

**Instructions:**

There are five questions in total. Complete the first question, and then complete three of the four remaining questions. Each question is worth 25% of the total mark (i.e., 5 marks out of a total possible 20 marks). There is a bonus question at the end worth an additional **2.0 marks** that you may attempt if you have time remaining. Place all answers in the test booklets provided, **surrounding final answers with a clearly marked box**. Please refer to the attached information sheets for physical constants and useful equations. Good luck!

1. **(5 marks, you must attempt this question)**
- (a) For the reversible adiabatic expansion of a perfect gas, state (where possible) whether  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta S_{\text{sur}}$ ,  $\Delta S_{\text{univ}}$ ,  $\Delta A$  and  $\Delta G$  are positive, negative or equal to zero. Show all reasoning.
- (b) Given that  $T_{\text{fus}} = 0\text{ }^\circ\text{C}$ , state whether  $\Delta S$ ,  $\Delta S_{\text{sur}}$  and  $\Delta S_{\text{univ}}$  are equal to, greater than or less than zero (where possible) for:
- (i) melting of ice at  $T = 0\text{ }^\circ\text{C}$
- (ii) melting of ice at  $T = 10\text{ }^\circ\text{C}$
- and briefly explain your answers.
- (c) Derive the fundamental equation  $dG = Vdp - SdT$  and the associated Maxwell relation.

2. **(5 marks)** Consider a system consisting of 1.5 mol of  $\text{CO}_2$  (g), initially at  $15\text{ }^\circ\text{C}$  and 9.0 atm, confined to a cylinder of gas of cross section  $100.0\text{ cm}^2$ . The sample is allowed to expand adiabatically against an external pressure of 1.5 atm until the piston has moved outwards through 15 cm. Assume that  $\text{CO}_2$  can be treated as a perfect gas with  $C_{v,m} = 28.8\text{ J K}^{-1}\text{ mol}^{-1}$ . Calculate (a)  $q$ , (b)  $w$ , (c)  $\Delta U$ , (d)  $\Delta T$  and (e)  $\Delta S$ .

3. **(5 marks)** Starting from the fundamental equation for  $dH$ , and show that

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1 - \alpha T)$$

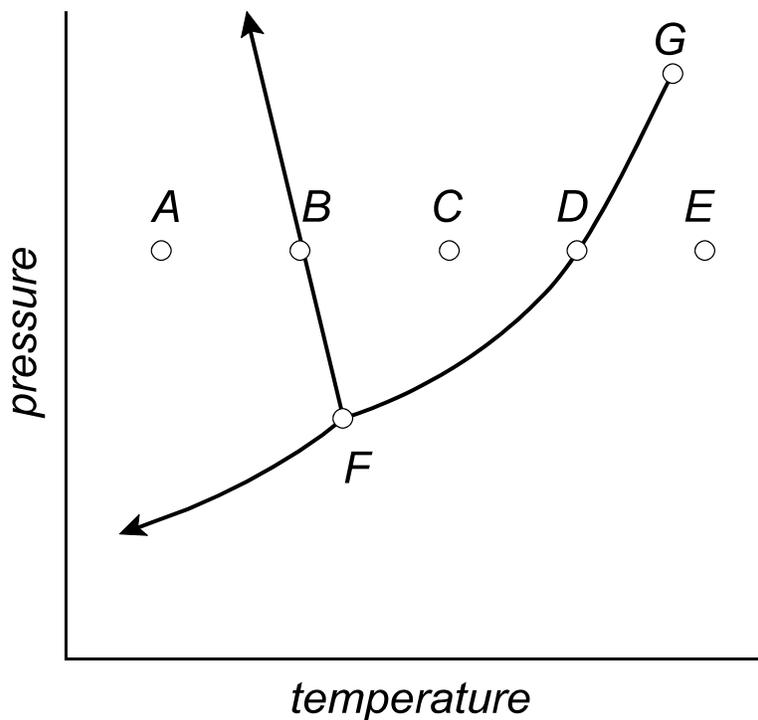
where  $\alpha$  is the expansion coefficient.

4. **(5 marks)** The standard enthalpy of combustion of solid urea,  $\text{CO}(\text{NH}_2)_2$  is  $-632\text{ kJ mol}^{-1}$  at 298 K ( $\text{CO}(\text{NH}_2)_2$  (s) +  $(3/2)\text{O}_2$  (g)  $\rightarrow$   $\text{CO}_2$  (g) +  $2\text{H}_2\text{O}(\ell)$  +  $\text{N}_2$ (g)) and its standard molar entropy is  $S_m^\circ = 104.60\text{ J K}^{-1}\text{ mol}^{-1}$ . Calculate the standard Gibbs energy of formation of urea at 298 K.

*(continued next page)*

5. **(5 marks) (Phase diagram problem)**

- (a) In the low pressure phase diagram of H<sub>2</sub>O below, explain the significance of points A through E.
- (b) Explain the what the points F and G signify.
- (c) Why is the slope of the line along FB negative for H<sub>2</sub>O?
- (d) Respond true or false to the following statements, and explain your reasoning:
- (i) The chemical potential at point E,  $\mu(E)$ , is always greater than the chemical potential at point C,  $\mu(C)$ .
  - (ii) At point B,  $\mu(A) = \mu(C)$ .
  - (iii) For an increase in temperature at constant pressure (i.e., A to E), the entropy increases.
  - (iv) It is possible to obtain supercritical fluid in an open vessel.



6. **(2 marks)** Given that  $\phi = f/p$  and  $Z = pV_m/RT$ , prove that

$$\ln \phi = \int_0^p \left( \frac{Z - 1}{p} \right) dp$$

***End of Mid-Term #2***

## Useful information

### Units of pressure:

<i>Name</i>	<i>Symbol</i>	<i>Value</i>
pascal	1 Pa	1 N m <sup>-2</sup> , 1 kg m <sup>-1</sup> s <sup>-2</sup>
bar	1 bar	10 <sup>5</sup> Pa
atmosphere	1 atm	101325 Pa
torr	1 Torr	101325/760 Pa = 133.32 Pa
mm of mercury	1 mm Hg	133.322 Pa
pound per sq inch	1 psi	6.894 757 kPa

### *R with different units*

8.31451	J K <sup>-1</sup> mol <sup>-1</sup>
8.20578 x 10 <sup>-2</sup>	L atm K <sup>-1</sup> mol <sup>-1</sup>
8.31451 x 10 <sup>-2</sup>	L bar K <sup>-1</sup> mol <sup>-1</sup>
8.31451	Pa m <sup>3</sup> K <sup>-1</sup> mol <sup>-1</sup>
62.364	L Torr K <sup>-1</sup> mol <sup>-1</sup>
1.98722	cal K <sup>-1</sup> mol <sup>-1</sup>

$R$  is related to the Boltzmann constant,  $k$ , by  $R = k \cdot N_A$ , where

$$k = 1.3806 \times 10^{-23} \text{ J K}^{-1}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\text{amu} = 1.66057 \times 10^{-27} \text{ kg}$$

$$1 \text{ m} = 100 \text{ cm}, 1 \text{ m}^2 = 10000 \text{ cm}^2, 1 \text{ m}^3 = 1000000 \text{ cm}^3, 1 \text{ m}^3 = 10^3 \text{ L}$$

### Unit prefixes

m	milli	10 <sup>-3</sup>
μ	micro	10 <sup>-6</sup>
n	nano	10 <sup>-9</sup>
p	pico	10 <sup>-12</sup>

<b>Data Table</b>	<b><math>M</math></b>	<b><math>\Delta_f H^\circ</math> (kJ mol<sup>-1</sup>)</b>	<b><math>S_m^\circ</math> (J K<sup>-1</sup> mol<sup>-1</sup>)</b>
Ar	39.948	0	154.84
C (s)	12.011	0	5.740
H <sub>2</sub> (g)	2.016	0	130.684
O <sub>2</sub> (g)	31.999	0	205.138
N <sub>2</sub> (g)	28.013	0	191.61
CO <sub>2</sub> (g)	44.010	-393.51	213.74
H <sub>2</sub> O (l)	18.015	-285.83	69.91