

5 Chapter 5: The Phenomenological Laws, Interference of Irreversible Processes

5.1 Domain of Validity of Phenomenological Laws, Chemical Reactions Near Equilibrium

Examine the domain of validity of linear phenomenological laws.

Eg. Transport process – heat flow in continuous systems.

Entropy production per unit time and volume is given by;

$$\sigma = -\frac{W_x}{T^2} \frac{\partial T}{\partial x} > 0 \quad (1)$$

with the phenomenological relation

$$W_x = -\frac{L}{T^2} \frac{\partial T}{\partial x} \quad (2)$$

which is Fourier's law with heat conductivity

$$\lambda = -\frac{L}{T^2} \quad (3)$$

Therefore, domain of validity of the phenomenological law (2) same as validity of Fourier's law. From statistical theory, Fourier's law valid if relative variation of temperature is small within length of mean free path ϕ ,

$$\frac{\phi}{T} \frac{\partial T}{\partial x} \ll 1. \quad (4)$$

Satisfied in most cases.

Consider now a single chemical reaction, the phenomenological relation is

$$v = L \frac{A}{T} \quad (5)$$

with entropy production

$$\frac{d_i S}{dt} = L \left(\frac{A}{T} \right)^2 \quad (6)$$

To consider the accuracy of phenomenological law (5), consider reaction for hydriodic acid,



The affinity

$$A = \mu_{H_2} + \mu_{I_2} - 2\mu_{HI} \quad (8)$$

For a mixture of perfect gases (see 3.24 and 3.25) and neglecting the pressure dependence

$$\mu_\gamma = \eta_\gamma(T) + RT \log C_\gamma \quad (9)$$

where the C_γ are the molar concentrations.

Introducing the equilibrium constant K , from (3.41) and (3.25)

$$RT \log K(T) = -\sum_\gamma \nu_\gamma \eta_\gamma(T) \quad (10)$$

and the affinity (3.40) becomes

$$A = -\sum_{\gamma} \nu_{\gamma} \eta_{\gamma}(T) - RT \sum_{\gamma} \nu_{\gamma} \log C_{\gamma} \quad (11)$$

$$= RT \log \frac{K(T)}{C_1^{\nu_1} \dots C_c^{\nu_c}} \quad (12)$$

For the synthesis of HI therefore,

$$A = RT \log \frac{K(T)}{C_{I_2}^{-1} C_{H_2}^{-1} C_{HI}^2} \quad (13)$$

Usual kinetic expression for the reaction rate is

$$v = \overrightarrow{v} - \overleftarrow{v} = \overrightarrow{k} C_{I_2} C_{H_2} - \overleftarrow{k} C_{HI}^2 = \overrightarrow{k} C_{I_2} C_{H_2} \left(1 - \frac{\overleftarrow{k}}{\overrightarrow{k}} \left(\frac{C_{HI}^2}{C_{I_2} C_{H_2}} \right) \right) \quad (14)$$

Ratio of the kinetic constants $\overrightarrow{k} / \overleftarrow{k} = K(T)$. Using (10) in (11) and comparing with (14) gives,

$$v = \overrightarrow{v} \left(1 - \exp \left(-\frac{A}{RT} \right) \right) \quad (15)$$

For reactions close to equilibrium

$$\left| \frac{A}{RT} \right| \ll 1 \quad (16)$$

and (15) reduces to

$$v = \frac{\overrightarrow{v}^e}{R} \frac{A}{T} \quad (17)$$

where \overrightarrow{v}^e is the value of the partial rate \overrightarrow{v} at equilibrium ($\overrightarrow{v}^e = \overleftarrow{v}^e$ for $A = 0$).

Therefore, the physical meaning of the phenomenological coefficient in eqn. (5) is

$$L = \overrightarrow{v}^e / R \quad (18)$$

its value depending on only the value of \overrightarrow{v} at equilibrium.

