

**Chapter 9**

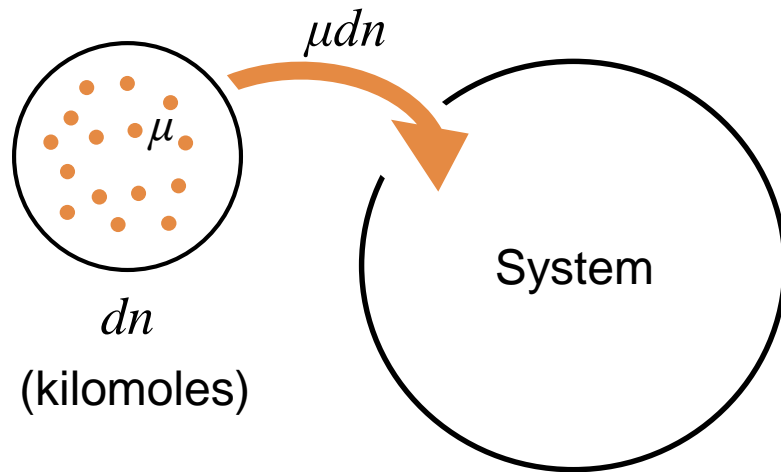
**The Chemical Potential  
and Open Systems**

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# 9.1 The Chemical Potential

Suppose that  $dn$  kilomoles of matter are introduced into a system.



Chemical reaction  $\longrightarrow$  Internal energy ( $\sim T$ )

Added energy  $\sim \mu dn$

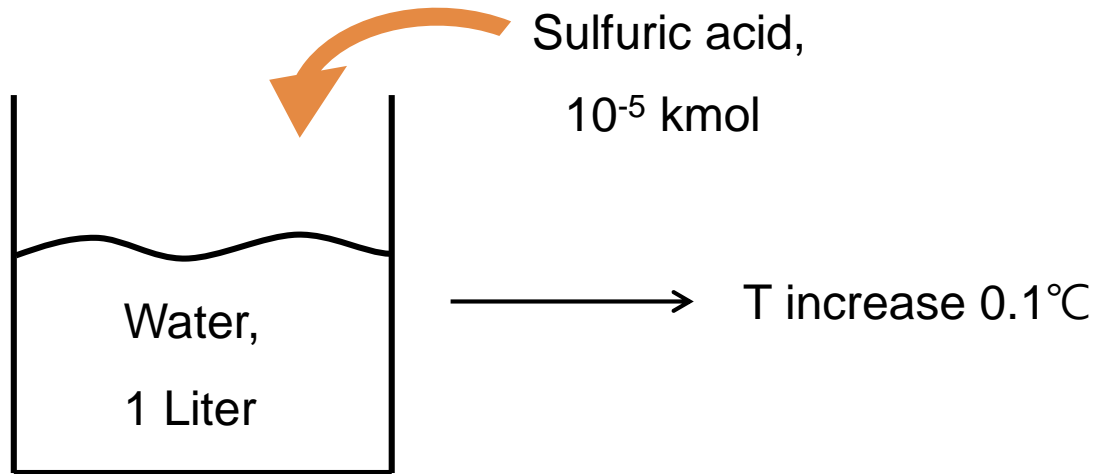
Each kilomole of added matter has its own internal energy that is released to the rest of the system, possibly in a chemical reaction.

The added energy is proportional to  $dn$  and may be written as  $\mu dn$ .

The quantity  $\mu$  is called the **chemical potential**.

