Ch7

PHASE EQUILIBRIUM IN A ONE-COMPONENT SYSTEM

7.1 Introduction

Temp. of a sys
= a measure of the potential at intensity of heat in the system.

Pressure of a sys
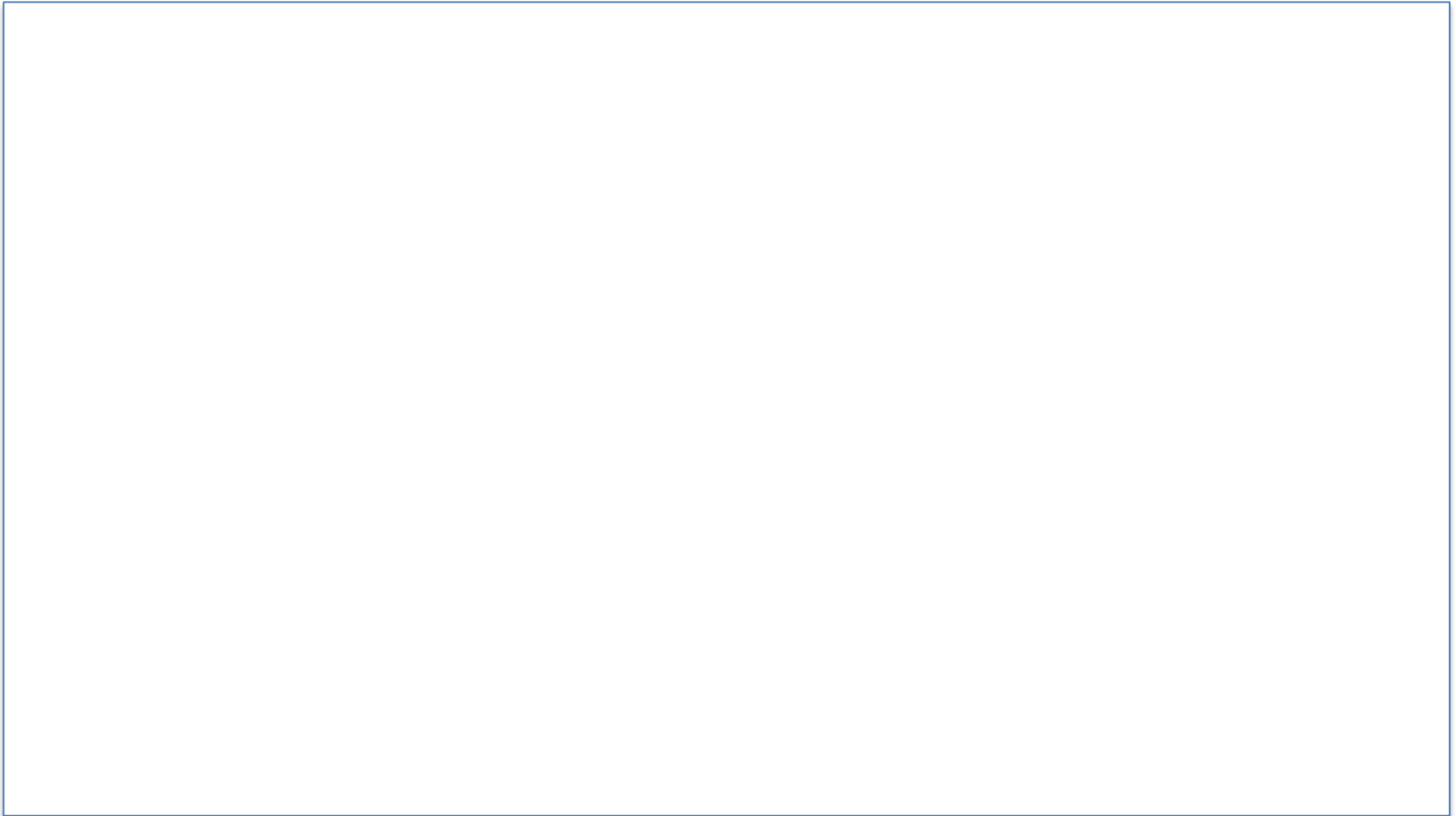= a measure of its tendency toward movement

Chemical potential of a sys
= a measure of its tendency toward of the spec to leave the phase.

G – T – P to examine the equil'm

7.2 The Variation of Gibbs Free Energy with T at Const. P

P= 1 atm T=0°C, ice and water equil'm

7.2 The Variation of Gibbs Free Energy with T at Const. P

$$dG = -SdT + VdP + \sum \mu_i dn_i \qquad (5.25)$$

at const. T, P $\qquad$ dG=$\sum\mu$idni

Integrate for min G'

$$G' = \sum \mu_i n_i$$

- For the ice & water sys.

$$G' = \mu_{H_2O_{(l)}} n_{H_2O_{(l)}} + \mu_{H_2O_{(l)}} n_{H_2O_{(l)}} \qquad (7.3)$$

7.2 The Variation of Gibbs Free Energy with T at Const. P

$$G' = n_{H_2O_{(s)}}G_{H_2O_{(s)}} + n_{H_2O_{(l)}}G_{H_2O_{(l)}}$$
$$G' = \mu_{H_2O_{(s)}}n_{H_2O_{(s)}} + \mu_{H_2O_{(l)}}n_{H_2O_{(l)}}$$

7.2 The Variation of Gibbs Free Energy with T at Const. P

$$\Delta G = G_{H_2O_{(l)}} - G_{H_2O_{(s)}} < 0 \qquad G_{H_2O_{(l)}} < G_{H_2O_{(s)}} \qquad T_m > T$$

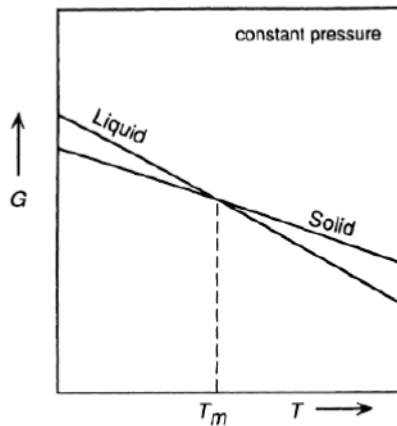$$G_{H_2O_{(l)}} > G_{H_2O_{(s)}} \qquad T_m < T$$

Figure 7.1 Schematic representation of the variations of the molar Gibbs free energies of solid and liquid water with temperature at constant pressure.

