

材料熱力學一

Thermodynamics of Materials I



Chapter1 Introduction and definition of terms

What determines how matter behaves? \Leftrightarrow Thermodynamics.

1. What determines how matter behaves?

Final Stable State \Leftrightarrow Equilibrium State

Gibbs free energy: Minimum (at specific T, P)

2. $\left\{ \begin{array}{l} \text{Classical thermodynamics} \Rightarrow \text{Macroscopic phenomena.} \\ \text{Statistical thermodynamics} \Rightarrow \text{Microscopic description} \end{array} \right.$

$\left\{ \begin{array}{l} \text{Particles : atoms, electrons, molecules.} \\ \text{Quantum mechanics} \\ \text{Probability (distribution function)} \end{array} \right.$

3. Thermodynamics V.S. Kinetics

Thermodynamics: $\left\{ \begin{array}{l} \text{Energy} \\ \text{Equilibrium state} \end{array} \right.$

Kinetics: $\left\{ \begin{array}{l} \text{Reaction rate} \\ \text{Metastable state} \end{array} \right.$

4. Thermodynamic systems of materials

① material system:

- Unary or/ multi-component (binary, ternary, quaternary)
- Homogeneous/ Heterogeneous
- Closed/ Open
- Non-reacting/ Reacting
- Simple/ Complex

② $\left\{ \begin{array}{l} \text{Simple system : energy changes due to mechanical, thermal,} \\ \quad \text{and chemical variation.} \\ \text{Complex system : energy changes due to gravitational, electrical, magnetic} \\ \quad \text{and surface effects.} \end{array} \right.$

5. Thermodynamic Variables

{ State functions or process variables
 { Intensive or extensive variables

- State function: a quantity that depends on the condition of the system and not on how the system arrived at that condition.

⇒ State function is independent of path.

$$\Rightarrow \Delta Z = Z_{final} - Z_{initial} = \int_{Z_i}^{Z_f} dZ$$

e.g. P, V, T, X_k, S, U, G, H, A

⇒ For a very complex process, ΔZ can be computed by the simplest path connecting the initial and the final states.

⇒ State function can be expressed by exact differential, dZ.

- Process variable: a quantity that only has meaning for a changing system and its value for a process depends explicitly on the path.

e.g. $\begin{cases} \text{Work,} & W(\Delta W), & \delta W \\ \text{Heat,} & Q(\Delta Q), & \delta Q \end{cases}$

$$\delta W = \vec{F} \cdot d\vec{x}$$

$$W = \int_{path} \vec{F} \cdot d\vec{x} \quad \left(\int \text{ or } \oint \right)$$

$$1. \oint dZ = 0, \text{ but } \oint \delta W \neq 0$$

$$2. \text{ Force : } \begin{cases} \text{Pressure : } P(+ PdV) \\ \text{Stress : } \sigma(+ \sigma d\epsilon) \\ \text{Electric : } \epsilon(+ \epsilon dq) \\ \text{Magnetic : } H(+ HdM) \\ \text{Surface tension : } \gamma(+ \gamma dA) \end{cases}$$

- “Intensive” property may be defined to have a value at a point in the system. It does not depend on the size of the system.

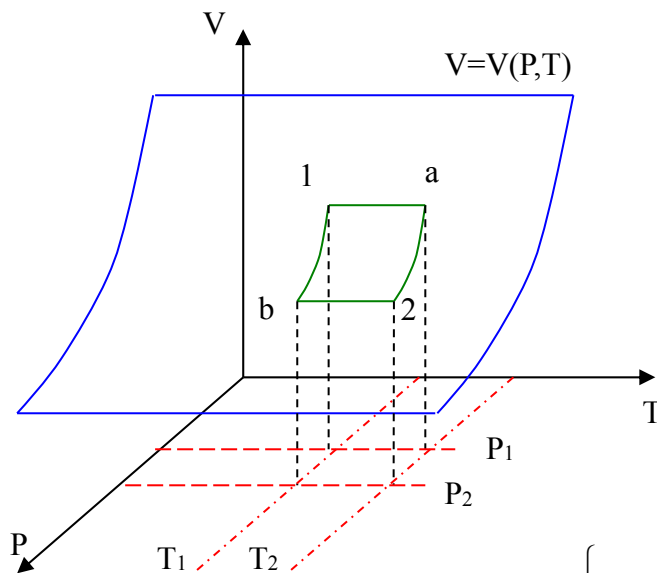
e.g. P, T, X_k, ρ(density), $\bar{V}, \bar{S}, \bar{U}, \bar{H}, \bar{A}, \bar{G}$

- “Extensive” property depends on the size of the system

e.g. V, S, U, H, A, G, n_k

6. Concept of state

- * $\left\{ \begin{array}{l} \text{Microscopic state : statistical distribution of all constituent particles.} \\ \text{Macroscopic state : phenomenological property of a system.} \end{array} \right.$
- * Thermodynamic state of the simple unary system is uniquely fixed when the values of two independent variables are fixed.
- * Any two properties could be chosen as the independent variables. P, T are the most amenable to control.
- * Consider a pure gas $V = V(P,T)$. Equation of state?
If Eq. of state is known, we can calculate ΔV .
 $(P_1, T_1) \rightarrow (P_2, T_2)$, $\Delta V = (V_2 - V_1) = ?$



