

3 Chapter 3: Entropy Production – Second Principle of Thermodynamics

3.1 Reversible and Irreversible Processes

Consider some time dependent physical process.

If eqns. describing process are invariant with respect to change of sign of the time variable, process is called *reversible*. If not, process is *irreversible*.

Give an example of a naturally occurring or man-made reversible process.

Eg.

$$\frac{1}{c^2} \frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \quad (1)$$

Equation is invariant under $t \rightarrow -t$ – reversible.

Fourier equation for temperature;

$$\frac{1}{\alpha} \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \quad (2)$$

– irreversible.

Most physiochemical processes, diffusion, conduction (heat or electricity) chemical reactions, etc. are irreversible processes.

Therefore, a theory of irreversible thermodynamics essential.

3.2 Entropy

From Greek word $\epsilon\nu\tau\rho\omega\pi\eta$ meaning “evolution”.

Postulate the following properties

1. is an *extensive* property of a system
- 2.

$$dS = d_e S + d_i S$$

$$d_i S = 0 \quad (\text{reversible process})$$

$$d_i S > 0 \quad (\text{irreversible process})$$

For *isolated* systems;

$$dS = d_i S \geq 0 \quad (3)$$

Second law of thermodynamics.

Most general evolution criterion of natural processes.

Other criterion, eg. $F = E - TS$ decreases when irreversible changes occur.

However, functions like F and G exist only for specific conditions (eg., changes at constant temperature and volume, or, at constant temperature and pressure).

3.3 Local Formulation of Second Law

Consider system I inside a larger system II such that the global system is isolated.

Second law

$$dS = dS^I + dS^{II} \geq 0 \quad (4)$$

Postulate

$$d_i S^I \geq 0, \quad d_i S^{II} \geq 0 \quad (5)$$

Situation in which

$$d_i S^I > 0, \quad d_i S^{II} < 0 \quad \text{with} \quad d(S^I + S^{II}) > 0 \quad (6)$$

excluded.

No possibility for compensation – in every macroscopic region (microscopic fluctuations are negligible) of the system the entropy production due to irreversible processes is positive.

Interference of irreversible processes only possible when they occur in same macroscopic region.

Local formulation of second law is postulate on which course is based.

Has been verified through statistical mechanics and experiment.

3.4 Absolute Temperature

Consider closed system containing a single component, irreversible processes excluded.

Entropy defined by

$$dS = \frac{dQ}{T} \quad (7)$$

T is called *absolute temperature*. Satisfies

1. T is positive
2. T is an intensive property obtained by measuring some arbitrary property like electrical resistance
3. T is an increasing function of the “empirical” temperature of the system.

To fix scale, set $T = 273.16^\circ\text{K}$ for triple point of water.

Note that

$$dS = \frac{dE + pdV}{T} \quad (8)$$

3.5 Entropy Production Due to Heat Flow

Consider two closed subsystems I and II (total system therefore also closed) maintained at uniform temperature T^I and T^{II} respectively.

Being an extensive variable

$$dS = dS^I + dS^{II} \quad (9)$$

For each phase

$$d^I Q = d_i^I Q + d_e^I Q, \quad d^{II} Q = d_i^{II} Q + d_e^{II} Q \quad (10)$$

For whole system

$$dS = \frac{d^I Q}{T^I} + \frac{d^{II} Q}{T^{II}} \quad (11)$$

$$= \frac{d_e^I Q}{T^I} + \frac{d_e^{II} Q}{T^{II}} + d_i^I Q \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) \quad (12)$$

Where we have used (3.24).

Then,

$$d_e S = \frac{d_e^I Q}{T^I} + \frac{d_e^{II} Q}{T^{II}} \quad (13)$$

and

$$d_i S = d_i^I Q \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) \quad (14)$$

results from irreversible heat flow inside the system.

Now, empirically, can show that entropy production $d_i S$ is always positive; therefore,

$$d_i^I Q > 0 \quad \text{when} \quad \frac{1}{T^I} - \frac{1}{T^{II}} > 0 \quad (15)$$

and

$$d_i^I Q < 0 \quad \text{when} \quad \frac{1}{T^I} - \frac{1}{T^{II}} < 0 \quad (16)$$

Entropy production is only zero when thermal equilibrium is established, i.e. when $T^I = T^{II}$.