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{c_p}{T}$$
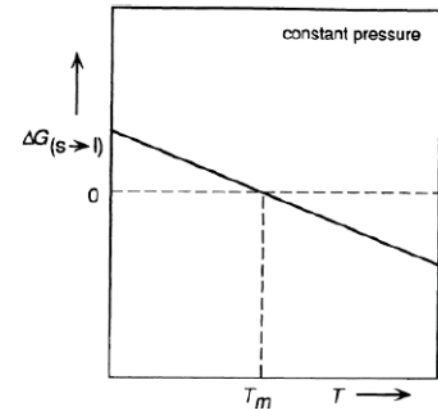

Figure 7.2 Schematic representation of the variation of the molar Gibbs free energy of melting of water with temperature at constant pressure.

7.2 The Variation of Gibbs Free Energy with T at Const. P

slope $\left(\dfrac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$ the energy change in rxn

The slope = negative → means $S_{H_2O_{(l)}} > S_{H_2O_{(s)}}$

- For the state in which the solid and liquid phases of a one-comp. sys are in equil'm w/ one another

$$G = H - TS \qquad\qquad G_{(l)} = H_{(l)} - TS_{(l)}$$

$$G_{(s)} = H_{(s)} - TS_{(s)}$$

For the rxn s→ l.

$$\Delta G_{(s \to l)} = \Delta H_{(s \to l)} - T\Delta S_{(s \to l)}$$

Since $\Delta G_{(s \to l)} = 0$ at T_m.

$$\Delta H_{(s \to l)} = T_m \Delta S_{(s \to l)} \qquad\qquad (7.4)$$

7.2 The Variation of Gibbs Free Energy with T at Const. P

For H_2O figure 7.3 (a, b)
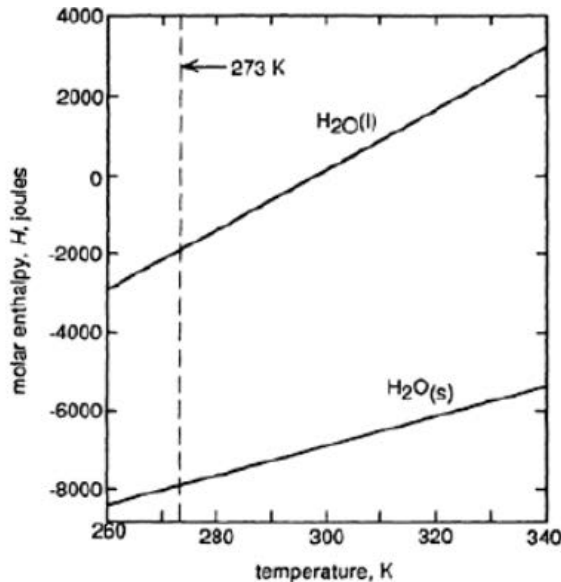
for convenience $H_{(l), 298} = 0$

Figure 7.3 The variations, with temperature, of the molar enthalpies of solid and liquid water at 1 atm pressure. The molar enthalpy of liquid water at 298 K is arbitrarily assigned the value of zero.

$$\Delta H_m = \Delta H_{(s \to l)} = 6008 \text{ joules at } 273 \text{ K}$$

$$S_{H_2O(l), 298 \text{ K}} = 70.08 \text{ J/K}$$

$$S_{H_2O(s), 298 \text{ K}} = 44.77 \text{ J/K}$$

$$c_{p, H_2O(l)} = 75.44 \text{ J/K}$$

$$c_{p, H_2O(s)} = 38 \text{ J/K}$$

$$H_{(l), T} = \int_{298}^{T} c_{p,(l)} dT = 75.44(T - 298) \text{ J}$$

$$H_{(s), T} = \int_{298}^{273} c_{p,(l)} dT - \Delta H_m + \int_{273}^{T} c_{p,(s)} dT$$

$$= 75.44(273 - 298) - 6008 + 38(T - 273) \text{ J}$$

(7.4)

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7.2 The Variation of Gibbs Free Energy with T at Const. P

Similarly $\Delta S_{s \to l, T} = S_{(l), T} - S_{(s), T}$

$$S_{(l), T} = S_{(l), 298} + \int_{298}^{T} \frac{Cp(l)}{T}\, dT$$

$$S_{(s), T} = S_{(S), 298} + \int_{298}^{T} \frac{Cp(s)}{T}\, dT$$

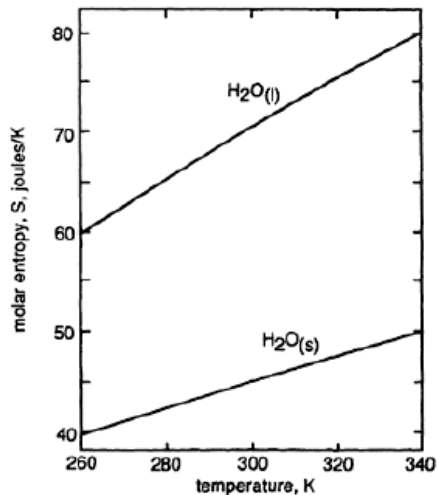Above Tm, the S contribution outweighs the H contribution to ΔG

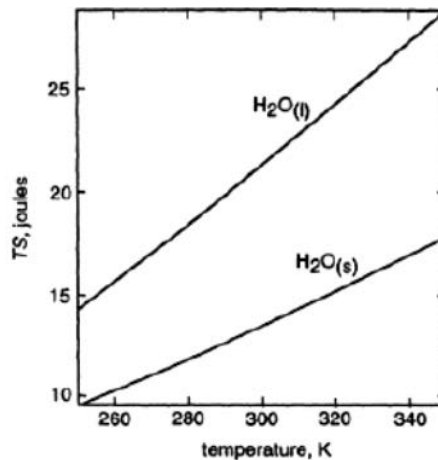**Figure 7.4** The variations, with temperature, of the molar entropies of solid and liquid water at 1 atm pressure.

