

※ 注意：請用 2B 鉛筆作答於答案卡，並先詳閱答案卡上之「畫記說明」。

There are two parts in the exam sheet. The first part is True/False questions, and the second part contains multiple choice questions. Short explanation will be given in each part.

You may find the following constants and conversion factors useful:

*Physical Constants*

Avogadro's number	$N_0 = 6.0221415 \times 10^{23}$
Rest mass of the electron	$m_e = 9.1093826 \times 10^{-31}$ (kg)
Elementary charge	$e = 1.60217653$ C
Plank's constant	$h = 6.6260693$ (J s)
Gas constant	$R = 8.314313$ (J/mol K)
	$R = 1.98727$ (cal/mol K)
	$R = 82.0589$ (cc atm/mol K)
	$R = 0.0820589$ (l atm/mol K)
Boltzmann's constant ( $k = R/N_0$ )	$k = 1.3806505 \times 10^{-23}$ (J/K)

*Conversion Factors*

Length	$1 \text{ m} = 100 \text{ cm} = 1000 \text{ mm} = 10^6 \mu\text{m} = 10^9 \text{ nm}$
Volume	$1 \text{ l} = 1000 \text{ ml} = 1000 \text{ cm}^3 = 10^{-3} \text{ m}^3$
Temperature	$T^\circ\text{C} = T \text{ K} - 273.15 = (5/9)(T^\circ\text{F} - 32)$
Pressure	$1 \text{ atm} = 101325 \text{ Pa} = 0.101325 \text{ MPa} = 0.06805 \text{ psi}$
Energy	$1 \text{ J} = 1 \text{ N m} = 4.184 \text{ cal} = 9.8699 \text{ cc atm} = 0.0098699 \text{ l atm}$

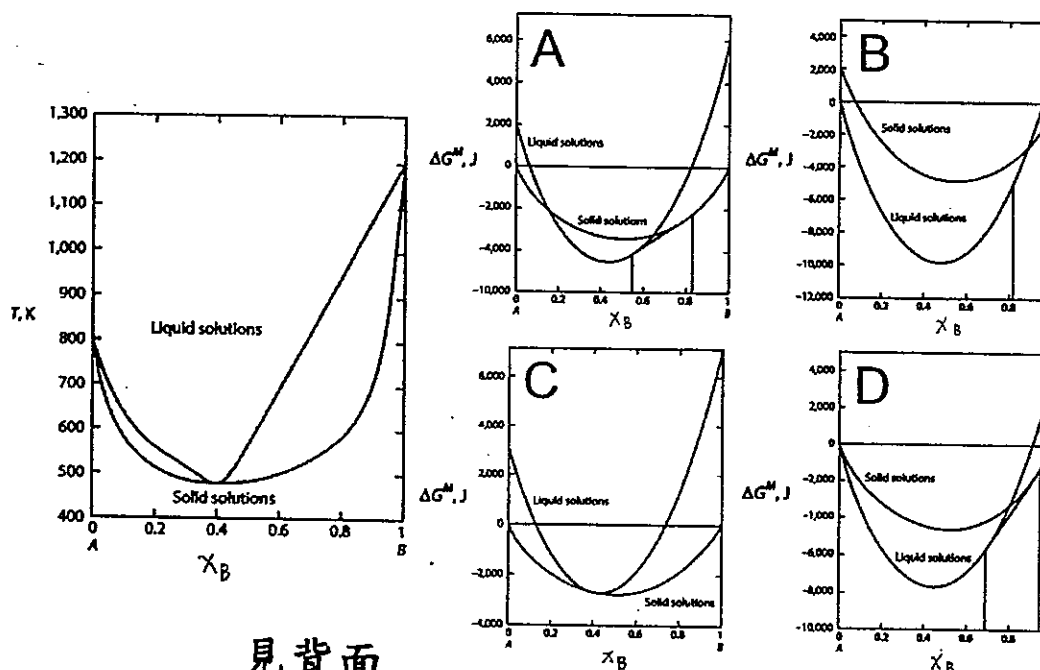
*Hint:* A useful method for converting energy units is to multiply by the ratio of two  $R$ -values that contain the units to be converted.

