Part A: [10 marks] There is **only one** correct answer for each of the following questions. Please circle it.

1. [1 mark] Which of the following quantity is equal to the exact amount of all energy of an isolated system, *nothing more nothing less*?

1) S 2) G 3) H [✓ 4) U] 5) PV

2. [1 mark] For a constant-volume process in a closed system, there is no expansion work.

[✓ 1) True] 2) False

3. [1 mark] An isolated system undergoes an isothermal process, then,

1) $\Delta S = 0$ 2) $\Delta G = 0$ 3) $\Delta V = 0$ 4) $\Delta P = 0$ [✓ 5) $q = 0$]

4. [1 mark] Nonspontaneous process can never happen.

1) True [✓ 2) False]

5. [1 mark] For a certain process, if $w = -3$ Joules, which of the following must be true for this process:

1) $q = +3$ Joules.
2) $\Delta U = -3$ Joules.
3) $\Delta H = +3$ Joules.
[✓ 4) There is +3 Joules of work being done on the surroundings.]

6. [1 mark] An ideal gas is undergoing an isothermal expansion/compression process in which both the volume and pressure of the gas are to change, indicate which of the following can be used by itself to decide whether or not the process is spontaneous:

1) ΔS_{sys} 2) ΔG 3) ΔU 4) ΔH [✓ 5) $\Delta S_{\text{universe}}$]

7. [1 mark] A gas undergoes a process reversibly at a constant temerature of 298 K. In the course of the process, 298 J of heat is transferred to the surroundings. What is the ΔS for the system?

1) 1 J/K 2) 2 J/K [✓ 3) −1 J/K] 4) −2 J/K

8. [1 mark] For systems containing 1 mole of molecules, which following system has the highest temperature?

1) System containing the fastest moving molecule.
2) System containing a few molecules going at 90% of the speed of light.
3) System with all molecules moving very fast.
[✓ 4) System with highest mean square velocity.]
5) System with lowest mean square velocity.

9. [1 mark] An ideal gas is compressed adiabatically. Which of the following is always true?

[✓ 1) $\Delta U = w$] 2) $\Delta T = 0$ 3) $\Delta U = q$ 4) $q = w$ 5) $\Delta U = \Delta H$

10. [1 mark] The initial and final states of process 1 are the same as initial and final states of process 2. Which of the following is **not** true?

1) $\Delta H_1 = \Delta H_2$ 2) $\Delta G_1 = \Delta G_2$ [✓ 3) $q_1 = q_2$] 4) $\Delta S_1 = \Delta S_2$ 5) $q_1 + w_1 = \Delta U_2$

Part B: **[15 marks]** Two moles of an ideal gas with molar heat capacity $C_{V,m} = 3R/2$, initially confined to a container of volume 6 L and at a temperature 298.15 K, irreversibly expand (or are compressed) against a constant external pressure of 7.10 atm until the final pressure of the gas is equal to the external pressure and the final temperature of the gas is equal to the temperature of the surroundings. During this process the system does 4000 J of work on the surroundings. (**Note:** 1 L = 1.0×10^{-3} m^3)

(a) [5 marks] Evaluate the volume and temperature of the final state of the system.

$$\text{(a)}\begin{cases} w = -p_{ex}\cdot\Delta V = -p_f\cdot\Delta V \;\Rightarrow\; \Delta V = -\dfrac{w}{p_f} = -\dfrac{-4000\times10^3}{7.10\times101325} = 5.56\ \text{L} \\ \Delta V = V_f - V_i \;\Rightarrow\; V_f = \Delta V + V_i = 5.56 + 6 = 11.56\ \text{L}\ (1.156\times10^{-2}\ \text{m}^3) \\ p_f V_f = nRT_f \;\Rightarrow\; T_f = \dfrac{p_f V_f}{nR} = \dfrac{7.10\times11.56}{2\times0.08206} = 500.1\ \text{K}\ (227\,^\circ\text{C}) \\ \text{or: } T_f = \dfrac{p_f V_f}{nR} = \dfrac{7.10\times101325\times11.56\times10^{-3}}{2\times8.314} = 500.1\ \text{K}\ (227\,^\circ\text{C}) \end{cases}$$

(b) [10 marks] Calculate ΔU, ΔH, ΔS, and q for this process.