Figure 7.5 The variation h, with temperature, of TS for solid and liquid water at 1 atm pressure.
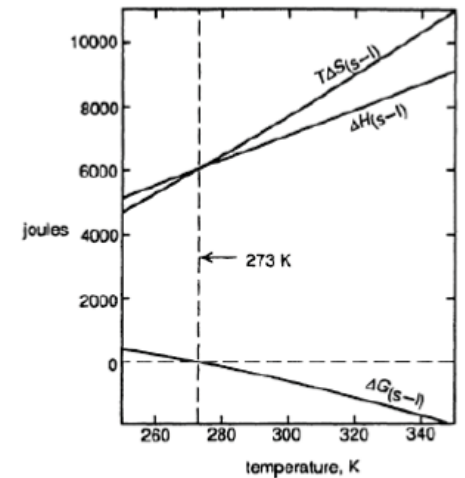
Figure 7.6 The variations, with temperature, of the molar Gibbs free energy of melting, the molar enthalpy of melting, and $T \times$ the molar entropy of melting of water at 1 atm pressure.

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7.3 The Variation of Gibbs F. E. with P at Const. T

- Mixture of ice and water at 0°C, 1 atm as P↑ than 1 atm the sys. try to be w/ less ice at 0°C that has a larger molar vol. than water.

$$\left(\frac{\partial G_{(l)}}{\partial P}\right)_T = V_{(l)} \quad \text{and} \quad \left(\frac{\partial G_{(s)}}{\partial P}\right)_T = V_{(s)}$$

- i.e., the rate of increase of G with increase in P at const. T = the molar V of the phase at T and the P

7.3 The Variation of Gibbs F. E. with P at Const. T

- For the change of the state solid →liquid

$$\left(\frac{\partial \Delta G_{(s \to l)}}{\partial P} \right)_T = \Delta V_{(s \to l)}$$