Entropy production per unit time

$$\frac{d_i S}{dt} = \frac{d_i^I Q}{dt} \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) > 0 \quad (17)$$

Equation will be shown to be very general. Product of rate of irreversible process ($d_i^I Q/dt$) by function of state ($1/T^I - 1/T^{II}$).

Generalized flow and corresponding force.

3.6 Entropy of Multicomponent Systems - Chemical Potentials

Generalize the total differential of the entropy for multi-component systems.

$$dS = \frac{dE}{T} + \frac{p}{T}dV - \sum_{\gamma} \frac{\mu_{\gamma}}{T}dn_{\gamma} \quad (18)$$

μ_{γ} are the *chemical potentials* defined by

$$\mu_{\gamma} = -T \left(\frac{\partial S}{\partial n_{\gamma}} \right)_{EVn'_{\gamma}} \quad (19)$$

The chemical potentials are intensive variables (like other partial derivatives of S , eg. $1/T = \partial S/\partial E$, $p/T = \partial S/\partial V$).

Chemical potential can be expressed in other ways; eg. energy representation

$$\mu_{\gamma} = \left(\frac{\partial E}{\partial n_{\gamma}} \right)_{SVn'_{\gamma}} \quad (20)$$

Introducing the enthalpy $H = E + pV$, Helmholtz free energy $F = E - TS$, Gibbs free energy $G = H - TS$,

$$\mu_{\gamma} = \left(\frac{\partial H}{\partial n_{\gamma}} \right)_{Spn'_{\gamma}} = \left(\frac{\partial F}{\partial n_{\gamma}} \right)_{TVn'_{\gamma}} = \left(\frac{\partial G}{\partial n_{\gamma}} \right)_{Tpn'_{\gamma}} \quad (21)$$

Show that the above relations are correct.

Relations involving the chemical potentials

$$\left(\frac{\partial \mu_{\gamma}}{\partial T} \right)_{pn_{\gamma}} = -s_{\gamma}, \quad \left(\frac{\partial \mu_{\gamma}}{\partial p} \right)_{Tn_{\gamma}} = v_{\gamma}, \quad \left(\frac{\partial(\mu_{\gamma}/T)}{\partial T} \right)_{pn_{\gamma}} = \frac{h_{\gamma}}{T^2} \quad (22)$$

where s_{γ} , v_{γ} and h_{γ} are respectively specific molar entropy, volume and enthalpy of component γ as defined by

$$s_{\gamma} = \left(\frac{\partial S}{\partial n_{\gamma}} \right)_{pTn'_{\gamma}}, \quad v_{\gamma} = \left(\frac{\partial V}{\partial n_{\gamma}} \right)_{pTn'_{\gamma}}, \quad h_{\gamma} = \left(\frac{\partial H}{\partial n_{\gamma}} \right)_{pTn'_{\gamma}} \quad (23)$$

Prove relations (22) using definitions (23).

For ideal systems

$$\mu_{\gamma} = \zeta_{\gamma}(p, T) + RT \log N_{\gamma} \quad (24)$$

where $\zeta_{\gamma}(p, T)$ is independent of composition and N_{γ} is the mole fraction ($= n_{\gamma}/n$).

For ideal gasses

$$\zeta_{\gamma}(p, T) = RT \log p + \eta_{\gamma}(T) \quad (25)$$

For non-ideal systems

$$\mu_{\gamma} = \zeta_{\gamma}(p, T) + RT \log f_{\gamma}N_{\gamma} \quad (26)$$

where f_{γ} is the *activity coefficient*.

3.7 Entropy Production due to Chemical Reactions - Affinity- Coupling of Chemical Reactions – Closed Systems

Expression for entropy flow and production due to single chemical reaction in a closed system. Using eqns. (2.6) $d\xi = dn_\gamma/\nu_\gamma$ and (18), can write

$$dS = \frac{dQ}{T} + \frac{Ad\xi}{T} \quad (27)$$

where A is the *affinity* of the chemical reaction, related to the chemical potentials by

$$A = - \sum_{\gamma} \nu_{\gamma} \mu_{\gamma} \quad (28)$$

The total entropy change can thus be divided into two parts

$$d_e S = \frac{dQ}{T} \quad (29)$$

and

$$d_i S = \frac{Ad\xi}{T} > 0 \quad (30)$$

Prove that $d_i S$ as given by eqn. (30) is always > 0 except in equilibrium, in which case it is $= 0$.