$$\text{(b)}\begin{cases} \Delta T = T_f - T_i = 500.1 - 298.15 = 202\ \text{K} \\ \Delta U = nC_{V,m}\Delta T = 2\dfrac{3R}{2}\Delta T = 2\times\dfrac{3\times8.314}{2}\times202\ \text{J} = 5.04\ \text{kJ}\ (5038\ \text{J}) \\ q = \Delta U - w = 5.04 - (-4) = 9.04\ \text{kJ}\ (9038\ \text{J}) \\ \Delta H = nC_{p,m}\Delta T = 2\dfrac{5R}{2}\Delta T = 2\times\dfrac{5\times8.314}{2}\times202\ \text{J} = 8.40\ \text{kJ}\ (8397\ \text{J}) \end{cases}$$

$$\begin{cases} \Delta S = nC_{V,m}\ln\dfrac{T_f}{T_i} + nR\ln\dfrac{V_f}{V_i} \\ \quad = 2\times\dfrac{3\times8.314}{2}\times\ln\dfrac{500.1}{298.15} + 2\times8.314\times\ln\dfrac{11.56}{6} = 23.8\ \text{J/K} \end{cases}$$

$$\text{or: }\begin{cases} p_i V_i = nRT_i \;\Rightarrow\; p_i = \dfrac{nRT_i}{V_i} = \dfrac{2\times0.08206\times298.15}{6} = 8.16\ \text{atm} \\ \Delta S = nC_{p,m}\ln\dfrac{T_f}{T_i} + nR\ln\dfrac{p_i}{p_f} = 5R\ln\dfrac{500.1}{298.15} + 2R\ln\dfrac{8.16}{7.10} = 23.8\ \text{J/K} \end{cases}$$

Part C: [12 marks] Consider the following reaction (**Note:** 0 °C = 273.15 K):

$$CH_4\,(g) \leftrightarrows C\,(s,\ \textit{diamond}) + 2\,H_2\,(g)$$

(a) [6 marks] Use the following table to calculate ΔH^0, ΔS^0, and ΔG^0 of the above reaction at 25 °C:

	$\Delta H^0{}_{\text{f,m}}$ [kJ mol^{-1}]	$S^0{}_{\text{f,m}}$ [J K^{-1} mol^{-1}]
C (*s*, *diamond*)	1.895	2.377
CH_4 (*g*)	−74.810	186.260
H_2 (*g*)		130.700

$$\text{(a)}\ \begin{cases} \Delta H^0 = 1.895-(-74.810) = 76.705\ \text{kJ}\ \ (76705\ \text{J}) \\ \Delta S^0 = 2.377+2\times 130.700-186.260 = 77.517\ \text{J/K} \\ \Delta G^0 = \Delta H^0 - T\cdot\Delta S^0 = 76705-298.15\times 77.517\ \text{J} = 53.60\ \text{kJ}\ \ (53593\ \text{J}) \end{cases}$$

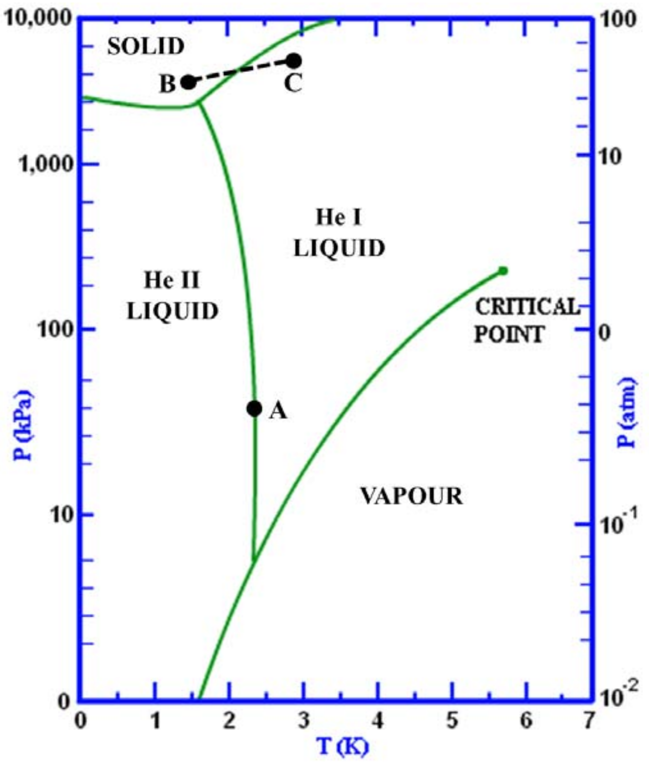
(b) [3 marks] Calculate the equilibrium constant, *K*, of the above reaction at 25 °C. Is this reaction spontaneous at 25 °C and under 1 atm partial pressure for all gases? Justify your answer.