constant temperature, 0°C

- $\Delta V_{(s \to l)}$ for H_2O at 0°C is negative, the ice melts when the P is increased
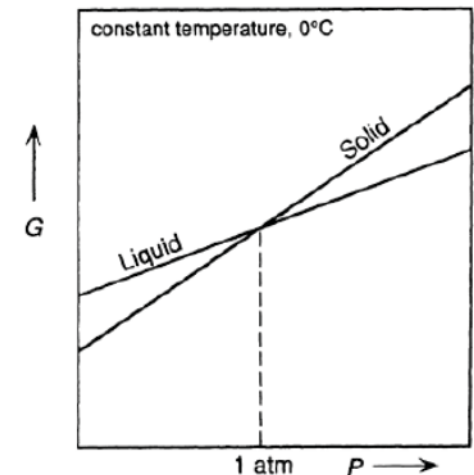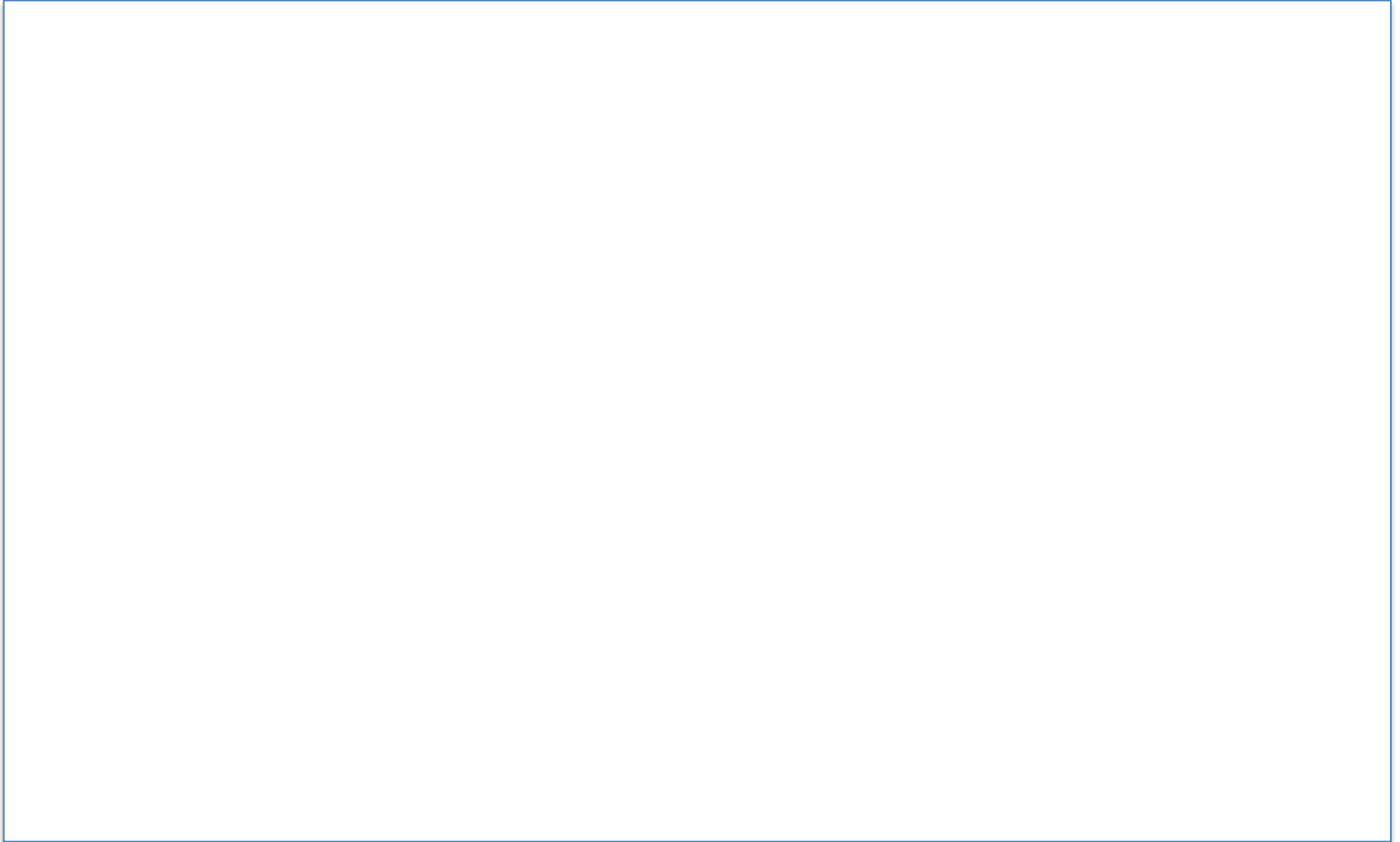
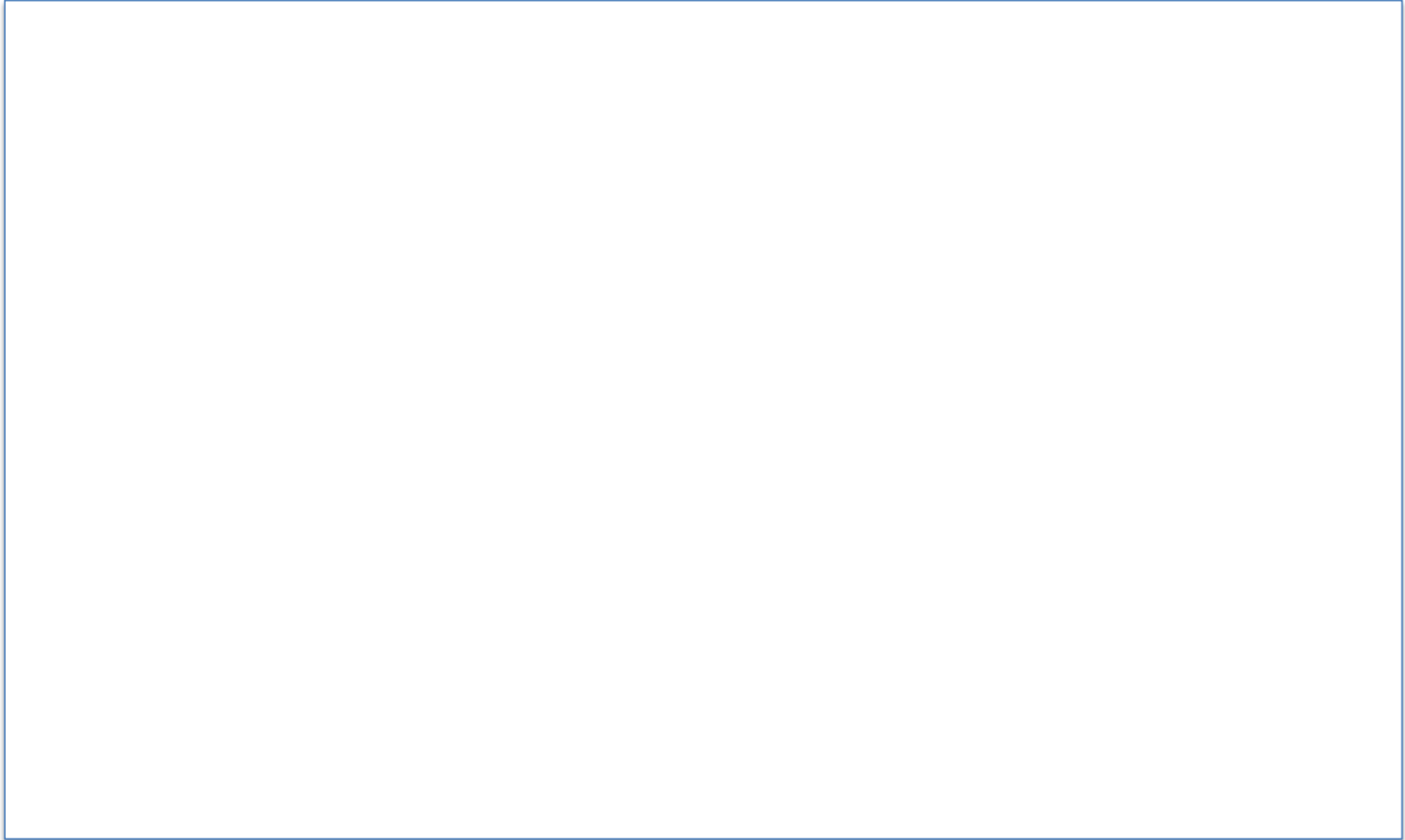**Figure 7.7** Schematic representation of the variations of the molar Gibbs free energies of solid and liquid water with pressure at constant temperature.

