浙江大学 2016 – 2017 学年 秋冬 学期

《物理化学》课程期末考试试卷

课程号： 061B9030，开课学院： 理学院

考试试卷：√ A 卷、B 卷（请在选定项上打√）

考试形式：√ 闭、开卷（请在选定项上打√），允许带 计算器 入场

考试日期：2017 年 1 月 19 日，考试时间： 120 分钟

诚信考试，沉着应考，杜绝违纪。

考生姓名：_____ 学号：_____ 所属院系：_____

题　序	一	二	三	四	五	六	七	总分
得　分								
评卷人								

1. The osmotic pressure of an aqueous solution at 300 K is 120 kPa. Calculate the freezing point of the solution. Given that the cryoscopic constant of water, K_f is 1.86 K·kg·mol^{-1}. (15 scores)

2. A sample of 1.00 mol perfect gas molecules at 298 K with $C_{p,m} = 7R/2$ is put through the following cycle: (a) constant−volume heating to twice its initial temperature, (b) reversible, adiabatic expansion back to its initial temperature, (c) reversible isothermal compression back to 1.00 atm. Calculate q, w, ΔU, and ΔH for each step and overall. (15 scores)

① a) $C_{V,m} = C_{p,m} - R = \frac{7}{2}R - R = \frac{5}{2}R$, $\Delta T = 298$

$\Delta U = n C_{V,m} \Delta T = \frac{5}{2} \times 8.314 \times 298 = 6.19\ kJ$ (1)

$w = 0$ (1)

$q = \Delta U - w = 6.19\ kJ$ (1)
 (1)
$\Delta H = \Delta U + \Delta(PV) = \Delta U + n R \Delta T = 6.19 + 8.314 \times 298 = 8.67\ k$

b) $q = 0$ (1) $\Delta U(b) = -\Delta U(a) = -6.19\ kJ$ (1)

$w = \Delta U(b) = -6.19\ kJ$ $\Delta H(b) = -\Delta H(a) = -8.67\ kJ$ (1)
 (1)

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

$q = -w = -nRT \ln \frac{V_1}{V_3}$

$V_2 = V_1 = \frac{nRT_1}{P_1} = \frac{0.08206 \times 298}{1.00} = 24.45\ L$ (1)

$V_2 T_2^c = V_3 T_3^c$, $c = \frac{5}{2}$

$V_3 = V_2 \left(\frac{T_2}{T_3}\right)^{5/2} = 24.45 \times \left(\frac{2 \times 298}{298}\right)^{5/2} = 138.3\ L$ (1)
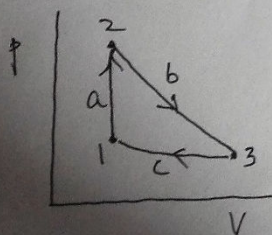
$w = -8.314 \times 298 \ln \frac{22.45}{138.3} = 4.29\ kJ$ (1)

$q = 4.29\ kJ$ (1)

For the overall cycle: (3)

$\Delta U = \Delta H = 0$

$q = 6.19 + 0 + (-4.29) = 1.90\ kJ$ $w = -1.90\ kJ$

3. An adiabatic container is divided by an adiabatic partition into two compartments. One compartment has a volume of 50 dm³ and contains 2 mol O_2 at 200 K; the other has a volume of 75 dm³ and contains 4 mol N_2 at 500 K. Calculate the entropy change of mixing when the partition is removed. Assuming perfect behavior. (15 scores)

②

N_2	N_2
$2\,mol = n_1$	$n_2 = 4\,mol$
$200\,K = T_1$	$T_2 = 500\,K$
$50\,dm^3 = V_1$	$V_2 = 75\,dm^3$

$\because q=0, \quad \Delta V = 0.$

$\Delta U = 0 = n\,C_{V,m}(T-T_1) + n\,C_{V,m}(T-T_2)$

$T = \dfrac{n_1\,C_{V,m}T_1 + n_2\,C_{V,m}T_2}{n_1\,C_{V,m} + n_2\,C_{V,m}} = \dfrac{n_1 T_1 + n_2 T_2}{n_1 + n_2} = \dfrac{2\times200 + 4\times500}{6} = 400\,K$