# 9.1 The Chemical Potential

Ex) Let's assume sulfuric acid is added to water, producing an increase in temperature.



$$Q = mc_p \Delta T = 1 \text{ kg} \times \frac{1 \text{ kmol}}{18 \text{ kg}} \times 80 \text{ kJ/kmol} \cdot \text{K} \times 0.1 \text{ K} = 400 \text{ J}$$
$$\text{chemical potential, } \mu = \frac{Q}{\Delta n} = \frac{400 \text{ J}}{10^{-5} \text{ kmol}} = 4 \times 10^7 \text{ J/kmol}$$

# 9.1 The Chemical Potential

To account for the effect of adding mass to a system,  
we need to add a term to our fundamental equation of thermodynamics:

$$dU = TdS - PdV + \mu dn$$

from 
$$dU = \left(\frac{\partial U}{\partial S}\right) dS + \left(\frac{\partial U}{\partial V}\right) dV + \left(\frac{\partial U}{\partial n}\right) dn,$$

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

# 9.1 The Chemical Potential

## Euler's theorem

if  $\lambda f(x, y, z) = f(\lambda x, \lambda y, \lambda z)$

then  $f = x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} + z \frac{\partial f}{\partial z}$

$$\longrightarrow U = S \left( \frac{\partial U}{\partial S} \right)_{V,n} + V \left( \frac{\partial U}{\partial V} \right)_{S,n} + n \left( \frac{\partial U}{\partial n} \right)_{S,V}$$

$$\left( \frac{\partial U}{\partial S} \right)_{V,n} = T, \quad \left( \frac{\partial U}{\partial V} \right)_{S,n} = -P, \quad \left( \frac{\partial U}{\partial n} \right)_{S,V} = \mu$$

# 9.1 The Chemical Potential

then

$$U = ST - PV + \mu n,$$

and

$$dU = Tds + SdT - PdV - VdP + \mu dn + nd\mu,$$

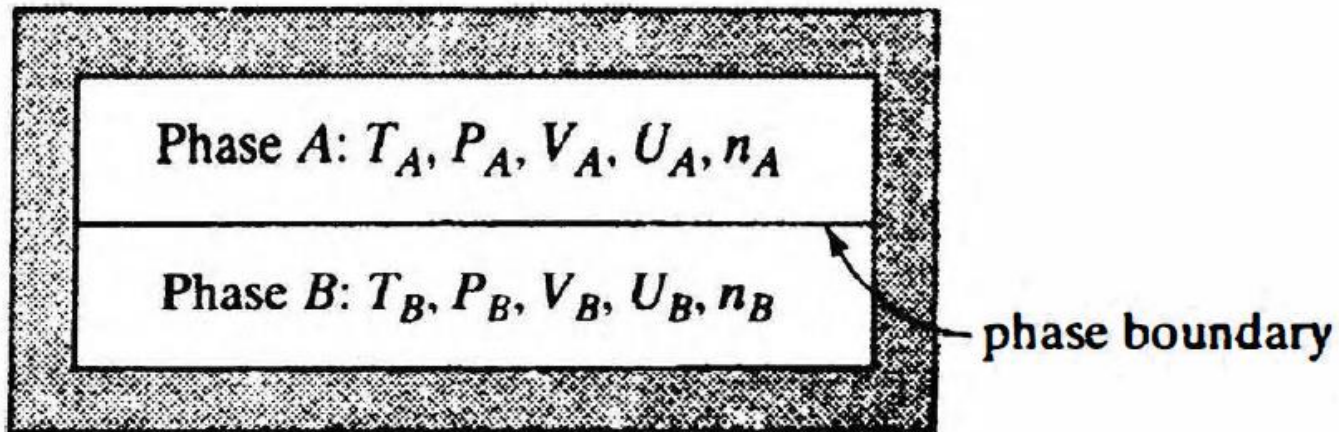
Since

$$dU = TdS - PdV + \mu dn,$$

$$SdT - VdP + nd\mu = 0$$

Gibbs-Duhem equation!