7.4 Gibbs Free Energy as a Function of T & P

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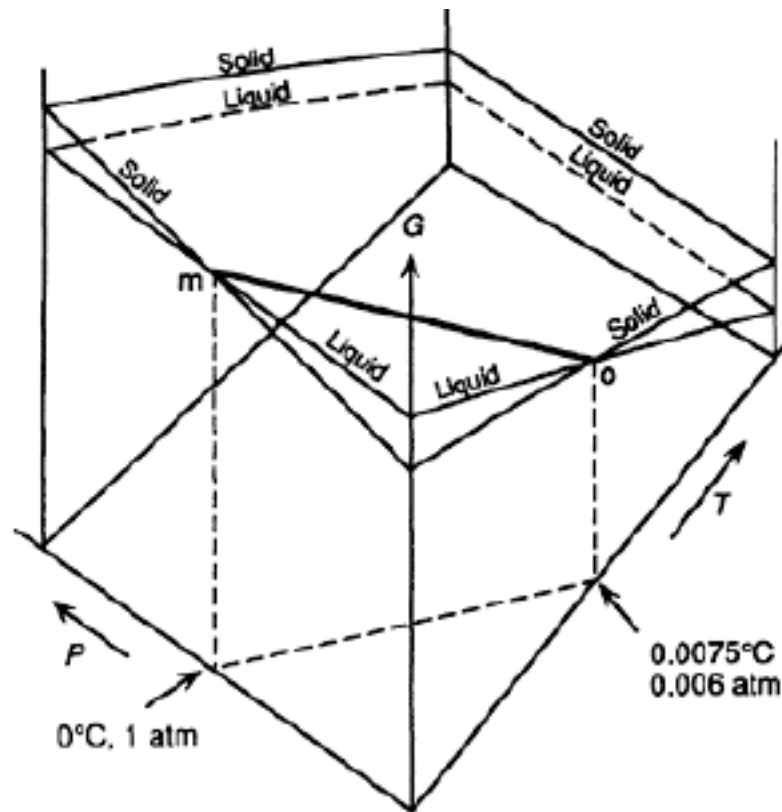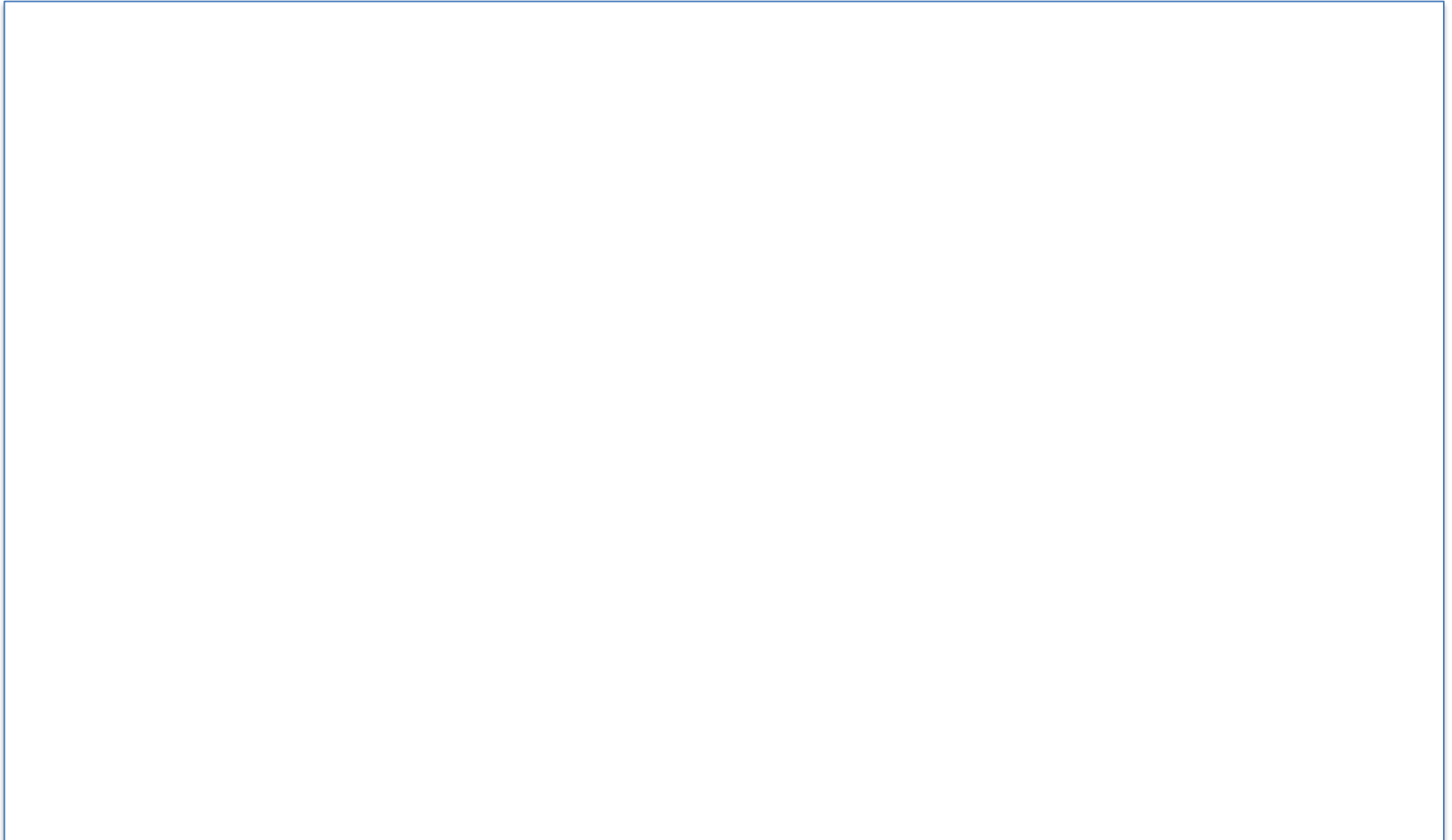**Figure 7.8** Schematic representation of the equilibrium surfaces of the solid and liquid phases of water in *G-T-P* space.

7.5 Equil'm Between the Vapor Phase and a Condensed Phase

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Chapter 8

The behavior of Gases.