For the other extreme case of

$$\frac{A}{RT} \rightarrow \infty \quad (19)$$

from eqn. (13),

$$\frac{C_{I_2} C_{H_2}}{C_{HI}^2} \rightarrow \infty \quad \text{or} \quad C_{HI} \rightarrow 0 \quad (20)$$

which for a closed system corresponds to the initial stage of the reaction. The corresponding value of v is

$$v \rightarrow \overrightarrow{v} \quad (21)$$

which is independent of the affinity. The entropy production $\frac{d_i S}{dt} = v \frac{A}{T} = \overrightarrow{v} \frac{A}{T}$ thus becomes a linear function of the affinity.

Thus, in contrast to the simple behavior of transport processes, linear relations between rates and affinities are not always justified, and it is necessary to take into account the non-linear relations, like eqn. (15).

However, if affinity of a chemical reaction is large, it may be possible to divide the reaction into a number of more elementary reactions, each having an affinity sufficiently small to justify the application of linear phenomenological laws.

Eg., Consider the reaction



which proceeds in a number of steps



Entropy production due to these successive reaction is

$$T \frac{d_i S}{dt} = A_1 v_1 + A_2 v_2 \dots + A_r v_r \quad (29)$$

If the intermediate components $N, O, \dots P$ are unstable, a steady state

$$v_1 = v_2 = \dots = v_r = v \quad (30)$$

is reached after a short time so that

$$T \frac{d_i S}{dt} = Av \quad (31)$$

where

$$A = \sum_{\rho} A_{\rho} \quad (32)$$

is the macroscopic affinity.

If

$$\frac{|A_{\rho}|}{RT} \ll 1 \quad (33)$$

then *we are still in the domain of the linear phenomenological laws between reaction rates and affinities, even if the total affinity*

$$\frac{|A|}{RT} \gg 1 \quad (34)$$

This appears to be the case for many biological reactions which occur in steps.

Near equilibrium, the kinetic equations become very simple, even for complicated reactions. Consider a closed system

$$v = \frac{d\xi}{dt} = \frac{L}{T} A \approx \frac{L}{T} \left(\frac{\partial A}{\partial \xi} \right)_e (\xi - \xi_e) \quad (35)$$

Introduce the relaxation time τ

$$\tau = -\frac{T}{L \left(\frac{\partial A}{\partial \xi} \right)_e} \quad (36)$$

Integration of eqn. (35) gives

$$\xi - \xi_e = (\xi - \xi_e)_0 \exp -\frac{t}{\tau} \quad (37)$$

Note that the relaxation time τ is positive since $\partial A / \partial \xi < 0$.

For the general case of r simultaneous reactions, it is possible to show that

$$\xi_\rho - \xi_{\rho,e} = \sum_{\rho'} a_{\rho\rho'} \exp -\frac{t}{\tau_{\rho'}} \quad (38)$$

Based on the form of eqn. (38), it is possible to state that, independent of the initial conditions, ξ_ρ can only cross its equilibrium value $\xi_{\rho,e}$, at most $(r - 1)$ times. Therefore, a periodic behavior in time is impossible with a finite number of reactions.

Show that the above statement is correct.

5.2 Electrokinetic Effects – Saxen’s Relation

Will use Onsager’s reciprocity relation to study interference between irreversible processes. Consider system of two phases I and II connected by means of a porous wall. Temperature and compositions uniform throughout entire system. Difference is in the pressure and electrical potential. Entropy production due to the transfer of constituents from vessel I to vessel II is

$$d_i S = \frac{1}{T} \sum_{\gamma} \tilde{A}_{\gamma} d\xi_{\gamma} = -\frac{1}{T} \sum_{\gamma} \tilde{A}_{\gamma} dn_{\gamma}^I \quad (39)$$

where \tilde{A}_{γ} is the electrochemical affinity (see eqn. (3.62))

$$\tilde{A}_{\gamma} = (\mu_{\gamma}^I - \mu_{\gamma}^{II}) + z_{\gamma} \mathcal{F}(\phi^I - \phi^{II}) \quad (40)$$

$$\tilde{A}_{\gamma} = \Delta\mu_{\gamma} + z_{\gamma} \mathcal{F} \Delta\phi \quad (41)$$