*Source:* From Lide, D.R., Ed., *CRC Handbook of Chemistry and Physics*, 71st ed., Boca Raton, FL, 1991.

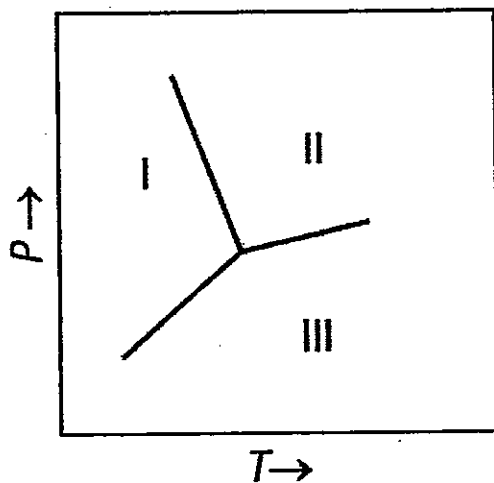
**I. True/False questions 30% (3 points for each)**

Short explanation: True: Select A; False: Select B

1. In the figure shown below, A, B, C, and D are four isothermal plots of molar Gibbs free energy of mixing of a binary phase diagram on the left. Out of these four temperatures, two are greater than 700K.



2. At 1 atm, 0K, we set enthalpies (H) of all elements to 0.
3. Kelvin-Planck statement describes work-heat relationship of an engine.
4. Entropy, volume, pressure, length, Gibbs free energy, and enthalpy all have absolute values.
5. For one mole of ideal gas undergoing an isothermal process, the work done by the system equals  $RT \ln \frac{V_1}{V_0}$ , where  $V_1$  and  $V_0$  stand for final and initial volumes, respectively.
6. During a reversible process, the entropy change of a system is not necessarily 0.
7. For gas decomposition  $2A \rightarrow B + 3C$ ,  $\Delta G^0 = 87030 - 25.8T \ln T - 31.7T$  (J). The equilibrium constant for the reaction at 400 °C is around 4750.
8. Three allotropes,  $\alpha$ ,  $\beta$ ,  $\gamma$  of a certain element are in equilibrium at its triple point (shown below). It is known that  $V_m^\gamma > V_m^\alpha$  and  $S_m^\gamma < S_m^\beta$ . It is correct to say that region I is  $\gamma$ ; region II is  $\alpha$ ; region III is  $\beta$ .



9. The isotopic composition of lead (atomic percent) is as follows:

Atomic Weight	Atomic Percent
204	1.5
206	23.6
207	22.6
208	52.3

The molar configurational entropy of Pb is calculated to be 7.98 J/K.

10. Richard's and Trouton's rules demonstrate that face-centered cubic metals have greater entropy changes than body-centered cubic metals, and in general, the entropy changes of melting are greater than those of boiling.

II. Multiple choices 70% (attention: There may be more than one correct answer)  
Short explanation: There will be 7 questions, each of which is 10 points. One error will cost you 5 points, until there is no more point in that particular question.

- Which statement is correct?
  - When mixing ideal gases in an isolated system, enthalpy of the system increases, while Gibbs free energy decreases.
  - For a binary, regular solution, the change in entropy is equal to the case when the solution is ideal.
  - If the solution is formed exothermically, then activity coefficient ( $\gamma$ ) < 1
  - At constant temperature and pressure, ordering/clustering in a binary solution system can be implied from the value  $\alpha$ . When  $\alpha$  is far larger than 0, then clustering tends to happen.
  - In a binary solution containing A and B, when solute A obeys Henry's law, the solvent B obeys Raoult's law.
- About the application of molar  $c_V$  and  $c_P$ ,
  - $dH = c_P dT + (1 - \alpha T) V dP$
  - $c_P = c_V + \frac{TV\alpha^2}{\beta}$
  - For one mole of ideal gases,  $c_P - c_V = \frac{1}{R}$
  - $c_P - c_V = \left(\frac{\partial V}{\partial T}\right)_P \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$
  - Taking the following table for references, for body-centered cubic iron (molar volume =  $7.1 \text{ cm}^3$ ,  $\alpha = 3 \times 10^{-5} \text{ K}^{-1}$ ), the enthalpy change by increasing the pressure from 1 atm to 100 atm at 298K almost equals that of increasing the temperature from 298K to 300K at constant 1 atm.