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES
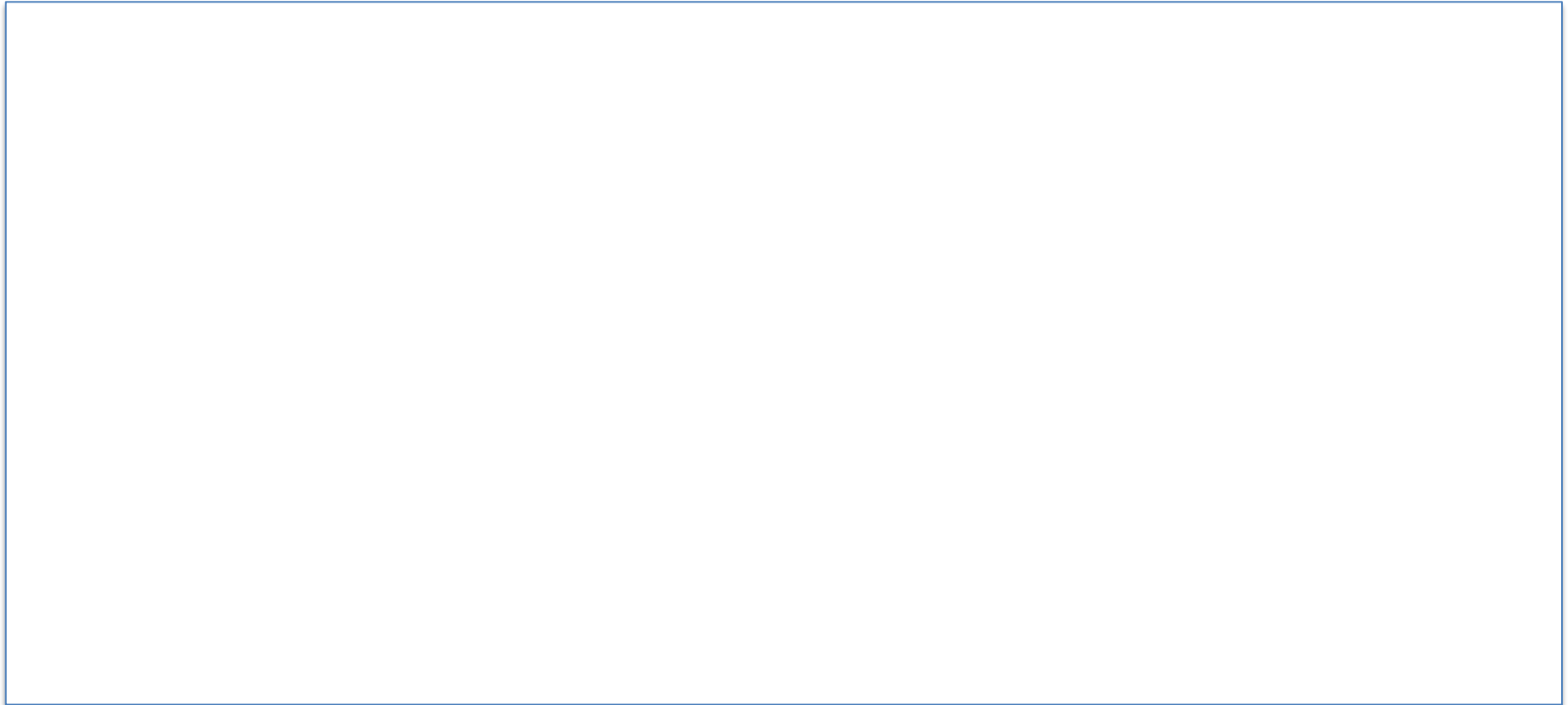
8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

As no absolute values for Gibbs free energies (only ΔG can be measured), it is convenient to choose an arbitrary reference state.

This reference state called "the standard state": the state of 1 mole of pure gas at 1 atm and the T of interest.

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

(A) Mixtures of Ideal Gases

(1) Mole fraction

: The mole fraction, X_i, of the component i defined as the ratio of the number of moles of i in the system to the total number of moles of all of the components in the system.

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

$$X_B = \frac{n_B}{n_A + n_B + n_C}$$

$$X_C = \frac{n_C}{n_A + n_B + n_C}$$

$$X_A + X_B + X_C = 1$$

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

(2) Dalton's law of partial pressures.

The *P* exerted by a mixture of ideal gases = the sum of the pressures exerted by each of the individual component gases.

$$P = p_A + p_B + p_C$$

Consider a fixed V', at T, with n_A moles of an ideal gas A.

$$P = \frac{n_A RT}{V'} \qquad (8.11)$$

If, to this const. V containing n_A moles of gas A, n_B moles of ideal gas B are added,

$$P = p_A + p_B = (n_A + n_B)\frac{RT}{V'} \qquad (8.12)$$

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

From (8.11) & (8.12)

$$\frac{p_A}{p_A + p_B} = \frac{n_A}{n_A + n_B}$$

thus, for the gas A in the mixture,

$$\frac{p_A}{P} = X_A \qquad \text{or} \qquad p_A = X_A P \qquad (8.13)$$

Eq. (8.13): Dalton's law of partial pressures.
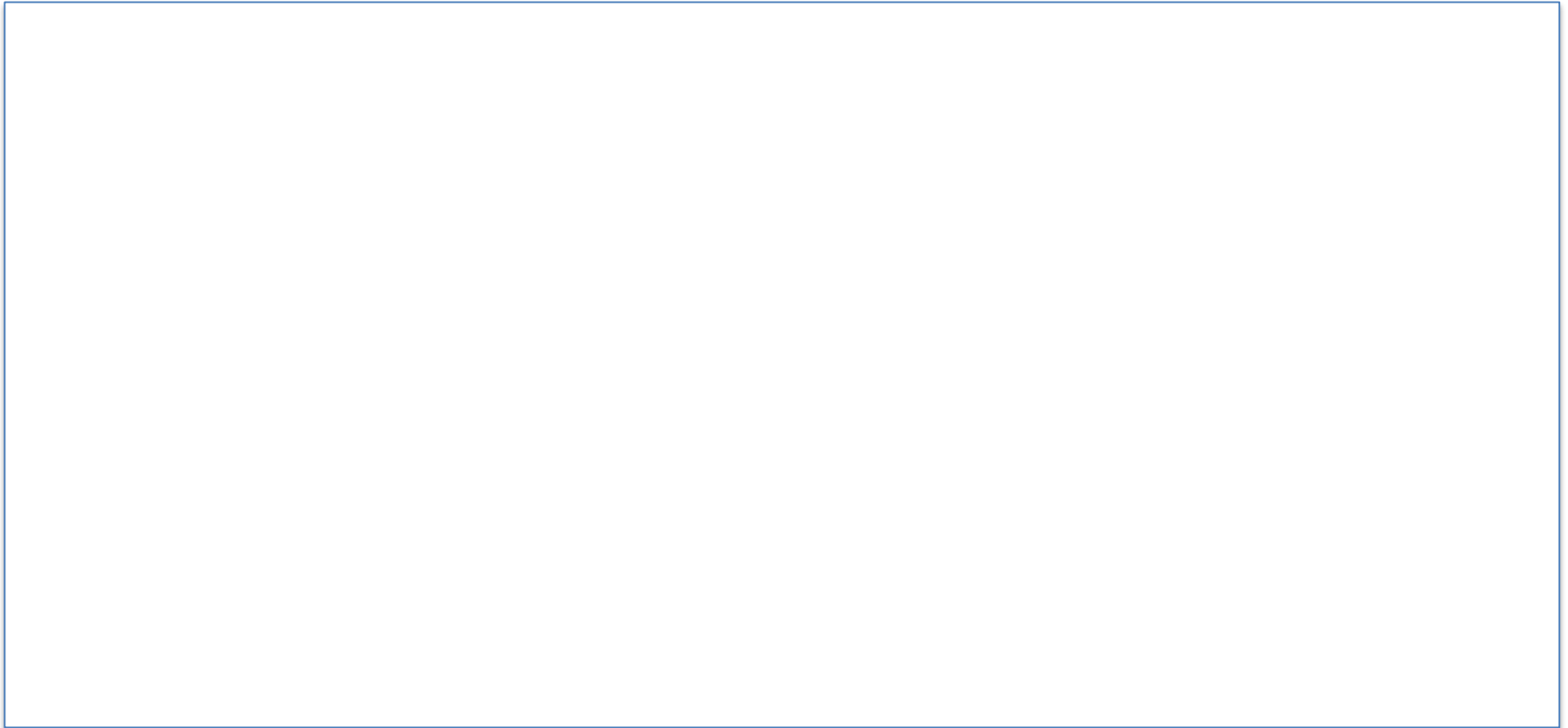
8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

