

$$1 \text{ atm} = 760 \text{ mmHg} = 1.01 \times 10^5 \text{ N m}^{-2}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

- 1 The vapor pressure of water is given in the following relation:

$$\ln P = 25.275 - \frac{5132}{T}$$

The vapor pressure of ice is given in the following relation:

$$\ln P = 28.868 - \frac{6133}{T}$$

The units of  $P$  and  $T$  are  $\text{Pa}$  and  $\text{K}$  for these two equations, respectively.

- 1.1 Estimate the normal boiling temperature.
- 1.2 Estimate the pressure and the temperature at the triple point.
- 1.3 Calculate the enthalpy of vaporization at the normal boiling temperature.
- 1.4 Calculate the enthalpy of fusion at the triple point.
- 1.5 Calculate the difference between the heat capacity of water and that of ice.

1.1 By  $\ln P = 25.275 - \frac{5132}{T} \Rightarrow \text{put } P = 1.01 \cdot 10^5 \text{ N m}^{-2} \Rightarrow 11.52 = 25.275 - \frac{5132}{T}, T = \underline{373.1 \text{ K}}$

1.2 By  $P_{\text{triple } S \rightarrow V} = P_{\text{triple } L \rightarrow V} \Rightarrow 25.275 - \frac{5132}{T} = 28.868 - \frac{6133}{T} \Rightarrow T_{\text{triple}} = \underline{273.6 \text{ K}}$

1.3  $\frac{d \ln P}{dT} = \frac{5132}{T^2} = \frac{\Delta H_{L \rightarrow V}}{RT^2} \Rightarrow \Delta H_{L \rightarrow V} = 5132 \cdot 8.314 = \underline{42667.45 \text{ J/mol}}$

1.4  $\Delta H_{S \rightarrow L} = \Delta H_{S \rightarrow V} - \Delta H_{L \rightarrow V}, \frac{d \ln P}{dT} = \frac{6133}{T^2} = \frac{\Delta H_{S \rightarrow V}}{RT^2} \Rightarrow \Delta H_{S \rightarrow V} = \underline{6133 R}$

$\therefore \Delta H_{S \rightarrow L} = 6133 R - 5132 R = 1001 R = \underline{8322.3 \text{ J/mol}}$

1.5  $C_{pL} - C_{pS} = \Delta C_{pS \rightarrow L} = \left( \frac{\partial \Delta H_{S \rightarrow L}}{\partial T} \right)_P = \underline{0 \text{ J/mol} \cdot \text{K}}$

$\ln P_{\text{triple}} = 25.275 - \frac{5132}{273.6} = 6.854$   
 $P_{\text{triple}} = \underline{947.8 \text{ N/m}^2}$

2 Two ideal gases are mixed in the container at the constant temperature of T. The initial states of the two gases are:

Gas A: 2 atm,  $V \text{ m}^3$

Gas B: 1 atm,  $V \text{ m}^3$

The volume of the container is  $2V \text{ m}^3$ . Assume that T and V are known parameters.

2.1 Calculate the change of the total Gibbs free energy.

2.2 Calculate the change of the total enthalpy.

2.3 Calculate the change of the total entropy.

$$2.1 \text{ By } \Delta G'_{\text{mix}} = n_A RT \ln \frac{P_A}{P_A'} + n_B RT \ln \frac{P_B}{P_B'} \quad n_A = \frac{2V}{RT}, \quad n_B = \frac{V}{RT}, \quad n_A : n_B = 2 : 1$$

$$\Rightarrow x_A = \frac{2}{3}, \quad x_B = \frac{1}{3}, \quad P'(2V) = \left( \frac{2V}{RT} + \frac{V}{RT} \right) RT, \quad P' = \frac{3}{2} \text{ atm}$$

$$\therefore P_A = x_A P' = \frac{2}{3} \times \frac{3}{2} = 1 \text{ atm}, \quad P_B = x_B P' = \frac{1}{3} \cdot \frac{3}{2} = \frac{1}{2} \text{ atm}$$

$$\Rightarrow \Delta G'_{\text{mix}} = \left( \frac{2V}{RT} \right) RT \ln \left( \frac{1}{2} \right) + \left( \frac{V}{RT} \right) RT \ln \left( \frac{1/2}{1} \right) = 3V \ln \frac{1}{2} = -2.08 V (\text{atm} \cdot \text{m}^3) = \underline{\underline{-2.1 \cdot 10^5 \text{ J}}}$$

$$2.2 \text{ Because of ideal gas, } \Delta H_{\text{mix}} = 0 \text{ J} *$$

$$2.3 \quad \Delta S'_{\text{mix}} = \frac{-\Delta G'_{\text{mix}}}{T} = \frac{2.1 \cdot 10^5 \cdot V}{T} \text{ J/K} *$$