For the equilibrium state

$$A = - \sum_{\gamma} \nu_{\gamma} \mu_{\gamma} = 0 \quad (31)$$

Prove that if the transformation represented by ξ consists in the passage of component γ from phase I to phase II, then the equilibrium condition (31) becomes

$$\mu_{\gamma}^I = \mu_{\gamma}^{II} \quad (32)$$

In terms of the chemical reaction rate v we have for the entropy production per unit time of the reaction

$$\frac{d_i S}{dt} = \frac{1}{T} Av > 0 \quad (33)$$

A and v thus always have the same sign. The right-hand side of this equation is again a product of a generalized flow (chemical reaction rate v) and corresponding force (affinity A/T). It is of the same general form as eqn. (4.17) for the irreversible process of heat flow.

Extension to the case of several simultaneous reactions

$$d_i S = \frac{1}{T} \sum_{\rho} A_{\rho} d\xi_{\rho} > 0 \quad (34)$$

where

$$A_{\rho} = - \sum_{\gamma} \nu_{\gamma\rho} \mu_{\gamma} \quad (35)$$

In equilibrium

$$A_1 = A_2 = \dots = A_r = 0 \quad (36)$$

Entropy production per unit time

$$\frac{d_i S}{dt} = \frac{1}{T} \sum_{\rho} A_{\rho} v_{\rho} > 0 \quad (37)$$

Second law of TD requires that entropy production resulting from all simultaneous reactions is positive. However, could have system undergoing two simultaneous reactions such that

$$A_1 v_1 < 0, \quad A_2 v_2 > 0 \quad (38)$$

provided that

$$A_1 v_1 + A_2 v_2 > 0 \quad (39)$$

Reactions called “coupled” reactions. One reaction can thus go in a direction contrary to that described by its own affinity.

This is a coupling of two distinct irreversible processes. Is of great importance to biological processes.

Another example (to be seen later) – thermodiffusion – diffusion of matter against its concentration gradient results in a negative entropy production but this effect is compensated by the positive entropy production due to the flow of heat.

Suggest three other possibly coupled irreversible process which might be important to biological or physical phenomena.

3.8 Chemical Affinity

Using eqn. (26), $\mu_\gamma = \zeta_\gamma(p, T) + RT \log N_\gamma$, and (28), $A = -\sum_\gamma \nu_\gamma \mu_\gamma$

$$A = -\sum_\gamma \nu_\gamma \zeta_\gamma(p, T) - RT \sum_\gamma \nu_\gamma \log N_\gamma \quad (40)$$

Define the *equilibrium constant* $K(p, T)$ by

$$RT \log K(p, T) = -\sum_\gamma \nu_\gamma \zeta_\gamma(p, T) \quad (41)$$

Then the affinity becomes $A = RT \log K(p, T) - RT \sum_\gamma \nu_\gamma \log N_\gamma$, N_γ = molar fraction

$$A = RT \log \frac{K(p, T)}{N_1^{\nu_1} \dots N_c^{\nu_c}} \quad (42)$$

In equilibrium, $A = 0$, so

$$K(p, T) = N_1^{\nu_1} \dots N_c^{\nu_c} \quad (43)$$

Called “law of mass action”.