$$\text{(b)}\ \begin{cases} \Delta G^0 = -RT\ln K \ \Rightarrow\ \ln K = \dfrac{-\Delta G^0}{RT} = \dfrac{-53.60\times 10^3}{8.314\times 298.15} = -21.6 \\ K = e^{-21.6} = 4\times 10^{-10} \\ \text{Everything is in standard state} \Rightarrow Q=1 \ \Rightarrow\ \Delta G = \Delta G^0 > 0 \\ \text{Forward reaction is not spontaneous, because } \Delta G^0 > 0 \text{ or } K < 1. \end{cases}$$

(c) [3 marks] In a galaxy far, far away, scientists recently discovered an alien planet. It has been observed that its atmosphere contains CH_4 (*g*) and H_2 (*g*) and its surface temperature can reach 900 °C during some period of the day. Can it rain diamonds on that planet at 900 °C and under 1 atm partial pressure for all gases? Assume ΔH^0 and ΔS^0 are both independent of the temperature. Justify your answer.

$$\text{(c)}\ \begin{cases} \text{Assume } \Delta H^0 \text{ and } \Delta S^0 \text{ are both independent of } T: \\ \Delta G^0_{900^\circ\text{C}} = \Delta H^0 - T\cdot\Delta S^0 = 76705-1173.15\times 77.517\ \text{J} = -14.2\ \text{kJ}\ \ (-14234\ \text{J}) \\ \text{Everything is in standard state } (Q=1) \ \Rightarrow\ \Delta G_{900^\circ\text{C}} = \Delta G^0_{900^\circ\text{C}} < 0 \\ \text{Thus, forward reaction becomes spontaneous.} \\ \text{Therefore, it can rain diamonds at } 900^\circ\text{C} \text{ \& standard states.} \end{cases}$$

Part D: [3 marks] In the phase diagram for helium (He) below, there are two distinct liquid phases, “He I” and “He II”, in addition to the solid phase and vapour phase.



(a) [1 mark] The broken line connecting points **B** and **C** signifies a constant-volume process between the solid (**B**) and the liquid He I (**C**) phases, **B** → **C**. Should the change in internal energy (ΔU) for **B** → **C** be positive, negative, or zero? (circle one below)

[✓ 1) positive] 2) negative 3) zero

$$\boxed{\text{(a)}\ \ \Delta T_{\mathrm{B}\to\mathrm{C}} > 0 \quad \Rightarrow \quad q_V = C_V \cdot \Delta T_{\mathrm{B}\to\mathrm{C}} > 0 \quad \Rightarrow \quad \Delta U = q_V > 0}$$

(b) [1 mark] At point **A** on the boundary curve separating the two liquid phases, is $\Delta S_{\text{universe}}$ positive, negative, or zero for the phase transition: He I (l) → He II (l) at constant pressure? (circle one below)

1) positive 2) negative [✓ 3) zero]

$$\boxed{\text{(b)}\ \ \Delta G_{\mathrm{A}} = 0 \quad \Rightarrow \quad \Delta S_{\text{universe}} = 0}$$

(c) [1 mark] At point **A** on the boundary curve separating the two liquid phases, is ΔS_{system} positive, negative, or zero for the phase transition: He I (l) → He II (l) at constant pressure? (circle one below)

1) positive [✓ 2) negative] 3) zero

$$\boxed{\text{(c)}\ \ \Delta H_{\mathrm{I}\to\mathrm{II}} < 0 \quad \Rightarrow \quad \Delta S_{\mathrm{A}} = \frac{\Delta H_{\mathrm{I}\to\mathrm{II}}}{T_{\mathrm{A}}} < 0}$$