## 9.2 Phase Equilibrium



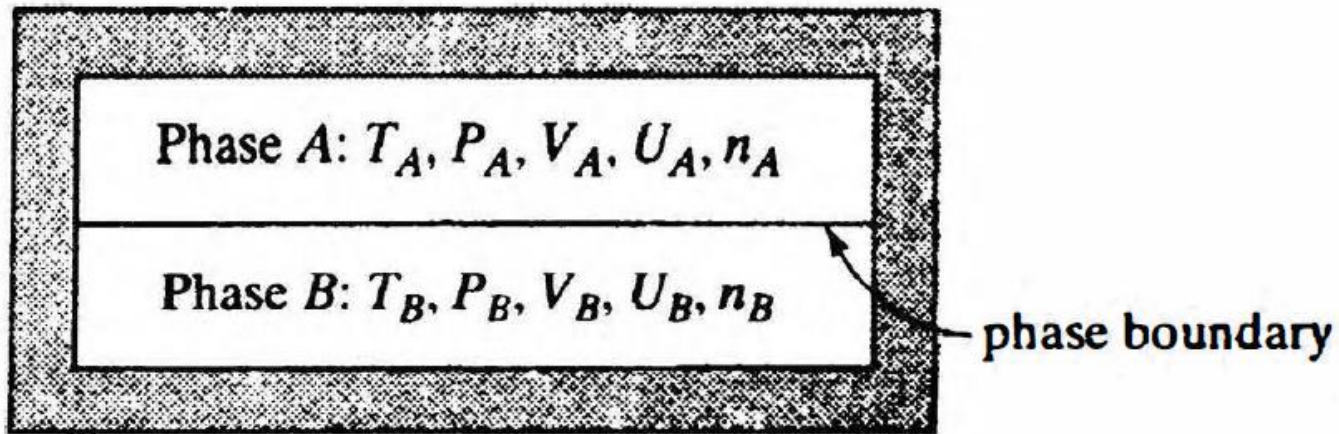
We wish to find the **condition of equilibrium** for two subsystems under particle exchange where the subsystems are **two phases of the same substance**.

$$n_A + n_B = n = \text{constant} \quad (\text{conservation of mass})$$

$$V_A + V_B = V = \text{constant} \quad (\text{conservation of volume})$$

$$U_A + U_B = U = \text{constant} \quad (\text{conservation of energy})$$

## 9.2 Phase Equilibrium



At equilibrium, the entropy of the combined system will be a maximum:

$$S_A + S_B = S \quad (\text{maximum})$$

Let all the quantities  $n$ ,  $V$ ,  $U$  and  $S$  change by infinitesimal amounts. Then,

$$dS = dS_A + dS_B = 0$$



## 9.2 Phase Equilibrium

Here,

$$dS_A = \frac{1}{T_A} (dU_A + P_A dV_A - \mu_A dn_A)$$

and

$$dS_B = \frac{1}{T_B} (dU_B + P_B dV_B - \mu_B dn_B)$$

We can eliminate three infinitesimals

$$dn_B = -dn_A, \quad dV_B = -dV_A, \quad dU_B = -dU_A$$

Then,

$$0 = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) dU_A + \left( \frac{P_A}{T_A} - \frac{P_B}{T_B} \right) dV_A + \left( \frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} \right) dn_A$$

## 9.2 Phase Equilibrium

Since the equation must be true for arbitrary increments  $dU_A$ ,  $dV_A$ ,  $dn_A$ , all of the coefficients must be zero:

$$T_A = T_B \quad (\text{thermal equilibrium})$$

$$P_A = P_B \quad (\text{mechanical equilibrium})$$

$$\mu_A = \mu_B \quad (\text{diffusive equilibrium})$$

We conclude that if we have two phases or subsystems in thermal and mechanical equilibrium, then they will also be in diffusive equilibrium (equilibrium against particle exchange) if their chemical potentials are equal.

## 9.3 The Gibbs Phase Rule

Consider a system in equilibrium with  $k$  constituents in  $\pi$  phases.

\*note

1. Only one gaseous phase can exist because of diffusion.
2. Several liquids can coexist in equilibrium if they are immiscible.
3. Several solids can coexist.
4. Only rarely do more than three phases of a given constituent coexist.

