Chapter 6 — Chemical Potential

Contents

1 Chemical Potential **2**

1.1 Fundamental Relations . . . 2
1.1.1 Definition of Chemical Potential . . . 2
1.1.2 Equivalent Expressions of Chemical Potential . . . 2
1.1.3 Euler Equation and Gibbs-Duhem Relation . . . 2
1.1.4 Expression of Chemical Potential for an Ideal Gas . . . 3
1.2 Phase Coexistence . . . 3
1.2.1 Equilibrium Condition Between Phases . . . 3
1.2.2 Clausius-Clapeyron Equation . . . 3
1.2.3 Phase Diagram and Triple Point . . . 4
1.3 Equilibrium Conditions at Constant Pressure . . . 4
1.3.1 Equilibrium at Constant T and P: Minimum of G . . . 4
1.3.2 Differential Equilibrium Condition . . . 4
1.3.3 Liquid-Vapor Equilibrium at Constant Pressure . . . 5
1.4 Equilibrium and Stability at Fixed Chemical Potential . . . 5
1.4.1 The Grand Potential Ω . . . 5
1.4.2 Stability Condition . . . 5
1.4.3 Local Stability and Fluctuations . . . 5
1.5 Chemical Reactions . . . 5
1.5.1 Chemical Equilibrium Condition . . . 5
1.5.2 Law of Mass Action and Equilibrium Constant . . . 6
1.5.3 Spontaneous Evolution and Chemical Affinity . . . 6
1.5.4 Displacement of Equilibria: Le Chatelier's Principle . . . 7
1.5.5 Example: Ammonia Synthesis (Haber-Bosch Process) . . . 7

1 Chemical Potential

The chemical potential is a fundamental quantity in thermodynamics that plays, for matter transfer, a role analogous to that of temperature for heat transfer and pressure for volume transfer. It allows the description of phase equilibrium, chemical reactions, and the stability of systems with variable composition.

1.1 Fundamental Relations

1.1.1 Definition of Chemical Potential

For a system with several constituents, the internal energy U depends not only on S and V, but also on the amounts of matter N_i of each species i. The fundamental relation is written:

$$dU = TdS - PdV + \sum_i \mu_i dN_i \qquad (1.1) \tag{1}$$

The chemical potential of species i, denoted μ_i, is defined as the partial derivative of U with respect to N_i, at fixed S, V, and $N_{j\neq i}$:

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j\neq i} \qquad (1.2) \tag{2}$$

It represents the variation of internal energy when one particle (or one mole) of species i is added to the system, at constant entropy and volume.

1.1.2 Equivalent Expressions of Chemical Potential

By Legendre transformation, equivalent expressions of the chemical potential are obtained from the other thermodynamic potentials:

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j\neq i} \quad (S, V \text{ fixed})$$

$$\mu_i = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_j\neq i} \quad (S, P \text{ fixed})$$

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_j\neq i} \quad (T, V \text{ fixed})$$

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j\neq i} \quad (T, P \text{ fixed})$$

This last expression is particularly useful because it relates the chemical potential to the free enthalpy $G(T, P, N_i)$, which is the most natural function for transformations at constant T and P (the usual conditions in chemistry).

1.1.3 Euler Equation and Gibbs-Duhem Relation

Since U is an extensive function, Euler's theorem gives:

$$U = TS - PV + \sum_i \mu_i N_i \qquad (1.7) \tag{3}$$

Differentiating this relation and comparing it with $dU = TdS - PdV + \sum_i \mu_i dN_i$, we obtain the Gibbs-Duhem relation:

$$S\,dT - V\,dP + \sum_i N_i\,d\mu_i = 0 \qquad (1.8) \tag{4}$$

For a single-component system, this relation reduces to $SdT - VdP + Nd\mu = 0$, i.e.:

$$d\mu = -s\,dT + v\,dP \tag{1.9}$$

where $s = S/N$ is the molar entropy and $v = V/N$ the molar volume.