Alternative expression for the affinity from eqn. (21)

$$A = -\sum_\gamma \nu_\gamma \left(\frac{\partial G}{\partial n_\gamma} \right)_{p, T, n'_\gamma} \quad (44)$$

But,

$$\left(\frac{\partial G}{\partial \xi} \right)_{p, T} = \sum_\gamma \left(\frac{\partial G}{\partial n_\gamma} \right)_{p, T, n'_\gamma} \frac{dn_\gamma}{d\xi} = \sum_\gamma \left(\frac{\partial G}{\partial n_\gamma} \right)_{p, T, n'_\gamma} \nu_\gamma \quad (45)$$

Therefore,

$$A = -\left(\frac{\partial G}{\partial \xi} \right)_{p, T} \quad (46)$$

Remembering that $G = H - TS$

$$A = -\left(\frac{\partial H}{\partial \xi} \right)_{p, T} + T \left(\frac{\partial S}{\partial \xi} \right)_{p, T} = r_{pT} + T \left(\frac{\partial S}{\partial \xi} \right)_{p, T} \quad (47)$$

In some cases, it may be possible to neglect the entropy variation term in (47), so that the entropy production due to a chemical change becomes simply proportional to the heat of reaction

$$\frac{d_i S}{dt} = \frac{A v}{T} \approx \frac{r_{\{p, T\}} v}{T} = -\frac{1}{T} \left(\frac{d_e Q}{dt} \right)_{pT} \quad (48)$$

Show that $\frac{r_{\{p, T\}} v}{T} = -\frac{1}{T} \left(\frac{d_e Q}{dt} \right)_{pT}$. Under what conditions can the entropy production term $\left(\frac{\partial S}{\partial \xi} \right)_{p, T} v$ can be neglected?

For simultaneous reactions

$$\frac{d_i S}{dt} \approx \frac{1}{T} \sum_\rho r_{p, T}^\rho v_\rho = -\frac{1}{T} \left(\frac{d_e Q}{dt} \right)_{pT} \quad (49)$$

In this approximation, the entropy of a living organism can be measured by its metabolism, as recorded by calorimetry.

Design a feasible experiment to measure the entropy production of an animal?

3.9 Entropy Production and Entropy Flow in Open Systems

Start with the Gibbs formula including flow of material from the exterior and chemical reactions occurring in the interior.

$$dS = \frac{d\phi}{T} - \sum_{\gamma} \frac{\mu_{\gamma}}{T} d_e n_{\gamma} + \frac{Ad\xi}{T} \quad (50)$$

$$d_e S = \frac{d\phi}{T} - \sum_{\gamma} \frac{\mu_{\gamma}}{T} d_e n_{\gamma} \quad (51)$$

Now, consider a system consisting of two open subsystems but which is closed as a whole. The change of the total entropy of the system is expressed by

$$dS = \frac{d^I \phi}{T^I} + \frac{d^{II} \phi}{T^{II}} - \sum_{\gamma} \left(\frac{\mu_{\gamma}^I}{T^I} - \frac{\mu_{\gamma}^{II}}{T^{II}} \right) d_e n_{\gamma}^I + \frac{A^I d\xi^I}{T^I} + \frac{A^{II} d\xi^{II}}{T^{II}} \quad (52)$$

where A^I and A^{II} are the affinities of the reactions taking place in each subsystem. Separating the flow of energy due to mass flow and heat internally, and heat from the exterior gives

$$dS = \frac{d_e^I Q}{T^I} + \frac{d_e^{II} Q}{T^{II}} + d_i^I \phi \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) - \sum_{\gamma} \left(\frac{\mu_{\gamma}^I}{T^I} - \frac{\mu_{\gamma}^{II}}{T^{II}} \right) d_e n_{\gamma}^I + \frac{A^I d\xi^I}{T^I} + \frac{A^{II} d\xi^{II}}{T^{II}} \quad (53)$$

Clearly,

$$d_e S = \frac{d_e^I Q}{T^I} + \frac{d_e^{II} Q}{T^{II}} \quad (54)$$

and

$$d_i S = d_i^I \phi \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) - \sum_{\gamma} \left(\frac{\mu_{\gamma}^I}{T^I} - \frac{\mu_{\gamma}^{II}}{T^{II}} \right) d_e n_{\gamma}^I + \frac{A^I d\xi^I}{T^I} + \frac{A^{II} d\xi^{II}}{T^{II}} \geq 0 \quad (55)$$

This entropy production results from the transport of heat and matter between the two phases and also from the chemical reaction taking part in each phase.