The Gibbs function is

$$G = \sum_{i=1}^k \sum_{\gamma=1}^{\pi} \mu_i^{\gamma} n_i^{\gamma}$$

component phase

## 9.3 The Gibbs Phase Rule

For equilibrium,  $(dG)_{T,P} = 0$

So,

$$dG = \sum_{i=1}^k \sum_{\gamma=1}^{\pi} \mu_i^{\gamma} dn_i^{\gamma} = 0, \quad T \text{ and } P \text{ fixed}$$

If we consider the special case of a closed system in which mass  $dn_i$  of the  $i$ -th constituent is transferred from one phase to another with the total mass of the constituent unchanged, then

$$\sum_{\gamma=1}^{\pi} dn_i^{\gamma} = 0, \quad \text{for all } i$$

## 9.3 The Gibbs Phase Rule

For a multiconstituent, multiphase system with  $T$  and  $P$  fixed, the condition for equilibrium is

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma \cdots = \mu_i^\pi, \quad i = 1, 2, \dots, k$$

The kilomole fractions are:

$$x_i^\gamma = \frac{n_i^\gamma}{\sum_{i=1}^k n_i^\gamma}$$

Thus, there would be  $k\pi$  kilomole fractions were it not for the identity

$$\sum_{i=1}^k x_i^\gamma = 1$$

## 9.3 The Gibbs Phase Rule

- Independent variable  $2 + k\pi - \pi$
- Equilibrium conditions  $k(\pi - 1)$

There are therefore  $2 + k\pi - \pi$  independent variables and  $k(\pi - 1)$  equilibrium conditions.

The number of remaining “degrees of freedom” called the variance  $f$ , is

$$f = [2 + k\pi - \pi] - [k(\pi - 1)]$$

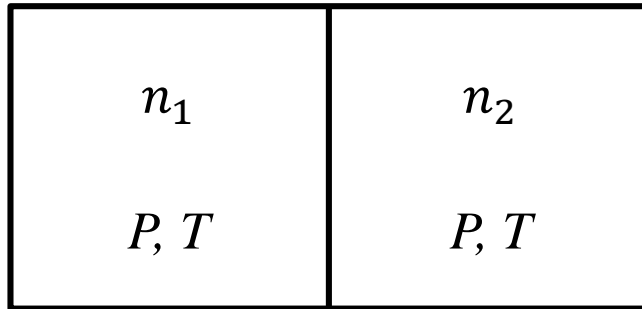
or

$$f = k - \pi + 2 \text{ (no chemical reaction)}$$

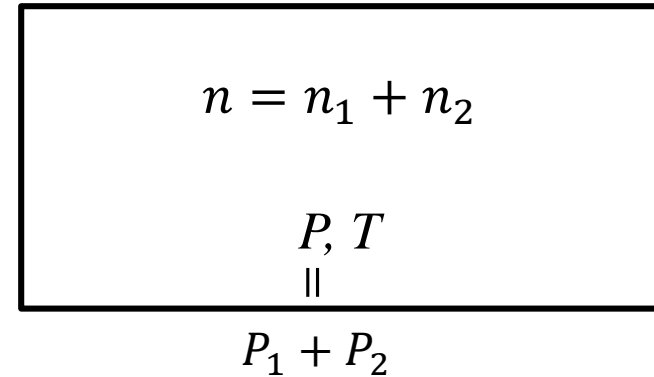
### Gibbs phase rule!