1.1.4 Expression of Chemical Potential for an Ideal Gas

For an ideal gas, the chemical potential is written:

$$\mu(T,P) = \mu^\circ(T) + RT\ln\left(\frac{P}{P^\circ}\right) \qquad (1.10) \tag{5}$$

where $\mu^\circ(T)$ is the standard chemical potential (at $P^\circ = 1$ bar) and R the ideal gas constant. For a mixture of ideal gases, with $p_i = x_i P$ the partial pressure:

$$\mu_i(T,P,x_i) = \mu_i^\circ(T) + RT\ln\left(\frac{p_i}{P^\circ}\right) = \mu_i^\circ(T) + RT\ln x_i + RT\ln\left(\frac{P}{P^\circ}\right) \qquad (1.11) \tag{6}$$

For an ideal solution, an analogous formula applies with the mole fraction x_i:

$$\mu_i = \mu_i^\circ + RT\ln x_i \qquad (1.12) \tag{7}$$

1.2 Phase Coexistence

1.2.1 Equilibrium Condition Between Phases

Consider a closed system consisting of two phases α and β of the same pure substance, in contact and capable of exchanging matter. At equilibrium, the condition of minimum free enthalpy G at fixed T and P imposes:

$$\mu^\alpha(T,P) = \mu^\beta(T,P) \qquad (1.13) \tag{8}$$

This equality means that the chemical potentials of the two phases are equal. It defines a coexistence curve in the P-T diagram (melting, vaporization, or sublimation curve).

Equilibrium conditions between phases

For two phases α and β in equilibrium:

$$T^\alpha = T^\beta, \quad P^\alpha = P^\beta, \quad \mu^\alpha = \mu^\beta$$

1.2.2 Clausius-Clapeyron Equation

Differentiating $\mu^\alpha(T,P) = \mu^\beta(T,P)$ along the coexistence curve, we obtain:

$$d\mu^\alpha = d\mu^\beta \implies -s^\alpha dT + v^\alpha dP = -s^\beta dT + v^\beta dP \qquad (1.14) \tag{9}$$

hence:

$$\frac{dP}{dT} = \frac{s^\beta - s^\alpha}{v^\beta - v^\alpha} = \frac{L}{T\Delta v} \qquad (1.15) \tag{10}$$

where $L = T(s^\beta - s^\alpha)$ is the latent heat of transition and $\Delta v = v^\beta - v^\alpha$ the variation of molar volume.

Case of vaporization

For liquid-vapor equilibrium, neglecting the molar volume of the liquid compared to that of the vapor and assuming the vapor to be ideal ($v_{vap} \approx RT/P$):

$$\frac{d\ln P}{dT} = \frac{L_{vap}}{RT^2} \qquad (1.16) \tag{11}$$

Integrating between two states (assuming L_{vap} constant):

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{L_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (1.17) \tag{12}$$

This equation allows, for example, the calculation of the saturated vapor pressure of a liquid at different temperatures.

1.2.3 Phase Diagram and Triple Point

The P-T diagram of a pure substance presents three coexistence curves (fusion, vaporization, sublimation) that meet at the triple point, where the three phases solid, liquid, and gas coexist simultaneously:

$$\mu_{solid}(T_{tr}, P_{tr}) = \mu_{liquid}(T_{tr}, P_{tr}) = \mu_{gas}(T_{tr}, P_{tr}) \qquad (1.18) \tag{13}$$

For water, the triple point is located at $T_{tr} = 273.16$ K and $P_{tr} = 611.657$ Pa.

Figure 1: P-T phase diagram of a pure substance

1.3 Equilibrium Conditions at Constant Pressure

1.3.1 Equilibrium at Constant T and P: Minimum of G

At constant temperature and pressure (the most common conditions in chemistry and biology), the relevant thermodynamic potential is the free enthalpy $G(T, P, N_i)$. For a closed system evolving spontaneously, we have:

$$(dG)_{T,P} \leq 0 \qquad (1.19) \tag{14}$$

Equality corresponds to a state of equilibrium. The system therefore evolves toward a minimum of G.

Evolution principle

At constant T and P, a closed system evolves spontaneously toward the state that minimizes its free enthalpy G.