Entropy production per unit time

$$\frac{d_i S}{dt} = \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) \frac{d_i^I \phi}{dt} - \sum_{\gamma} \left(\frac{\mu_{\gamma}^I}{T^I} - \frac{\mu_{\gamma}^{II}}{T^{II}} \right) \frac{d_e n_{\gamma}^I}{dt} + \frac{A^I v^I}{T^I} + \frac{A^{II} v^{II}}{T^{II}} \geq 0 \quad (56)$$

Again, entropy production is a bilinear form of the rates of irreversible processes and of some functions of state which may be called the “generalized forces”.

3.10 Entropy Production Due to Electrochemical Reactions

Generalization to include electrochemical or photochemical reactions.

Include the presence of an electrical or radiation field in the conservation of energy.

Example

Transport of electrically charged component from position at potential φ^I to position at potential φ^{II} .

Consider open subsystems I and II in contact, but closed as a whole.

Degree of advancement

$$-dn_\gamma^I = dn_\gamma^{II} = d\xi_\gamma \quad (57)$$

Let z_γ denote electrovalency of the ionic component γ being transported by the field.

Let \mathcal{F} be the electric charge associated with one gram-ion of a species having an electrovalency of 1 ($\mathcal{F} = 0.9649$).

The electric current is then ($q = z_\gamma \mathcal{F}$)

$$I = z_\gamma \mathcal{F} \frac{d\xi_\gamma}{dt} = z_\gamma \mathcal{F} v_\gamma \quad (58)$$

Including the change of electrical energy into internal energy

$$dE = dQ - pdV + (\varphi^I - \varphi^{II}) I dt \quad (59)$$

(remember that power $P = dE/dt = VI$)

Assume that the Gibbs equation is still valid in presence of field.

True if polarization of matter can be neglected. Orientation of molecules in electric field associated with decrease in entropy.

If temperature uniform throughout whole system, Gibbs equation becomes

$$dS = \frac{dE}{T} + \frac{p}{T} dV - \sum_\gamma \left(\frac{\mu_\gamma^I}{T} dn_\gamma^I + \frac{\mu_\gamma^{II}}{T} dn_\gamma^{II} \right) \quad (60)$$

Using the above equations show that ...

$$dS = \frac{dQ}{T} + \frac{\tilde{A}_\gamma d\xi_\gamma}{T} \quad (61)$$

with

$$\tilde{A}_\gamma = A_\gamma + z_\gamma \mathcal{F} (\varphi^I - \varphi^{II}) = (\mu_\gamma^I + z_\gamma \mathcal{F} \varphi^I) - (\mu_\gamma^{II} + z_\gamma \mathcal{F} \varphi^{II}) \quad (62)$$

$$\bar{\mu}_\gamma = \mu_\gamma + z_\gamma \mathcal{F} \varphi \quad (63)$$

called the "electrochemical potential".

The internal entropy production due to the transport of the electrically charge component is thus

$$d_i S = \frac{\tilde{A}_\gamma d\xi_\gamma}{T} \quad (64)$$

Presence of electrical potential manifests itself only by altering the value of the affinity.

At equilibrium,

$$\tilde{A}_\gamma = 0 \quad \text{or} \quad \mu^I - \mu^{II} = z_\gamma \mathcal{F} (\varphi^I - \varphi^{II}) \quad (65)$$

3.11 Entropy Production in Continuous Systems

Until now we have considered *discontinuous systems* – where the intensive variables have the same value throughout each homogeneous region, but different values in each region.

Now we will consider intensive variables which are not only a function of time, but also of space coordinates, *continuous systems*.

eg. metal bar heated at one end and cooled at the other, a mixture of diffusing components.

Continuous Systems

No new physical principles required.

Conservation of Mass

$$\frac{\partial \rho}{\partial t} = -\text{div } \rho \omega \quad (66)$$

Equation of continuity, ρ is mass density and ω is macroscopic velocity.

$$\text{div } \rho \omega = \frac{\partial \rho \omega_x}{\partial x} + \frac{\partial \rho \omega_y}{\partial y} + \frac{\partial \rho \omega_z}{\partial z} \quad (67)$$

Eqn. (66) holds also for a mixture. Define

$$\omega = \left(\sum_{\gamma} \rho_{\gamma} \omega_{\gamma} \right) / \rho \quad (68)$$

ω is thus velocity of center of gravity.

In general, local change of a physical quantity is due not only to the divergence of a current but also to a *source* term.

For example, consider a chemical reaction, equation of continuity for the density ρ_{γ} of component γ is thus

$$\frac{\partial \rho_{\gamma}}{\partial t} = -\text{div } \rho_{\gamma} \omega_{\gamma} + \nu_{\gamma} M_{\gamma} v_v \quad (69)$$

where v_v is the rate of the chemical reaction per *unit volume*.

Flow of component γ can be decomposed into a flow with velocity of center of mass and a diffusion flow relative to ω .

$$\rho_{\gamma} \omega_{\gamma} = \rho_{\gamma} \omega + \rho_{\gamma} (\omega_{\gamma} - \omega) = \rho_{\gamma} \omega + \rho_{\gamma} \Delta_{\gamma} \quad (70)$$

Δ_{γ} represents diffusion velocity with respect to ω .

Note that

$$\sum_{\gamma} \rho_{\gamma} \Delta_{\gamma} = 0 \quad (71)$$

For every extensive variable, can write an eqn. similar to (69).

eg. Entropy per unit volume s_v

$$\frac{\partial s_v}{\partial t} = -div\Phi + \sigma \quad (72)$$

The above is the extension of $dS = d_eS + d_iS$ to continuous systems.

It is obvious that

$$\sigma = 0 \text{ (reversible processes) } , \sigma > 0 \text{ (irreversible processes) } \quad (73)$$

Calculation of local entropy production based on the local formulation of the Gibbs equation. For *discontinuous* systems (see (56))

$$\frac{d_iS}{dt} = \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) \frac{d_i\phi}{dt} - \sum_{\gamma} \left(\frac{\mu_{\gamma}^I}{T^I} - \frac{\mu_{\gamma}^{II}}{T^{II}} \right) \frac{d_e n_{\gamma}^I}{dt} + \frac{A^I v^I}{T^I} + \frac{A^{II} v^{II}}{T^{II}} \geq 0 \quad (74)$$

For a continuous system it can be shown (*try to derive this*) that

$$\sigma = - \sum_i \frac{W^i}{T^2} \frac{\partial T}{\partial x^i} + \sum_{\gamma} \sum_i \frac{1}{T} \left(\mathcal{F}_{\gamma}^i - T \frac{\partial \mu_{\gamma}^+ / T}{\partial x^i} \right) \rho_{\gamma} \Delta_{\gamma}^i + \frac{A v_v}{T} > 0 \quad (75)$$

summation over i ($i = 1, 2, 3$) refers to the geometrical coordinates. W^i is the heat flow in coordinate i , \mathcal{F}_{γ} is the force (per unit mass) acting on component γ . μ^+ is the chemical potential per unit mass.

In present description of continuous systems, must distinguish between bulk movement with velocity ω and the c diffusion flows $\rho_{\gamma} \Delta_{\gamma}$ out of which only $c - 1$ are linearly independent (see (71)).

For non-viscous systems (no friction), velocity of center of gravity ω does not appear in the eqn. for the entropy production, and is therefore considered a reversible phenomena. Irreversibility is related to the diffusion.

In a two component system, without temperature gradient, and without chemical reaction, eqn. (75) reduces to

$$\sigma = \frac{1}{T} \left(\mathcal{F}_1 - \frac{\partial \mu_1^+}{\partial x} \right) \rho_1 \Delta_1 + \frac{1}{T} \left(\mathcal{F}_2 - \frac{\partial \mu_2^+}{\partial x} \right) \rho_2 \Delta_2 > 0 \quad (76)$$

Assuming mechanical equilibrium and using eqn.(71) $\sum_{\gamma} \rho_{\gamma} \Delta_{\gamma} = 0$ gives

$$\left(\mathcal{F}_1 - \frac{\partial \mu_1^+}{\partial x} \right) \rho_1 + \left(\mathcal{F}_2 - \frac{\partial \mu_2^+}{\partial x} \right) \rho_2 = 0 \quad (77)$$

Note that instead of using the average mass velocity ω we could have used any reference velocity. Entropy production must remain invariant under such a change. Eg. if take as the reference velocity ω_2 then eqn. (76) becomes

$$\sigma = \frac{1}{T} \left(\mathcal{F}_1 - \frac{\partial \mu_1^+}{\partial x} \right) \rho_1 (\omega_1 - \omega_2) > 0 \quad (78)$$

Show that eqn. (78) is correct.