# 9.5 Mixing processes

Initial



Final

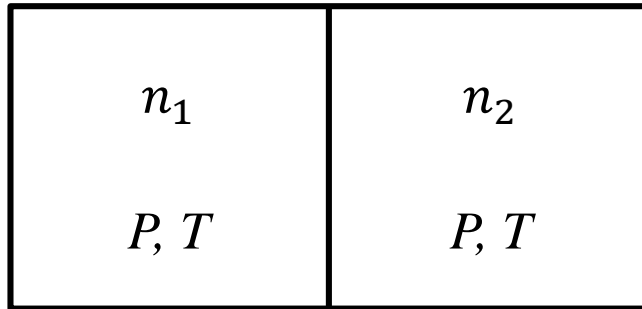


Dalton's law of partial pressure

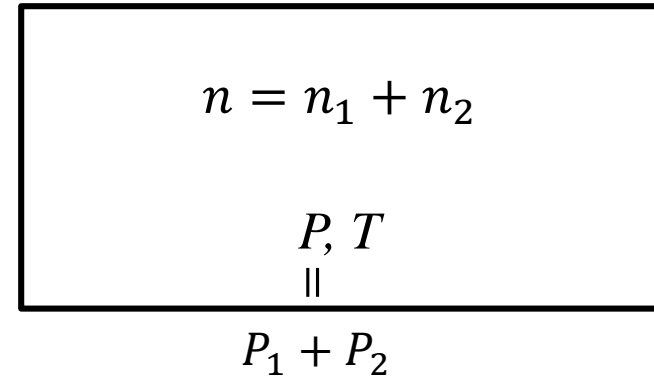
$$P_j = x_j P \longrightarrow \begin{array}{l} \text{Pressure of the mixture} \\ \text{mole fraction} \end{array}$$

# 9.5 Mixing processes

Initial



Final



For ideal gas,

$$h = c_p T + h_0$$

$$s = c_p \ln T + R \ln P + s_0$$

$$g = h - Ts = c_p T - c_p T \ln T + RT \ln P - Ts_0 + h_0$$



## 9.5 Mixing processes

$$G_i = n_1 g_{1,i} + n_2 g_{2,i} = n_1 RT(\ln P + \phi_1) + n_2 RT(\ln P + \phi_2)$$

$$G_f = n_1 g_{1,f} + n_2 g_{2,f} = n_1 RT(\ln P_1 + \phi_1) + n_2 RT(\ln P_2 + \phi_2)$$

$$\Delta G = RT(n_1 \ln x_1 + n_2 \ln x_2)$$

$$= nRT(x_1 \ln x_1 + x_2 \ln x_2)$$

$$\Delta S = -nR(x_1 \ln x_1 + x_2 \ln x_2)$$

└→ entropy of mixing

**Chapter 10**

**The Third Law of Thermodynamics**

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# 10.1 Statement of the Third Law

- The third law of thermodynamics is concerned with the behavior of systems in equilibrium as their temperature approaches zero
- The definition of entropy given by

$$S = \int_0^T \frac{dQ_r}{T} + S_0 \quad (10.1)$$

is incomplete because of the undetermined additive constant  $S_0$ , the entropy at absolute zero.

- In this chapter we shall introduce a principle that will enable us to determine  $S_0$ .

# 10.1 Statement of the Third Law

- Gibbs-Helmholtz equation

$$G = H + T \left( \frac{\partial G}{\partial T} \right)_P \quad (10.2)$$

- If this relation is applied to the initial and final states of a system undergoing an isothermal process, it takes the form

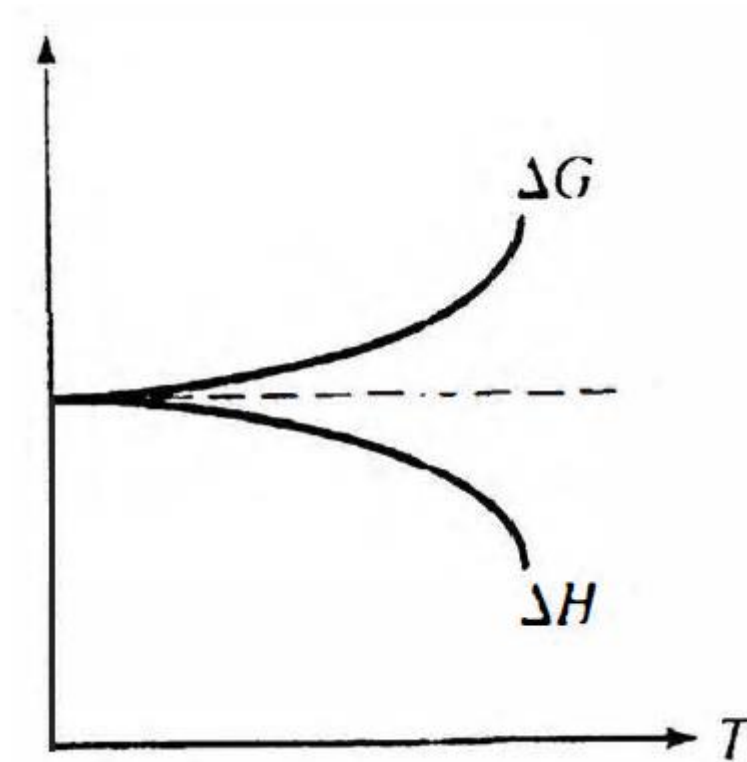
$$\Delta G = \Delta H + T \left[ \frac{\partial(\Delta G)}{\partial T} \right]_P \quad (10.3)$$