1.3.2 Differential Equilibrium Condition

At constant T and P, the differential of G is written:

$$(dG)_{T,P} = \sum_i \mu_i dN_i \qquad (1.20) \tag{15}$$

The equilibrium condition $(dG)_{T,P} = 0$ therefore imposes:

$$\sum_i \mu_i dN_i = 0 \qquad (1.21) \tag{16}$$

This condition is the basis for the study of chemical equilibria and equilibria between phases.

1.3.3 Liquid-Vapor Equilibrium at Constant Pressure

For a pure substance at constant T and P, the liquid-vapor coexistence is stable if:

$$\mu_{liq}(T, P) = \mu_{vap}(T, P) \qquad (1.22) \tag{17}$$

If $\mu_{liq} < \mu_{vap}$, the liquid is stable; if $\mu_{vap} < \mu_{liq}$, the vapor is stable. The transition occurs when the two chemical potentials become equal.

1.4 Equilibrium and Stability at Fixed Chemical Potential

1.4.1 The Grand Potential Ω

When a system can exchange matter with a reservoir at fixed chemical potential μ (open system), the relevant thermodynamic potential is the grand potential:

$$\Omega(T, V, \mu) = U - TS - \mu N = F - \mu N = -PV \qquad (1.23) \tag{18}$$

Its differential is written:

$$d\Omega = -SdT - PdV - Nd\mu \qquad (1.24) \tag{19}$$

1.4.2 Stability Condition

At fixed T, V, and μ, equilibrium corresponds to a minimum of Ω:

$$(d\Omega)_{T,V,\mu} = 0 \quad \text{and} \quad (d^2\Omega)_{T,V,\mu} > 0 \qquad (1.25) \tag{20}$$

This formulation is particularly useful in statistical physics (grand canonical ensemble) and for the study of systems in contact with a particle reservoir (adsorption, catalytic reactions, etc.).

1.4.3 Local Stability and Fluctuations

The stability of an equilibrium state is related to the sign of the second derivatives of the potentials. For example, the isothermal compressibility must be positive:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T > 0 \qquad (1.26) \tag{21}$$

Similarly, the heat capacity must be positive: $C_V > 0$ and $C_P > 0$.

These stability conditions guarantee that the system returns to its equilibrium state after a small perturbation.

1.5 Chemical Reactions

1.5.1 Chemical Equilibrium Condition

Consider a general chemical reaction:

$$\nu_1 A_1 + \nu_2 A_2 + \cdots = \nu_3 A_3 + \nu_4 A_4 + \cdots \qquad (1.27) \tag{22}$$

or, in condensed form:

$$\sum_i \nu_i A_i = 0 \qquad (1.28) \tag{23}$$

where the ν_i are the stoichiometric coefficients (positive for products, negative for reactants). The progress of the reaction is described by the variable ξ (extent of reaction):

$$dN_i = \nu_i d\xi \qquad (1.29) \tag{24}$$

At constant T and P, the equilibrium condition $(dG)_{T,P} = 0$ gives:

$$\sum_i \mu_i dN_i = \left(\sum_i \nu_i \mu_i \right) d\xi = 0 \qquad (1.30) \tag{25}$$

hence the chemical equilibrium condition:

$$\sum_i \nu_i \mu_i = 0 \qquad (1.31) \tag{26}$$

1.5.2 Law of Mass Action and Equilibrium Constant

For ideal gases, substituting $\mu_i = \mu_i^\circ + RT \ln(p_i/P^\circ)$, the equilibrium condition becomes:

$$\sum_i \nu_i \mu_i^\circ + RT \sum_i \nu_i \ln \left(\frac{p_i}{P^\circ} \right) = 0 \qquad (1.32) \tag{27}$$

Setting $\Delta_r G^\circ = \sum_i \nu_i \mu_i^\circ$ (standard free enthalpy of reaction), we obtain:

$$\Delta_r G^\circ = -RT \ln K_P \qquad (1.33) \tag{28}$$

where K_P is the equilibrium constant in partial pressures:

$$K_P = \prod_i \left(\frac{p_i}{P^\circ} \right)^{\nu_i} \qquad (1.34) \tag{29}$$

The law of mass action is therefore written:

$$K_P = \frac{(p_3/P^\circ)^{\nu_3} (p_4/P^\circ)^{\nu_4} \cdots}{(p_1/P^\circ)^{\nu_1} (p_2/P^\circ)^{\nu_2} \cdots} \qquad (1.35) \tag{30}$$

1.5.3 Spontaneous Evolution and Chemical Affinity

The chemical affinity $\mathcal{A}$ is defined by:

$$\mathcal{A} = -\sum_i \nu_i \mu_i = -\Delta_r G \qquad (1.36) \tag{31}$$

The spontaneous evolution of the reaction is given by:

- If $\mathcal{A} > 0$ (i.e., $\Delta_r G < 0$): the reaction evolves in the forward direction (ξ increases).
- If $\mathcal{A} < 0$ (i.e., $\Delta_r G > 0$): the reaction evolves in the reverse direction (ξ decreases).
- If $\mathcal{A} = 0$ (i.e., $\Delta_r G = 0$): the system is at equilibrium.

1.5.4 Displacement of Equilibria: Le Chatelier's Principle

Le Chatelier's principle states that when a system at equilibrium is subjected to a perturbation (variation of T, P, or concentrations), it evolves so as to oppose this perturbation.

- **Temperature variation**: if the reaction is endothermic ($\Delta_r H^\circ > 0$), an increase in T displaces the equilibrium in the forward direction. If it is exothermic, the effect is reversed.

  The variation of K_P with T is given by the van't Hoff relation:

$$\frac{d\ln K_P}{dT} = \frac{\Delta_r H^\circ}{RT^2} \qquad (1.37) \tag{32}$$

- **Pressure variation**: an increase in P displaces the equilibrium toward the side with the fewest gaseous moles ($\Delta\nu_{gas} < 0$).
- **Concentration variation**: adding a reactant displaces the equilibrium in the direction of its consumption.

1.5.5 Example: Ammonia Synthesis (Haber-Bosch Process)

The ammonia synthesis reaction is written:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \quad \Delta_r H^\circ = -92.4 \text{ kJ·mol}^{-1} \qquad (1.38) \tag{33}$$

The equilibrium constant is:

$$K_P = \frac{(p_{NH_3}/P^\circ)^2}{(p_{N_2}/P^\circ)(p_{H_2}/P^\circ)^3} \qquad (1.39) \tag{34}$$

- The reaction is exothermic: a low temperature favors the formation of NH_3.
- The number of gaseous moles decreases ($\Delta\nu_{gas} = -2$): a high pressure favors the formation of NH_3.
- In practice, one works at $T \approx 450$ °C and $P \approx 200$ bar, with an iron-based catalyst, to reconcile yield and kinetics.

Chapter Summary

Table 1: Summary of key concepts of Chapter 6

Concept	**Essential idea**
Chemical potential (μ_i)	Variation of U by adding N_i: $\mu_i = (\partial U/\partial N_i)_{S,V,N_{j\neq i}}$.
Equivalent expressions	$\mu_i = (\partial G/\partial N_i)_{T,P,N_{j\neq i}}$.
Gibbs-Duhem relation	$SdT - VdP + \sum_i N_i d\mu_i = 0$.
Ideal gas	$\mu = \mu^\circ(T) + RT\ln(P/P^\circ)$.
Ideal solution	$\mu_i = \mu_i^\circ + RT\ln x_i$.
Phase coexistence	$\mu^\alpha(T,P) = \mu^\beta(T,P)$.
Clausius-Clapeyron	$dP/dT = L/(T\Delta v)$.
Equilibrium at fixed T, P	Minimum of G, $\sum_i \nu_i\mu_i = 0$.
Grand potential Ω	$\Omega = -PV$, useful at fixed T, V, μ.
Stability	$C_V > 0$, $\kappa_T > 0$.
Chemical reactions	$\Delta_r G^\circ = -RT\ln K_P$.
Le Chatelier	The system opposes the perturbation.
van't Hoff	$d\ln K_P/dT = \Delta_r H^\circ/(RT^2)$.