3.12 Internal Degrees of Freedom

Irreversible processes related to internal degrees of freedom of molecule.

eg. orientation of spin, electric dipole moment, deformation (isomerization)

Starting point is Gibb's formula (18);

$$\frac{dS}{dt} = \frac{1}{T} \frac{dE}{dt} + \frac{p}{T} \frac{dV}{dt} - \frac{1}{T} \int_{\gamma} \mu(\gamma) \frac{\partial n(\gamma)}{\partial t} d\gamma \quad (79)$$

$n(\gamma)$ is density of molecules in state γ so $n(\gamma)d\gamma$ is number of molecules for which the internal parameter lies between γ and $\gamma + d\gamma$.

Consider a continuity eqn. for $(\partial n(\gamma)/\partial t)$

First assume that change of γ is discrete, i.e. γ changed by transformations from or into neighboring states $\gamma - 1$ or $\gamma + 1$. Then

$$\frac{dn_{\gamma}}{dt} + (v_{\gamma} - v_{\gamma-1}) = 0 \quad (80)$$

v_{γ} is rate $\gamma \rightarrow (\gamma + 1)$ and $v_{\gamma-1}$ is rate of $\gamma - 1 \rightarrow \gamma$.

If γ is a continuous parameter

$$\frac{\partial n(\gamma)}{\partial t} + \frac{\partial v(\gamma)}{\partial \gamma} = 0 \quad (81)$$

– is a continuity eqn. in the “internal coordinate space” γ .

$v(\gamma)$ is the reaction rate (flow) giving how the molecules change along coordinate γ .

In vector notation

$$\frac{\partial n(\gamma)}{\partial t} = -\text{div } \vec{v}(\gamma) \quad (82)$$

By partial integration, eqn. (79) can be transformed into

$$\frac{dS}{dt} = \frac{1}{T} \frac{dE}{dt} + \frac{p}{T} \frac{dV}{dt} - \frac{1}{T} \int_{\gamma} \frac{\partial \mu(\gamma)}{\partial \gamma} v(\gamma) d\gamma \quad (83)$$

so

$$\frac{d_i S}{dt} = -\frac{1}{T} \int_{\gamma} \frac{\partial \mu(\gamma)}{\partial \gamma} v(\gamma) d\gamma > 0 \quad (84)$$

We now postulate a further refinement in the second law of TD.

In each part of the internal coordinate space, the irreversible processes proceed in a direction such that a positive entropy production results. Implies

$$\sigma^* = -\frac{1}{T} \frac{\partial \mu(\gamma)}{\partial \gamma} v(\gamma) > 0 \quad (85)$$

σ^* is the entropy production per unit volume of the internal configuration space.

σ^* has usual form, product of an affinity (or force) $-\frac{1}{T}(\partial \mu(\gamma)/\partial \gamma)$ and a rate $v(\gamma)$ of irreversible process.

If there is a potential energy which varies with γ (eg. if γ is the angle θ of a dipole with respect to an external electric field e , then

$$E_{pot} = -me \cos(\theta) \quad (86)$$

where m is the dipole moment, there then appears a corresponding “force” $-\partial E/\partial\gamma$ in the entropy production (exactly as \mathcal{F}_γ appeared in eqn. (75),

$$\sigma^* = -\frac{1}{T} \left(\frac{\partial\mu(\gamma)}{\partial\gamma} + \frac{\partial E_{pot}}{\partial\gamma} \right) v(\gamma) > 0 \quad (87)$$

Assuming that there is a linear relation between the rate and the affinity, can obtain a formulation of Debye’s theory of the orientation of dipoles in an alternating electrical field.

What is the Debye theory in this context, and suggest how the results above for the entropy production due to changes in the internal coordinates may be used to provide an independent formulation of this theory.