- This shows that the change in enthalpy and the change in the Gibbs function are equal at  $T = 0$  for an isobaric process.

$$\lim_{T \rightarrow 0} \left[ \frac{\partial(\Delta G)}{\partial T} \right]_P = 0 \quad \lim_{T \rightarrow 0} \left[ \frac{\partial(\Delta H)}{\partial T} \right]_P = 0 \quad (10.4)$$

# 10.1 Statement of the Third Law

- Equation (10.4) is illustrated in Figure 10.1.



**Figure 10.1** Variation of  $\Delta G$  and  $\Delta H$  in the vicinity of absolute zero.

# 10.1 Statement of the Third Law

- We may write the equation (10.4) as

$$\lim_{T \rightarrow 0} \left[ \frac{\partial(G_2 - G_1)}{\partial T} \right]_P = \lim_{T \rightarrow 0} \left[ \left( \frac{\partial G_2}{\partial T} \right)_P - \left( \frac{\partial G_1}{\partial T} \right)_P \right] = 0 \quad (10.5)$$

where the subscripts 1 and 2 refer to the initial and final states, respectively.

- From the reciprocity relation, we have **the Nernst formulation of the third law**.

$$\lim_{T \rightarrow 0} (S_1 - S_2) = 0 \quad (10.6)$$

**All reactions in a liquid or solid in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero.**

$$Cf. G = U - TS + PV \rightarrow dG = -SdT + VdP \rightarrow S = - \left( \frac{\partial G}{\partial T} \right)_P$$

# 10.1 Statement of the Third Law

- Planck extended Nernst's hypothesis by assuming that it holds for  $G_1$  and  $G_2$  separately.

$$\lim_{T \rightarrow 0} G(T) = \lim_{T \rightarrow 0} H(T) \quad (10.7)$$

$$\lim_{T \rightarrow 0} \left( \frac{\partial G}{\partial T} \right)_P = \lim_{T \rightarrow 0} \left( \frac{\partial H}{\partial T} \right)_P \quad (10.8)$$

- For convenience, we temporarily introduce a variable  $\Phi \equiv G - H$ . Equation (10.2) then becomes

$$T \left( \frac{\partial G}{\partial T} \right)_P - \Phi = 0 \quad (10.9)$$

- Adding the term  $-T(\partial H/\partial T)_P$  to both sides of Equation (10.9), we get

$$T \left( \frac{\partial \Phi}{\partial T} \right)_P - \Phi = -T \left( \frac{\partial H}{\partial T} \right)_P \quad (10.10)$$

# 10.1 Statement of the Third Law

- By L'Hopital's rule,

$$\lim_{T \rightarrow 0} \left( \frac{\partial H}{\partial T} \right)_P = 0 \quad (10.11)$$

- Finally, by Equation (10.8), we obtain the result

$$\lim_{T \rightarrow 0} \left( \frac{\partial G}{\partial T} \right)_P = 0 \quad (10.12)$$

- Since  $\left( \frac{\partial G}{\partial T} \right)_P = -S$ , it follows **the Planck's statement of the third law.**

$$\lim_{T \rightarrow 0} S = 0 \quad (10.13)$$

**The entropy of a true equilibrium state of a system at absolute zero is zero**