Since temperature and composition are the same in each phase, (see eqn. (3.22)) $\left(\frac{\partial\mu_{\gamma}}{\partial p}\right)_{Tn_{\gamma}} = v_{\gamma}$ (specific molar volume)

$$\Delta\mu_{\gamma} = v_{\gamma} \Delta p \quad (42)$$

where v_{γ} is the specific molar volume of constituent γ . Thus

$$\frac{d_i S}{dt} = -\frac{1}{T} \sum_{\gamma} v_{\gamma} \frac{dn_{\gamma}^I}{dt} \Delta p - \frac{1}{T} \sum_{\gamma} z_{\gamma} \mathcal{F} \frac{dn_{\gamma}^I}{dt} \Delta\phi \quad (43)$$

Define the following flows

$$J = -\sum_{\gamma} v_{\gamma} \frac{dn_{\gamma}^I}{dt}; \quad I = -\sum_{\gamma} z_{\gamma} \mathcal{F} \frac{dn_{\gamma}^I}{dt} \quad (44)$$

where J is the flow of matter and I is the electrical current due to a transfer of charge from I to II. The entropy production is then

$$\frac{d_i S}{dt} = \frac{J \Delta p}{T} + \frac{I \Delta\phi}{T} \quad (45)$$

The phenomenological eqns. are then

$$I = L_{11} \frac{\Delta\phi}{T} + L_{12} \frac{\Delta p}{T} \quad (46)$$

$$J = L_{21} \frac{\Delta\phi}{T} + L_{22} \frac{\Delta p}{T} \quad (47)$$

with the Onsager relation $L_{12} = L_{21}$ which describes the interference of two irreversible processes; transport of matter under the influence of a difference of pressure; flow of electrical current due to a difference of electrical potential.

Definition of some electrokinetic effects;

Streaming potential – potential difference per unit pressure difference in state with zero electrical current

$$\left(\frac{\Delta\phi}{\Delta p}\right)_{I=0} = -\frac{L_{12}}{L_{11}} \quad (48)$$

Electro-osmosi – flow of matter per unit electrical current in state of uniform pressure

$$\left(\frac{J}{I}\right)_{\Delta p=0} = \frac{L_{21}}{L_{11}} \quad (49)$$

Electro-osmotic pressure – pressure difference per unit potential difference when the flow of matter is zero

$$\left(\frac{\Delta p}{\Delta\phi}\right)_{J=0} = -\frac{L_{21}}{L_{22}} \quad (50)$$

Streaming Current – flow of electrical current per unit flow of mass in the state of zero electrical potential

$$\left(\frac{I}{J}\right)_{\Delta\phi=0} = \frac{L_{12}}{L_{22}} \quad (51)$$

With the use of Onsager's relations,

$$\left(\frac{\Delta\phi}{\Delta p}\right)_{I=0} = -\left(\frac{J}{I}\right)_{\Delta p=0} \quad (52)$$

$$\left(\frac{\Delta p}{\Delta\phi}\right)_{J=0} = -\left(\frac{I}{J}\right)_{\Delta\phi=0} \quad (53)$$

Relate an osmotic effect to a streaming effect. Eqn. (52) was obtained before through kinetic considerations, but was based on a model of restricted generality.

5.3 Thermomolecular Pressure Difference and Thermochemical Effect

Consider system of two phases I and II which communicate via a small hole or porous membrane. System as a whole is closed. Temperature difference is maintained between the two. Will have flow of heat and may have flow of matter.