(3) Partial molar quantities

The molar value of any extensive state property of a component of a mixture is called "the partial molar value of the property."

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

the partial molar Gibbs free energy of a component in a mixture equals the chemical potential of the component in the mixture.

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

G, a state function: the order of partial differentiation-no influence on the result

$$\left[\frac{\partial}{\partial n_i} \left(\frac{\partial G'}{\partial P} \right)_{T.comp} \right]_{T.P.n_j} = \left[\frac{\partial}{\partial P} \left(\frac{\partial G'}{\partial n_i} \right)_{T.P.n_j} \right]_{T.comp}$$

$$= \left(\frac{\partial \overline{G}_i}{\partial P} \right)_{T.comp}$$

Hence

$$\left(\frac{\partial \overline{G}_i}{\partial P} \right)_{T.comp} = \overline{V}_i \qquad dG = -SdT + VdP + \sum \mu_i dn_i \quad (5.25)$$
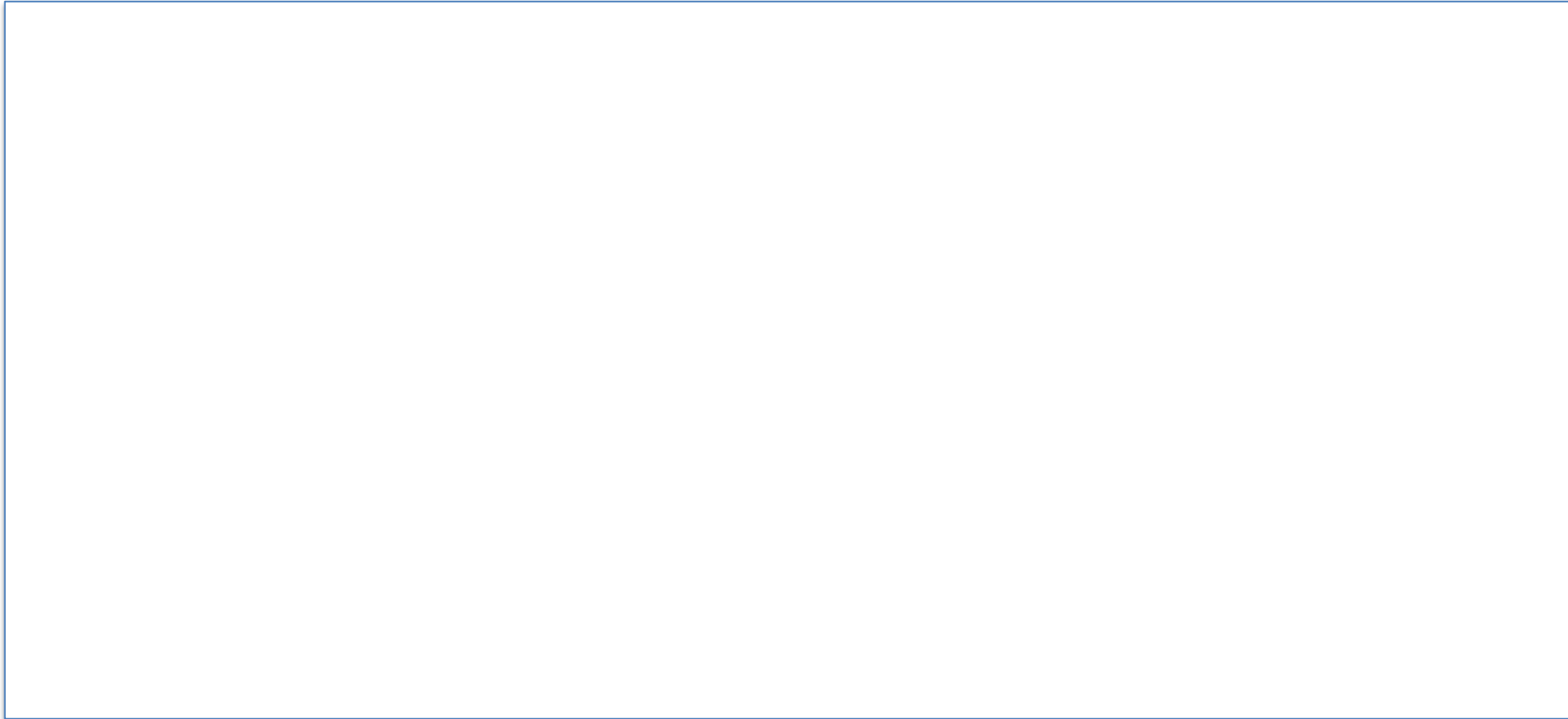
which is simply the application of Eq. (5.25) to the component i in the system.