求 先求 $P_1, P_2, P.$

$P_1 = \dfrac{n_1 RT_1}{V_1} = \dfrac{2\times8.314\times200}{50\times10^{-3}} = 66516\,Pa$

$P_2 = \dfrac{n_2 RT_2}{V_2} = \dfrac{4\times8.314\times500}{75\times10^{-3}} = 221720\,Pa$

$P = \dfrac{(n_1+n_2)RT}{V_1+V_2} = \dfrac{6\times8.314\times400}{(50+75)\times10^{-3}} = 159638\,Pa$

$\Delta S_1 = n_1 C_{p,m}\ln\dfrac{T}{T_1} + n_1 R\ln\dfrac{P_1}{P}$

$= 2\times8.314\times\dfrac{7}{2}\ln\dfrac{400}{200} + 2\times8.314\,\ln\dfrac{66516}{159638}$
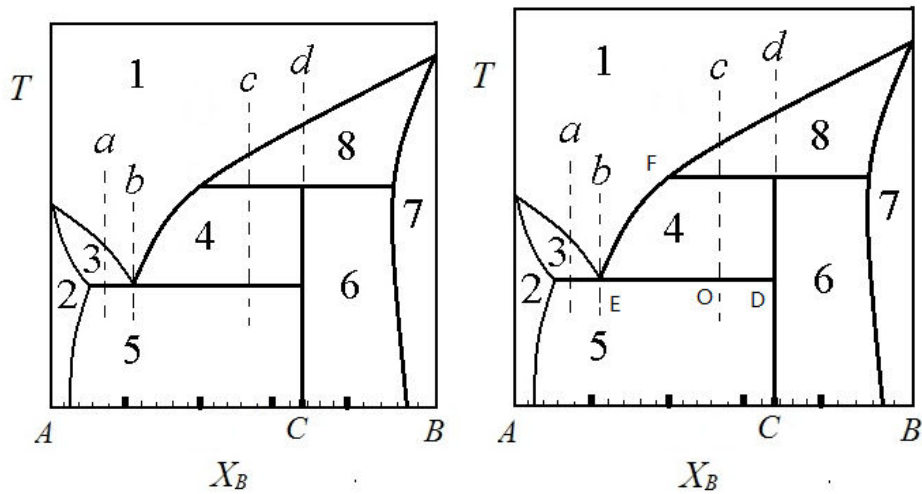
$= \cancel{28.8} - 14.56 = 25.78\ J\,K^{-1}$
$\quad 40.34$

$\Delta S_2 = n_2 C_{p,m}\ln\dfrac{T}{T_2} + n_1 R\ln\dfrac{P_2}{P}$

$= 4\times\dfrac{7}{2}\times8.314\,\ln\dfrac{400}{500} + 4\times8.314\,\ln\dfrac{221720}{159638}$

$= -25.97 + 10.92 = -15.05\ J\cdot K^{-1}$

$\Delta S = \Delta S_1 + \Delta S_2 = 25.78 - 15.05 = 10.73\ J\,K^{-1}$

4. The solid—liquid phase diagram is as follows:

(a) Indicate the substances and states in each region.

(b) Draw the cooling curves of a, b, c and d.

(c) Indicate the range of the composition in order to obtain the pure solid C.

(d) How many grams of the pure solid C can be obtained at most if 100 g of the solution c is cooled? (15 scores)

4. (a) 1: L   2: $\alpha(s)$
   3: $\alpha(s) + L$ 4: $C(s) + L$
   5: $\alpha(s) + C(s)$ 6: $C(s) + \beta(s)$
   7: $\beta(s)$ 8: $\beta(s) + L$ (5")

   $\alpha(s)$, $\beta(s)$ are solid solutions.
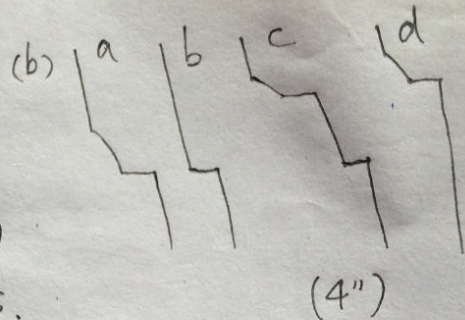 $C(s)$ is unstable compound.

   (c) EF or $0.22 \sim 0.40$ (2")

   (d) $n_\ell(\overline{OE}) = n_s(\overline{OD})$
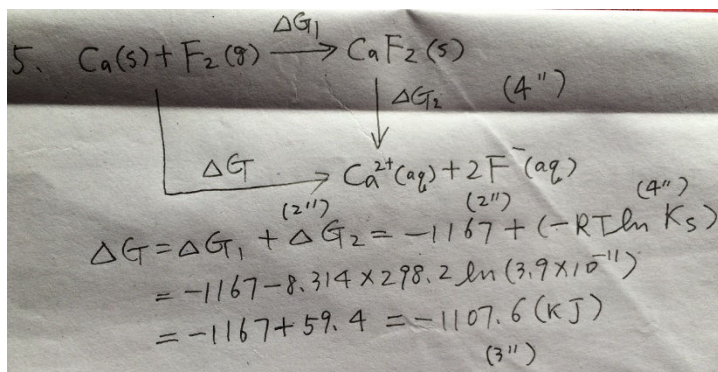 $n_\ell(0.53 - 0.22) = n_s(0.67 - 0.53)$ (2")
   $(100 - n_s) \times 0.31 = 0.14 n_s$
   $n_s = 68.8 \text{(g)}$ (2")

(b)   a   b   c   d

(4")

5. For CaF_2 (s), $K_s = 3.9 \times 10^{-11}$ at 298.2 K, and the standard Gibbs energy of formation of CaF_2 (s) is -1167 kJ mol^{-1}. Calculate the standard Gibbs energy of formation of CaF_2 (aq). (15 scores).

6. The adsorption of a gas is described by the Langmuir isotherm with the equilibrium constant $K = 0.85$ kPa $^{-1}$ at 298.2 K. Calculate the pressure at which the fractional surface coverage is 0.95. (10 scores)
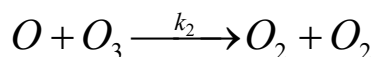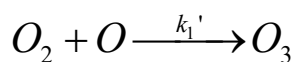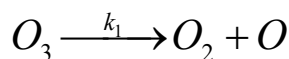
$$\theta = \frac{Kp}{1+Kp}$$

7. Derive the rate law for the decomposition of ozone in the reaction $2O_3(g) \rightarrow 3O_2(g)$ on the basis of the following proposed mechanism:

$$O_3 \xrightarrow{k_1} O_2 + O$$
$$O_2 + O \xrightarrow{k_1'} O_3$$
$$O + O_3 \xrightarrow{k_2} O_2 + O_2$$

(a) Use the consumption rate of O_3 to deduce the rate law.

(b) Under what approximation the reaction behaves a first$-$order reaction?

(15 scores)

(a)

$$-\frac{d[O_3]}{dt} = k_1[O_3] - k_1'[O_2][O] + k_2[O][O_3] \quad (3'')$$

$$\frac{d[O]}{dt} = k_1[O_3] - k_1'[O_2][O] - k_2[O][O_3] = 0 \quad (3'')$$

$$[O] = \frac{k_1[O_3]}{k_1'[O_2] + k_2[O_3]}$$

$$k_1[O_3] - k_1'[O_2][O] = k_2[O][O_3]$$

$$-\frac{d[O_3]}{dt} = 2k_2[O][O_3] = \frac{2k_1k_2[O_3]^2}{k_1'[O_2] + k_2[O_3]} \quad (2'')$$
$$(2'')$$

(b) $k_1'[O_2] \ll k_2[O_3]$

or $k_1' \ll k_2 \quad (3'')$

$$-\frac{d[O_3]}{dt} = 2k_1[O_3] \quad (2'')$$