritical fluid (24p)

1. Phase diagram in p-T representation: (5p)

   1/2 for each phase, 1/4 for each transition

   1 for triple point, 1 for critical point

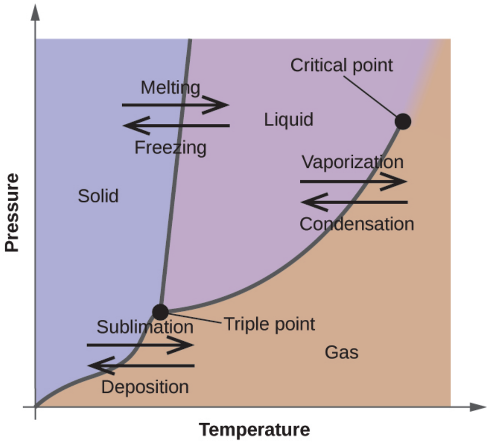

FIG. 4. Phase diagram diagram

2. Phase diagram in p-V representation: (2p)

   1/2 for each line with correct shape, 1/2 for correct temperature direction

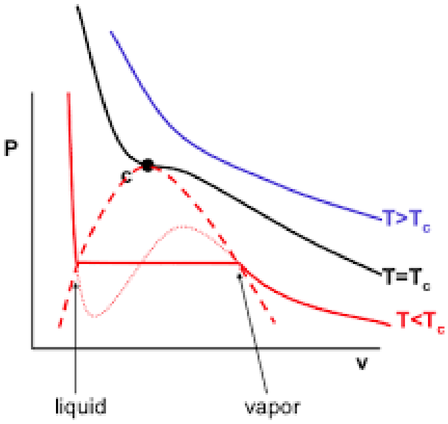

FIG. 5. Phase diagram diagram

3. - The point in each graph at which the pressure is constant in terms of volume change indicates the vapor pressure of the sample. (1p)

   - The volume difference of this area is the change in volume between the gas and the liquid phase. (1p)

4. At 26^{o}C, $p_{vapor} = 65.62$ bar (2p)

   At 30^{o}C, $p_{vapor} = 71.76$ bar (2p)

5. Using the Claperon equation:

   $$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \qquad \text{(2p)}$$

   $$\frac{dp}{dT} = 1.183 \cdot 10^{-4} \cdot T^2 + 4.6 \cdot T + 4.66564 \text{ Derivation of the given p(T)}$$

   At 26^{o}C, $\Delta H = 618.96\,\mathrm{J}$, $\Delta S = 2.07\,\mathrm{J\,K^{-1}}$ (2p)

   At 30^{o}C, $\Delta H = 211.87\,\mathrm{J}$, $\Delta S = 0.70\,\mathrm{J\,K^{-1}}$ (2p)

   consider numerical error

   - Near the critical point, $\Delta S = 0$. (1p)

6. - Using the van der Waals equation, p = 22.33 bar. (1p)

   - Using the ideal gas equation, p = 24.86 bar. (1p)

   In this situation, perfect gas approximation is nolonger valid (1p)

   because at high pressure, we can nolonger neglect intermolecular interaction. (1p)