Thus, for the ideal gas A in a mixture of ideal gases,

$$d\overline{G}_A = \overline{V}_A dP$$

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

The partial molar volume, $\overline{V}_A$, in a gas mixture is

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

- **The Heat of Mixing of Ideal Gases**

each component gas in a mixture of ideal gasses

$$\overline{G}_i = G_i^\circ + RT \ln X_i + RT \ln P$$

where P is the total pressure of the gas mixture at T.

Dividing by T and differentiating with respect to T at const. P and composition

But, from Eq. (5.37)

$$\frac{\partial(\overline{G}_i/T)}{\partial T} = \frac{\partial(G_i^\circ/T)}{\partial T}$$

$$\left[\frac{\partial(G_i^\circ/T)}{\partial T} \right]_{P.\text{comp}} = -\frac{H_i^\circ}{T^2} \quad \text{and} \quad \left(\frac{\partial \overline{G}_i/T}{\partial T} \right)_{P.\text{comp}} = -\frac{\overline{H}_i}{T^2} \quad (8.17)$$

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

And thus

$$\overline{H}_i = H_i^\circ \qquad (8.18)$$

i.e., the partial molar H of ideal gas i in a mixture of ideal gases = the molar H of pure i,

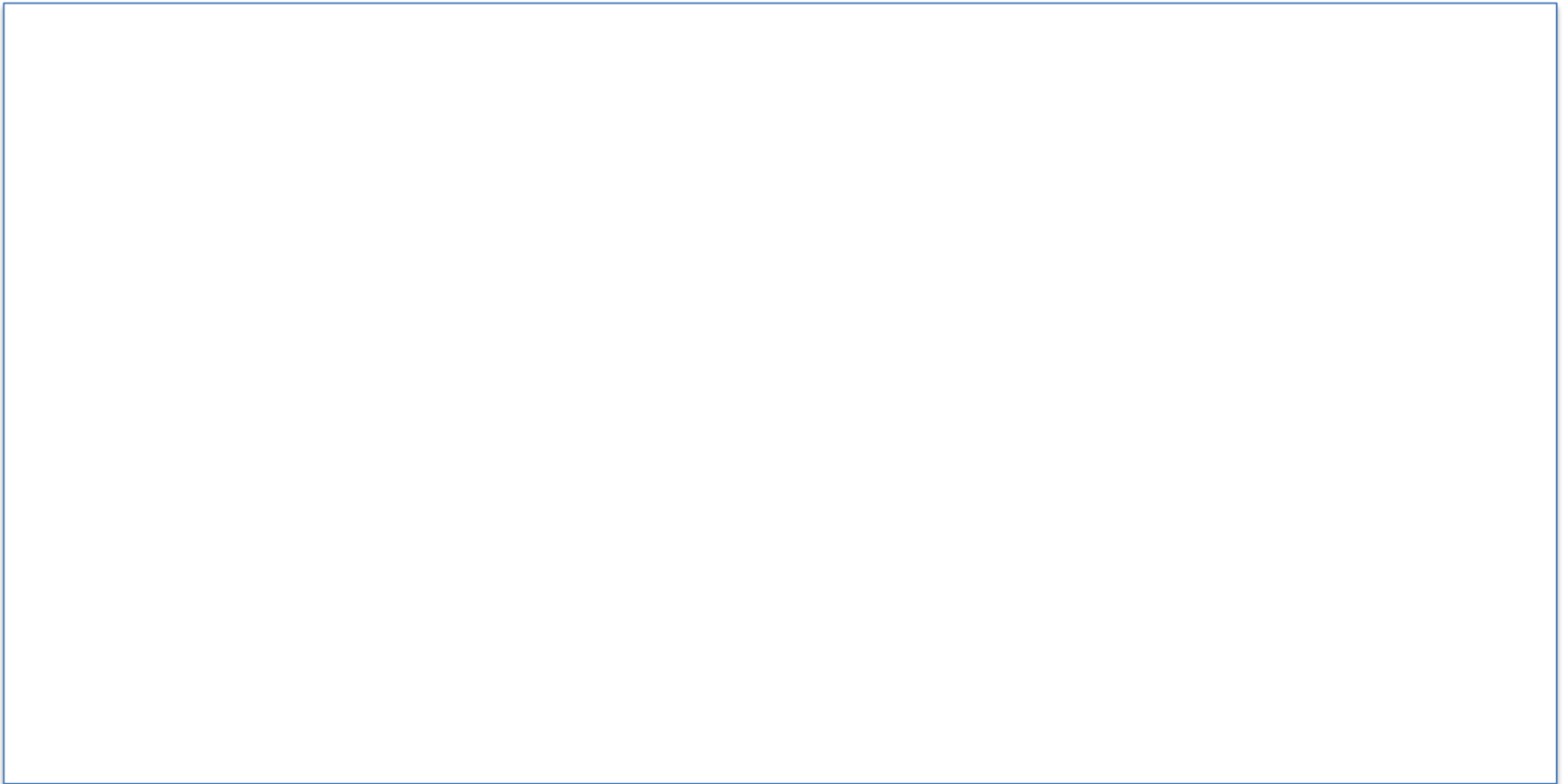the H of the gas mixture = the sum of the H of the component gases before mixing, i.e.,

$$\Delta H'^{mix} = \sum_i n_i \overline{H}_i - \sum_i n_i H_i^\circ = 0 \qquad (8.19)$$

$\overline{H}_i = f(T), \neq f(comp), \neq f(P)$

The zero heat of mixing of ideal gases: from the fact that the particles of an ideal gas do not interact with one another.

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

- **The Gibbs Free Energy of Mixing of Ideal Gases**

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

ΔG^{mix} depends on n_i and p_i for each gas.

If, before mixing, $p_i = p_j = p_k = \dots$ and mixing is carried out at total const. V such that p_{mix} = the initial pressures of the gases before mixing, then, as $p_i / p_{total} = X_i$,

$$\Delta G'^{mix} = \sum_i n_i RT \ln X_i \qquad (8.21)$$

As $X_i < 1$, $\Delta G_{mix} < 0$, the mixing of gases is a spontaneous process.

8.6 THE THERMODYNAMIC PROPERTIES OF IDEAL GASES AND MIXTURES OF IDEAL GASES

- **The Entropy of Mixing of Ideal Gases**