Curso

Optativo de Posgrado

Termodinamica Fuera de Equilibrio

Semestre 2008-1(11 agsto al 28 nov. 2008) 3 hrs/semana

Dr. Karo Michaelian, IFUNAM, Of. FE4, Ed. ColiSur, Tel: 5622-5165

Basado en "Thermodynamics of Irreversible Processes" – I. Prigogine

1 Capitulo 1: Conservation of Mass

1.1 Isolated, Closed and Open Systems

- **well defined geometrical volume**
- **macroscopic dimensions**

1. **Isolated systems - no energy, no matter, no work, exchange**
2. **Closed systems - energy exchange, but no matter, no work, exchanged**
3. **Open systems - energy, matter, and work exchanged**

What type of thermodynamic system is the planet Earth?
What type of thermodynamic system is the Universe?

Classical TD normally treats isolated or closed systems.

Open systems particularly important in meteorology and biology.

Give an example of a living biological system which is closed?

1. **Extensive properties or variables - defined by the system as a whole, eg. energy E, volume V,and number of moles N - are additive.**
2. **Intensive properties - take well defined values at each point in the system, eg. temperature T, pressure p, and chemical potential μ.**

   Give two other examples of extensive and intensive properties or variables of a system?

   Thermodynamic system described by "fundamental relation"

   $S(E, V, N, ...)$

   $E(S; V; N, ...)$

   Gibb's equation

   $dS = \left(\frac{\partial S}{\partial E}\right)_{V,N,...} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N,...} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V,...} dN + ...$

   $= \frac{1}{T} dE + \frac{P}{T} dV + \frac{\mu}{T} dN + ...$

2 Conservation of Mass in Closed Systems

Closed system containing c components ($\gamma = 1 \ldots c$).
Variation in masses result only from chemical reactions.
Change of mass dm_γ of component γ in time interval dt is

$$dm_\gamma = \nu_\gamma M_\gamma d\xi \tag{1}$$

ν_γ is stoichiometric coefficient (positive when component γ appears on right of reaction equation, negative whem on left), M_γ is the molar mass. ξ is degree of advancement or extent of reaction.
Eg.

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{2}$$

Therefore,

$$\frac{dm_{N_2}}{-M_{N_2}} = \frac{dm_{H_2}}{-3M_{H_2}} = \frac{dm_{NH_3}}{2M_{NH_3}} = d\xi \tag{3}$$

Total mass of system $m = \sum_\gamma m_\gamma$.
Principle of conservation of mass for a closed system

$$dm = (\sum_\gamma \nu_\gamma M_\gamma) d\xi = 0. \tag{4}$$

$$\sum_\gamma \nu_\gamma M_\gamma = 0 \tag{5}$$

called stoichiometric equation.
Often useful to consider mole numbers $n = m/M$

$$dn_\gamma = \nu_\gamma d\xi \tag{6}$$

Chemical reaction rate

$$v \equiv \frac{d\xi}{dt} \tag{7}$$

Change in number of moles is thus

$$\frac{dn_\gamma}{dt} = \nu_\gamma v \tag{8}$$

For r simultaneous reactions ρ

$$dm_\gamma = M_\gamma \sum_{\rho=1}^{r} \nu_{\gamma\rho} d\xi_\rho \tag{9}$$

or

$$dn_\gamma = \sum_{\rho=1}^{r} \nu_{\gamma\rho} d\xi_\rho \tag{10}$$

where $\nu_{\gamma\rho}$ is stoichiometric coefficient of component γ in the reaction ρ.
Rate of reaction ρ is

$$v_\rho = \frac{d\xi_\rho}{dt} \tag{11}$$

Eg.

$$2C + O_2 \rightarrow 2CO \quad (\rho = 1) \tag{12}$$
$$C + O_2 \rightarrow CO_2 \quad (\rho = 2) \tag{13}$$

gives

$$dn_C = -2d\xi_1 - d\xi_2 \tag{14}$$

2.1 Conservation of Mass in Open Systems

$$dm_\gamma = d_e m_\gamma + d_i m_\gamma \tag{17}$$

$$dm_\gamma = d_e m_\gamma + M_\gamma \sum_{\rho=1}^{r} \nu_{\gamma\rho} d\xi_\rho \tag{18}$$

or

$$dn_\gamma = d_e n_\gamma + \sum_{\rho=1}^{r} \nu_{\gamma\rho} d\xi_\rho \tag{19}$$

Summing equation (17) over γ and using the stoichiometric equations $\sum_\gamma \nu_{\gamma\rho} M_\gamma = 0$ gives

$$dm = d_e m \tag{20}$$

Principle of conservation of mass in open systems.
Process of splitting change of mass of γ into an external part and an internal part due to reactions inside the system can be performed for any extensive property, eg. entropy.