Two paths

① 1 \rightarrow a \rightarrow 2

② 1 \rightarrow b \rightarrow 2

$$\left\{ \begin{array}{l} 1 \rightarrow a \\ b \rightarrow 2 \end{array} \right\} \text{isobaric}$$

$$\left\{ \begin{array}{l} 1 \rightarrow b \\ a \rightarrow 2 \end{array} \right\} \text{isothermal}$$

$$\text{Path} \left\{ \begin{array}{l} 1 \rightarrow a : V_a - V_b = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T} \right)_P dT \\ a \rightarrow 2 : V_2 - V_a = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P} \right)_T dP \end{array} \right.$$

$$\therefore \Delta V = V_2 - V_1 = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T} \right)_P dT + \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P} \right)_T dP$$

$$\text{Path} \begin{cases} 1 \rightarrow b, & V_b - V_1 = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P} \right)_T dP \\ b \rightarrow 2, & V_2 - V_b = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T} \right)_P dT \end{cases}$$

$$\therefore \Delta V' = V_2 - V_1 = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P} \right)_T dP + \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T} \right)_P dT$$

$\Delta V = \Delta V'$ ΔV is indep. of path.

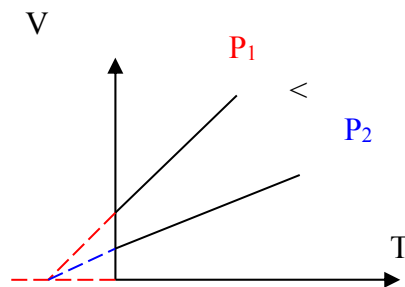
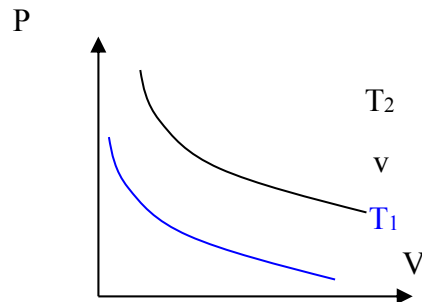
V is state function, dV is exact differential.

$$V = V(T, P) \quad dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

For any values of T_1 , P_1 , the gas system is at equilibrium only when it has that unique volume, V_1 , which corresponds to T_1 and P_1 .

7. Equation of state of an ideal gas

$$\left\{ \begin{array}{l} \text{Boyle's law : constant } T, \quad P \propto 1/V \\ \text{Charles's law : constant } P, \quad V \propto T \end{array} \right.$$



∴ at T ($P_o \rightarrow P$) Boyle's law : $P_o V(T, P_o) = PV(T, P)$

at P_o ($T_o \rightarrow T$) Charles's law : $\frac{V(P_o, T_o)}{T_o} = \frac{V(P_o, T)}{T}$

Take : $\begin{cases} T_o = 0^\circ C = 273.15 K \\ P_o = 1 \text{ atm} \end{cases}$

∴ $P_o \cdot \frac{T \cdot V(P_o, T_o)}{T_o} = P \cdot V(T, P)$

∴ $\frac{PV}{T} = \frac{P_o V_o}{T_o} = \text{Const.}$

Avogadro's hypothesis : Volume per "g - mole" of all "ideal gas" at $0^\circ C$, $P = 1 \text{ atm}$ is 22.414 l .

∴ gas constant = $R = \frac{1 \text{ atm} \times 22.414 \text{ l}}{\text{mole} \times 273.15 \text{ K}} = 0.082057 \frac{\text{atm} \cdot \text{l}}{\text{K} \cdot \text{mole}}$

∴ Ideal gas law (equation of state of ideal gas) :

For one mole gas : $PV = RT$

For n mole gas : $PV = nRT$

molar volume : $V = \frac{V'}{n}$

Note : (1) $1 \text{ atm} = 101325 \frac{\text{N}}{\text{m}^2} = 101325 \text{ Pa} = 1013.25 \text{ hPa}$

∴ $1 \text{ atm} \cdot \text{liter} = 101.325 \text{ J}$

$R = 0.082057 \frac{\text{atm} \cdot \text{liter}}{\text{K} \cdot \text{mole}} = 8.314 \frac{\text{J}}{\text{K} \cdot \text{mole}}$

(2) Absolute temperature scale (Kelvin)

$1 \text{ atm}, \text{H}_2\text{O} \begin{cases} \text{ice point : } 0^\circ C, 32^\circ F \\ \text{boil point : } 100^\circ C, 212^\circ F \end{cases}$

1802 Luis & Lussac : Thermal expansion coefficient of "permanent gas" is a constant.

Thermal expansion coefficient : $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$

Take $V = V_o$ at $0^\circ C$

∴ $\alpha = \frac{1}{273.15}$ for all gas when $P \rightarrow 0$

hypothetical gas : ideal gas

∴ When $T = -273.15^\circ C$, mole volume of gas is zero,
 \Rightarrow low temperature limit

∴ $T \equiv 0\text{K} = -273.15^\circ C$

$T(\text{K}) \equiv T(^{\circ}C) + 273.15$

Charles's law:

