題號: 266 國立臺灣大學 113 學年度碩士班招生考試試題

科目:熱力學

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一、選擇題(單選,請選出最適合的答案,每題5分,共40分)

- ※ 注意:請於試卷內之「選擇題作答區」依序作答。
- 1. Which of the following is not within the scope of thermodynamics?
- (A) The rate of a falling stone from Eiffel tower
- (B) The Curie temperature of iron
- (C) The melting temperature of ice
- (D) The efficiency of a refrigerator
- 2. Which of the following is a state function?
- (A) Heat
- (B) Work
- (C) Entropy
- (D) Velocity
- 3. Which system do you think has the lowest entropy (assuming of the same mass)?
- (A) A glass of water
- (B) Shaved ice
- (C) A pot of hot water
- (D) A pool of melting snow
- 4. Which of the following statement regarding Carnot cycle is NOT true?
- (A) Operate at the maximum efficiency of a heat engine
- (B) The entropy flows in is more than entropy flows out
- (C) Not practical
- (D) The expansion of working fluid is isothermal
- 5. Which of the following is least likely to be included in a refrigerator?
- (A) Turbine
- (B) Boiler
- (C) Pump
- (D) Condenser
- 6. Which of the following phase transformation can potentially involve a critical point?
- (A) Dry ice and carbon dioxide gas
- (B) Water and ice
- (C) Diamond and graphite
- (D) Helium liquid and helium gas
- 7. Why is the oxygen in the air not liquefied when the temperature is slightly below oxygen's boiling point?
- (A) Oxygen won't mix with nitrogen
- (B) Oxygen is heavier than nitrogen

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(C) There is a solubility gap for nitrogen/oxygen system

- (D) Mixing of gases increases entropy
- 8. Which of the following is NOT a colligative property of dilute solutions?
- (A) Osmotic pressure
- (B) Solubility
- (C) Vapor pressure
- (D) Freezing temperature
- 二、計算與問答題 (每小題 6 分,共 60 分)
- ※ 注意:請於試卷內之「非選擇題作答區」標明題號依序作答。
- 1. A gas mixture at one atmosphere total pressure has the following composition:

Component	H ₂	O ₂	H ₂ O	
Molar fraction	0.05	0.04	0.91	

At 700°C, for the reaction to form the product H₂O:

$$2H_2 + O_2 \rightarrow 2H_2O_1$$
, $\Delta G^0 = -393 \text{ KJ}$

(I)

Given the internal energy change $dU = TdS - PdV + \sum_{i=1}^{n} \mu_i dn_i$, where

 μ_i and n_i are the chemical potential and the molar number of species i, respectively.

- (a) Use Legendre transformation to derive the Gibbs free energy change dG from dU. (Hint: use product rule, d(XY) = YdX + XdY, to change variables.)
- (b) Providing the definition $\mu_k = G_k^0 + RT \ln a_k$, where a_k indicates the activity of species k. Derive the expression of ΔG for reaction (I) in terms of ΔG^0 and the activities of gas species.
- (c) At equilibrium the system free energy change $\Delta G = 0$, the equilibrium constant K can be derived from $0 = \Delta G^0 + RT \ln(K)$. What is the equilibrium constant of reaction (I) for the given conditions? Briefly explain the meaning of the results you acquired for reaction (I)
- (d) The activity of a gas species k, a_k , is defined as its partial pressure normalized by 1 atm. Following the second law of thermodynamics, determine whether reaction (I) will spontaneous occur for the given composition and conditions.
- (e) Explain why the chemical reaction (I) and most of the chemical reactions do not go to completion?

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2. Consider a fuel cell and a Carnot engine that both use methane as their fuel. The chemical and combustion reactions are the same as the following:

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$$

- (a) Use the data in **Table 1** to determine the values of ΔH and ΔG for this reaction occurred in the fuel cell (for one mole of methane). Assume that the reaction occurs at ambient temperature and pressure.
- (b) Assuming ideal performance, how much electrical work can you get out of the cell, for each mole of methane fuel?
- (c) The half reactions for the fuel cell are

at (-) electrode: $CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$

at (+) electrode: $2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O$

Wat is the voltage of the fuel cell?

- (d) Assuming the Carnot engine is powered by burning methane at 600° C, how much heat is expelled for each mole of combusted methane?
- (e) Basing on results in (b) and (c), compare the efficiency of a fuel cell and a Carnot engine. Explain why one technology is more efficient than the other.

見背面

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Constant:

Avogardo's number $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

Faraday constant F = 96485 C/mol

Gas constant $R = 8.314 \text{ J/mol} \cdot \text{K}$

Table 1. Thermodynamics Properties of Selected Substances

All of the values in this table are for one mole of material at 298 K and 1 bar. The form of the substance, either solid (s), liquid (l), gas (g) or aqueous solution (aq), is denoted after the chemical formula. Data for aqueous solutions are at a standard concentration of 1 mole per kilogram water. The enthalpy and Gibbs free energy of formation, $\Delta_f H$ and $\Delta_f G$, represent the changes in H and G upon forming one more of the material starting with elements in their most stable pure states (e.g., C (graphite), O₂ (g), etc.).

Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	$V (cm^3)$
H ₂ (g)	0	0	130.68	28.82	
$\mathbf{H}_{\mathbf{g}}$	217.97	203.25	114.71	20.78	
H ⁺ (aq)	0	0	0	0	
$H_2O(l)$	-285.83	-237.13	69.91	75.29	18.068
H_2O (g)	-241.82	-228.57	188.83	33.58	
O_2 (g)	0	0	205.14	29.38	
O_2 (aq)	-11.7	16.4	110.9		
OH ⁻ (aq)	-229.99	-157.24	-10.75	-148.5	
CH ₄ (g)	-74.81	-50.72	186.26	35.31	
C_2H_6 (g)	-84.68	-32.82	229.60	52.63	
C_3H_8 (g)	-103.85	-23.49	269.91	73.5	
$C_2H_5OH(1)$	-277.69	-174.78	160.7	111.46	58.4
C ₆ H ₁₂ O ₆ (glucose)	-1268	-91 0	212	115	
CO (g)	-110.53	-137.17	197.67	29.14	
CO_2 (g)	-393.51	-394.36	213.74	37.11	

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