

國立中山大學 106 學年度碩士暨碩士專班招生考試試題

科目名稱：熱力學【材光系碩士班乙組】

題號：439006

※本科目依簡章規定「可以」使用計算機（廠牌、功能不拘）（問答申論題）

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請於答案卷上依序作答，並清楚標明題號

1. (30%) (a, 5%) Define the partial molar property \overline{M}_i , the chemical potential μ_i , the fugacity (f_i), the activity (a_i) and activity coefficient (r_i) of species i in a solution. (b, 5%) What are the relationships of the chemical potential μ_i of each species in all phases when the multiple phases at the same T and P are in equilibrium? (c, 5%) Draw a schematic A-B binary T-x (temperature-composition) phase diagram with a liquid phase and a solid solution phase (label all phase regions). (d, 5%) Draw a schematic A-B binary T-x phase diagram with a vapor phase, a liquid phase and a minimum azeotrope (label all phase regions). (e, 5%) Draw a schematic A-B binary T-x phase diagram with a liquid phase, two terminal solid phases (α and β) and a *eutectic* reaction (label all phase regions). (f, 5%) Draw a schematic A-B binary T-x phase diagram with a liquid phase, two terminal solid phases (α and β) and a *peritectic* reaction (label all phase regions).

2. (20%) (a, 5%) The complete differential internal energy U can be written in terms of the partial derivative $dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$, please derive the relation $C_p - C_v = R$ for one mole of ideal gas. (b, 5%) Prove that the process path of an ideal gas undergoing a *reversible adiabatic* change of state is described by $PV^\gamma = \text{constant}$, where P is the pressure, V refers to the volume and $\gamma = C_p/C_v$. (c) Air at an initial state of 47°C , 0.2 MPa , follows a process until it reaches a final state 267°C , 0.8 MPa . Assume the air is an ideal gas with constant specific heat. The specific heat is $C_p = 1.017 \text{ (KJ/KgK)}$ and gas constant is $R = 0.287 \text{ (KJ/KgK)}$. Calculate the entropy change per unit mass during the process, assuming the following (i, 5%) The process is reversible. (ii, 5%) The process is irreversible.

3. (10%) Please prove the following statement: for two given heat reservoirs no engine can have a thermal efficiency higher than that of a Carnot engine.

4. (20%) A vessel, divided into two parts by a partition, contains 6 moles of nitrogen gas at 400K and 5 bar on one side and 4 moles of argon gas at 400K and 5 bar on the other side. The molar Gibbs free energies of nitrogen gas and argon gas at 400K and 5 bar are $\overline{G}_{\text{N}_2}$ and \overline{G}_{Ar} , respectively. (a, 5%) What is the molar Gibbs free energy of the gas in the vessel? (b, 5%) If the partition is removed and the gases mixed adiabatically and completely, what is the molar Gibbs free energy of the gas in the vessel after mixing? (c, 5%) What are the entropy of mixing, enthalpy of mixing, and Gibbs free energy of mixing? (d, 5%) What are the excess entropy of mixing, excess enthalpy of mixing, and excess Gibbs free energy of mixing? Assume nitrogen to be an ideal gas with $C_v = 2.5R$ and Argon to be an ideal gas with $C_v = 1.5R$. R is the gas constant.

5. (20%) The melting point T^m and the latent heat of fusing ΔH^m of Aluminum are 932K and 10.8 (KJ/mole) , respectively. The allotropic phase transformation from α -Mn to β -Mn occurs at 1000K and one atmosphere pressure. The entropy change for the phase transformation is 2.25 (J/mole K) . Calculate ΔS for the following reaction at 1400 K and one atmosphere pressure.

$$\text{MnSiO}_{3(s)} + 2\text{Al}_{(l)} = \text{Al}_2\text{O}_{3(s)} + \text{Mn}_{(s)} + \text{Si}_{(s)}$$

Given that the constant-pressure molar heat capacity of various substances as follows:

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$$MnSiO_{3(s)}: S_{298}=89.5 \text{ (J/mole K)}$$

$$Al_{(s)}: S_{298}=28.4 \text{ (J/mole K)}$$

$$Al_2O_{3(s)}: S_{298}=51.1 \text{ (J/mole K)}$$

$$Mn_{(s)}: S_{298}=31.9 \text{ (J/mole K)}$$

$$Si_{(s)}: S_{298}=18.9 \text{ (J/mole K)}$$

$$C_p(MnSiO_{3(s)}) = 110.0 + 16.1 \times 10^{-3} T - 25.8 \times 10^5 T^{-2} \text{ (J/mole K)} \quad 298K < T < 1300K$$

$$C_p(Al_{(s)}) = 20.7 + 12.4 \times 10^{-3} T \text{ (J/mole K)} \quad 298K < T < 1300K$$

$$C_p(Al_{(l)}) = 29 \text{ (J/mole K)} \quad 298K < T < 1300K$$

$$C_p(Al_2O_{3(s)}) = 106.6 + 7.8 \times 10^{-3} T - 28.5 \times 10^5 T^{-2} \text{ (J/mole K)} \quad 298K < T < 1300K$$

$$C_p(\alpha Mn_{(s)}) = 21.6 + 15.9 \times 10^{-3} T \text{ (J/mole K)} \quad 298K < T < 1300K$$

$$C_p(\beta Mn_{(s)}) = 34.9 + 2.8 \times 10^{-3} T \text{ (J/mole K)} \quad 298K < T < 1300K$$

$$C_p(Si_{(s)}) = 24.3 + 2.3 \times 10^{-3} T - 4.5 \times 10^5 T^{-2} \text{ (J/mole K)} \quad 298K < T < 1300K$$

Conversion factor:

$$\text{Pressure: } 1 \text{ bar} = 10^5 \text{ Kg m}^{-1} \text{ S}^{-2} = 10^5 \text{ Pa} = 0.986923 \text{ atm}$$

$$\text{Energy: } 1 \text{ J} = 1 \text{ Kg m}^2 \text{ s}^{-2} = 1 \text{ Nm} = 1 \text{ m}^3 \text{ Pa} = 0.239006 \text{ cal}$$

Gas constant:

$$R = 8.314 \text{ J/mole K} = 8.314 \text{ m}^3 \text{ Pa/mole K} = 1.987 \text{ Cal/mole K}$$