Using eqns. (4.22) and (4.26), the forces are given by

$$X_{th} = \Delta \left(\frac{1}{T}\right) \approx -\frac{1}{T^2} \Delta T \quad (54)$$

$$X_m = -\frac{(\Delta\mu)_T}{T} \approx -\frac{v}{T} \Delta p \quad (55)$$

where X_m is the transformed force (see chapter 4) and $\left(\frac{\partial\mu_\gamma}{\partial p}\right)_{Tn_\gamma} = v_\gamma$ (specific molar volume). And the fluxes of energy and matter are, using (4.19) and (4.20) with (4.17),

$$J_{th} = \frac{d_i^{II}\phi}{dt} - h \frac{dn^{II}}{dt} \quad (56)$$

$h_\gamma = \left(\frac{\partial H}{\partial n_\gamma}\right)_{pTn'_\gamma}$ (specific molar enthalpy), and J_{th} is the transformed flow including h ,

$$J_m = \frac{dn^{II}}{dt} = -\frac{dn^I}{dt} \quad (57)$$

with the phenomenological laws

$$J_{th} = -L_{11} \frac{\Delta T}{T^2} - L_{12} \frac{v}{T} \Delta p \quad (59)$$

$$J_m = -L_{21} \frac{\Delta T}{T^2} - L_{22} \frac{v}{T} \Delta p \quad (60)$$

with the Onsager relation

$$L_{12} = L_{21} \quad (61)$$

Define *Thermomolecular pressure* – difference of pressure which arises between two phases held at a finite temperature difference when the flow of matter goes to zero, i.e. $J_m = 0$

$$\left(\frac{\Delta p}{\Delta T} \right)_{J_m=0} = - \frac{L_{21}}{L_{22} v T} \quad (62)$$

In the *stationary state* ($J_m = 0$) the state variables of the system no longer depend on time. Flow of matter due to pressure difference is balanced by flow of matter due to temperature difference. This is not an equilibrium state since the flow J_{th} is different from zero and thus there is entropy production.

In the case of the system consisting of a gas separated by a small opening, the thermomolecular pressure difference is called the “Knudsen effect”.

This effect also occurs in liquid helium below the λ point ($2.19^\circ K$) and is called the “fountain effect”.

Investigate and describe the “fountain effect”.

In the case of a permeable membrane separating the two phases, the effect is called “*thermo-osmosis*”.

Define *Thermomechanical effect* – a pressure difference is maintained between the two phases and the temperature is maintained uniform throughout the whole system. Matter will flow from one phase to the other and will result in a corresponding, proportional flow of energy.

$$\left(\frac{J_{th}}{J_m} \right)_{\Delta T=0} = \frac{L_{12}}{L_{22}} \quad (63)$$

L_{12}/L_{22} has physical significance of energy transfer per unit transfer of mass. Often called *heat of transfer*.

$$Q^* \equiv \frac{L_{12}}{L_{22}} \quad (64)$$

Onsager’s reciprocity relation establishes the relation between the thermomolecular pressure difference and the thermomechanical effect

$$\left(\frac{\Delta p}{\Delta T} \right)_{J_m=0} = - \frac{1}{v T} \left(\frac{J_{th}}{J_m} \right)_{\Delta T=0} \quad (65)$$

Both effects depend on the heat of transfer Q^* . Further insight into this heat of transfer can be obtained by applying principle of conservation of energy to phase II.

$$\frac{dE^{II}}{dt} = \frac{d^{II}\phi}{dt} = \frac{d_e^{II}Q}{dt} + \frac{d_i^{II}\phi}{dt} \quad (66)$$

but from eqns. (56) and (57)

$$\frac{d_i^{II}\phi}{dt} = J_{th} + h \frac{dn^{II}}{dt} \quad (67)$$

so

$$\frac{dE^{II}}{dt} = \frac{d_e^{II}Q}{dt} + \left(\frac{J_{th}}{v} + h \right) \frac{dn^{II}}{dt} \quad (68)$$

$$\frac{dE^{II}}{dt} = \frac{d_e^{II}Q}{dt} + (Q^* + h) \frac{dn^{II}}{dt} \quad (69)$$

Thus, $Q^* + h$ is the average energy transferred to phase II per unit mass transfer, denote this by e^*

$$e^* = Q^* + h \quad (70)$$

or

$$Q^* = e^* - h \quad (71)$$

5.4 Kinetic Interpretation of Heat of Transfer – Knudsen Gas

Two phases connected by a small opening, the diameter of which is small compared to the mean free path.

From kinetic theory of gases, the number of molecules coming from phase I which pass through the opening is proportional to $p^I/\sqrt{T^I}$, and the corresponding molecules from phase II is $p^{II}/\sqrt{T^{II}}$. For the stationary state, in which the flow of matter is zero,

$$\frac{p^I}{p^{II}} = \sqrt{\frac{T^I}{T^{II}}} \quad (72)$$

Show that this equation can be derived from the kinetic theory of gases.

With $p^{II} = p^I + \Delta p$, $T^{II} = T^I + \Delta T$, ignoring terms of $(\Delta p)^2$ y $(\Delta T)^2$, can write differential form of the above as

$$\frac{\Delta p}{\Delta T} = \frac{1}{2} \frac{p}{T} = \frac{R}{2v} \quad (73)$$

With eqn. (62) $\left(\frac{\Delta p}{\Delta T}\right)_{J_m=0} = -\frac{L_{21}}{L_{22}vT}$ and (64) $Q^* \equiv \frac{L_{12}}{L_{22}}$, the heat transfer for a Knudsen gas is

$$Q^* = -\frac{RT}{2} \quad (74)$$

Heat of transfer can also be obtained through a direct *statistical* calculation by determining the mean energy e^* transported by a molecule crossing the opening.

Assume direction x is perpendicular to the opening. v_x is the velocity of a molecule and f is the corresponding velocity distribution function.

$$f \propto \exp -\frac{mv_x^2}{2kT} \quad (75)$$

Total flow of molecules through the unit area of the opening per unit time is (C is a constant proportional to size of opening)

$$C\bar{v}_x = \int_0^\infty f v_x dv_x \quad (76)$$

Each molecule passing the opening transports a kinetic energy

$$\frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \quad (77)$$

Total flow of energy (per unit time and unit area of the opening) corresponding to the coordinate x is

$$C \overline{\frac{1}{2}mv_x^2 \cdot v_x} = \frac{m}{2} \int_0^\infty f v_x^3 dv_x \quad (78)$$

The mean value of the energy transported per molecule is given by the ratio of the total flow of energy to the total flow of molecules

$$\frac{m \int_0^\infty f v_x^3 dv_x}{2 \int_0^\infty f v_x dv_x} = kT \quad (79)$$

This is exactly twice the equipartition value of $1/2kT$ and is a consequence of fact that molecules of high velocity have greater chance of crossing the opening than slow molecules.

The mean values of $1/2mv_y^2$ and $1/2mv_z^2$ are simply the equipartition value of $1/2kT$. So the total mean value of energy transported per molecule is $2kT$, so per mole

$$e^* = 2RT \quad (80)$$

Therefore, the heat of transfer is

$$Q^* = e^* - h = 2RT - (5/2)RT = -\frac{RT}{2} \quad (81)$$

which is the same as (74), obtained through noneq. TD methods.

In cases in which the mean energy of the molecules crossing the separating layer between two phases is different from the enthalpy h , there will be a heat of transfer, a thermomolecular pressure difference, and a thermomechanical effect.

5.5 Diffusion – Einstein's Relation

From equation for entropy production due to diffusion in a two component system, eqn. (4.78)

$$\sigma = \frac{1}{T} \left(\mathcal{F}_1 - \frac{\partial \mu_1^+}{\partial x} \right) \rho_1 (\omega_1 - \omega_2) > 0 \quad (82)$$

the corresponding phenomenological law is

$$\rho_1 (\omega_1 - \omega_2) = \frac{L}{T} \left(\mathcal{F}_1 - \frac{\partial \mu_1^+}{\partial x} \right) \quad (83)$$

For an ideal gas or a dilute solution,

$$\mu_1 = \eta_1(T) + RT \log C_1 \quad (84)$$

by multiplying (83) by the molar mass of component 1, M_1 , gives

$$C_1 (\omega_1 - \omega_2) = \frac{L}{T} \left(\mathcal{F}_1 M_1 - \frac{\partial \mu_1}{\partial x} \right) = -\frac{L}{T} \frac{RT}{C_1} \left(\frac{\partial C_1}{\partial x} - \frac{\mathcal{F}_1 M_1 C_1}{RT} \right) \quad (85)$$

$$C_1(\omega_1 - \omega_2) = \frac{L}{T} \left(\mathcal{F}_1 M_1 - \frac{\partial \mu_1}{\partial x} \right) = -\frac{L RT}{T C_1} \left(\frac{\partial C_1}{\partial x} - \frac{\mathcal{F}_1 M_1 C_1}{RT} \right) \quad (86)$$

Consider two particular cases.

1) A *uniform system*;

$$(\omega_1 - \omega_2) = \frac{L}{TC_1} \mathcal{F}_1 M_1 \quad (87)$$

coefficient of proportionality between the relative velocity $\omega_1 - \omega_2$ and the force $\mathcal{F}_1 M_1$ (per mole),

$$B = \frac{L}{TC_1} \quad (88)$$

is called the *mobility* of component 1.

2) A system without external forces;

$$C_1(\omega_1 - \omega_2) = -\frac{L RT}{T C_1} \frac{\partial C_1}{\partial x} \quad (89)$$

Coefficient of proportionality between flux of diffusion $C_1(\omega_1 - \omega_2)$ and concentration gradient is the *diffusion coefficient*

$$D = \frac{L RT}{T C_1} \quad (90)$$

Comparing eqns. (88) and (90), we obtain Einstein's relation between mobility and the diffusion coefficient,

$$D = RTB \quad (91)$$

Consider the general definition of the diffusion coefficient without external forces

$$C_1(\omega_1 - \omega_2) = -\frac{L}{T} \frac{\partial \mu_1}{\partial x} \quad (92)$$

or

$$C_1(\omega_1 - \omega_2) = -\frac{L}{T} \frac{\partial \mu_1}{\partial N_1} \frac{\partial N_1}{\partial x} \quad (93)$$

From an experimental point of view, the diffusion coefficient is measured from

$$C_1(\omega_1 - \omega_2) = -DC \frac{\partial N_1}{\partial x} \quad (94)$$

where C is some constant. Therefore,

$$D = \frac{1}{TC} L \frac{\partial \mu_1}{\partial N_1} \quad (95)$$

(For an ideal gas or dilute solution, this definition is the same as eqn. (90).) Note that the diffusion coefficient is a product of the phenomenological coefficient L and the thermodynamic quantity $(1/TC)(\partial \mu_1 / \partial N_1)$.

The coefficient L is always positive, and so is the quantity $\partial \mu_1 / \partial N_1$ for all ideal systems. Therefore the diffusion coefficient is positive and according to eqn. (94) the flow of diffusion is directed in a direction such that concentration gradients are compensated.

For systems containing two "non-miscible" liquids, like benzene and water, $\partial \mu_1 / \partial N_1$ is negative, in this case, the two concentration gradients are maintained.

5.6 Continuous and Discontinuous Formalism

General method for describing continuous systems through discontinuous formalism.

Consider the case of thermal conductivity

$$d_i S/dt = \int \sigma dV = - \int (W_x/T^2)(\partial T/\partial x)dV \quad (96)$$

Would like to put this continuous form into a discontinuous form, eg.

$$d_i S/dt = \sum_i J_i X_i \quad (97)$$

Expand W and T in a Fourier series

$$W = \sum_f W_f \exp(iffx) \quad T = \sum_f T_f \exp(iffx) \quad (98)$$

W_f and T_f complex. Introducing these into eqn. (96) gives

Show this as homework.

$$d_i S/dt = -1/t_0^2 \sum_{ff'} T_f if W_{f'} \int \exp[i(f+f')x] dx \quad (99)$$

$$= -1/t_0^2 \sum_f if T_f W_f \quad (100)$$

Thus, the flows J_i are the Fourier components of W , and the generalized forces are ifT_f . Eg., Fourier's law becomes

$$W_f = -\lambda if T_f \quad (101)$$