Substance	a	$b \times 10^3$	$c \times 10^{-5}$	Range, K
$\text{Cr}_2\text{O}_3$	119.37	9.30	-15.65	298-1800
$\text{Cu}_{(s)}$	22.64	6.28	—	298-1356( $T_m$ )
$\text{Fe}_{(\alpha\delta)}$	37.12	6.17	—	298-1183/1664-1809
$\text{Fe}_{(\gamma)}$	24.47	8.45	—	1187-1664
$\text{Fe}_{(\delta)}$	41.8	—	—	1809-1873

- A rigid and adiabatic container is divided into two compartments of the same volume by a partition.
  - One compartment contains 2 moles of ideal gas A at 2 atm, and the other compartment contains 1 mole of ideal gas B at 1 atm. The increase in entropy

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- when the partition is removed is about 17.3 J/K.
- (B) One compartment contains 1 mole of ideal gas A at 1 atm, and the other compartment contains 1 mole of ideal gas B at 1 atm. The increase in entropy when the partition is removed is about 11.6 J/K.
- (C) One compartment contains 2 moles of ideal gas A at 2 atm, and the other compartment contains 1 mole of the same ideal gas A at 1 atm. The increase in entropy when the partition is removed is about 1.41 J/K.
- (D) One compartment contains 1 mole of ideal gas A at 1 atm, and the other compartment is vacuum. The increase in entropy when the partition is removed is 5.76 J/K.
- (E) One compartment contains 1 mole of ideal gas A at 1 atm, and the other compartment contains 1 mole of the same ideal gas A at 1 atm. The increase in entropy when the partition is removed is 0.
4. 100 moles of hydrogen gas at 298 K are isothermally and reversibly compressed from 30 to 10 liters. While the van der Waals constants for hydrogen are  $a = 0.2461 \text{ liters}^2 \cdot \text{atm} \cdot \text{mole}^{-2}$  and  $b = 0.02668 \text{ liters/mole}$ , and in the range of pressure 0 – 1000 atm, the virial equation for hydrogen is expressed as  $PV = RT (1 + 6.4 \times 10^{-4} P)$ .
- (A) In van der Waals equation,  $b$  is used to correct the interactive forces between molecules.
- (B) By virial equation, the work (absolute value) that must be done on the system to effect the required change in volume is 275 (kJ).
- (C) By virial equation, when the volume equals 30 liters, the pressure is 86 atm.
- (D) Assuming that hydrogen behaves like an ideal gas, the work (absolute value) that must be done on the system to effect the required change in volume is 272 (kJ).
- (E) The ideal gas assumption gives acceptable prediction of the performed work, which is less than 5% deviated from the value calculated from the virial equation or the van der Waals equation.
5. Under constant pressure, when  $T \rightarrow 0\text{K}$ , which holds?
- (A)  $\Delta H \rightarrow \Delta G$
- (B)  $\frac{\partial \Delta S}{\partial T} \rightarrow 0$
- (C)  $\Delta S \rightarrow 0$
- (D)  $\Delta U \rightarrow 0$
- (E)  $\Delta C_p \rightarrow 0$

6. For a miscibility gap in a regular binary solution,

(A) At the critical temperature ( $T_c$ ) of the miscibility gap,  $T_c = \frac{2\alpha}{R}$

(B) The phase transformation mechanisms could be different within the region of miscibility gap.

(C) When plotting the change of Gibbs free energy versus composition, the third order derivative may not be zero at the critical temperature and at the composition where immiscibility becomes imminent.

(D) Spinodal decomposition is a congruent transformation.

(E) If  $T_c = 1000K$ , the Gibbs free energy of mixing at  $X = 0.5$  and  $T = 1100K$  is  $-1282 J$

7. Which is an intensive property?

(A) Molar volume (B) Gibbs free energy (C) Specific heat (D) Pressure (E) Constant volume heat capacity

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