

## Lecture 6: Irreversible Processes

In all our discussions of equilibrium thermodynamics, we have dealt with measurable properties of materials as formulated on the concept of equilibrium. Examples of such *material properties* include entropy, temperature and volume. These properties are convenient in the description of equilibrium, because on an appropriate scale, they are static and time-invariant. There are other material properties which are not relevant to the discussion of equilibrium: thermal conductivity, diffusivity and viscosity, but are interesting because they can describe a second kind of time independence, that of the steady-state (Denbigh, 1955). Thus, the concentration profile does not change during steady-state diffusion, even though energy is being dissipated by the diffusion.

The subject described as the “thermodynamics of irreversible processes” deals with systems which are not at equilibrium but are nevertheless *stationary*. We shall see that the methodology involved is remarkably simple and yet powerful, with major applications to phase transformations, for example in the theory of diffusion in multicomponent alloys. The theory in effect uses thermodynamics to deal with *kinetic* phenomena. However, there is an interesting distinction drawn by Denbigh between these thermodynamics of irreversible processes and kinetics. The former applies strictly to the steady-state, whereas there is no such restriction on kinetic theory.

The term “irreversible” in the ordinary language sounds too permanent, whereas its meaning in thermodynamics is really quite benign. We therefore proceed to define it better.

### *Reversibility*

A process whose direction can be changed by an infinitesimal alteration in the external conditions is called reversible. Consider the example illustrated in Fig. 1, which deals with the response of an ideal gas contained at uniform pressure within a cylinder, any change being achieved by the motion of the piston. For any starting point on the  $P/V$  curve, if the application of an infinitesimal force causes the piston to move slowly to an adjacent position still on the curve, then the process is reversible since energy has not been dissipated. The removal of the infinitesimal force will cause the system to reverse to its original state.

On the other hand, if there is friction during the motion of the piston in a cylinder, then deviations occur from the  $P/V$  curve as illustrated by the cycle in Fig. 1. An infinitesimal force cannot move the piston because energy is dissipated due to friction (as given by the area within the cycle). Such a process, *which involves the dissipation of energy*, is classified as irreversible with respect to an infinitesimal change in the external conditions.

More generally, reversibility means that it is possible to pass from one state to another without appreciable deviation from equilibrium. Real processes are not reversible so equilibrium thermodynamics can only be used approximately, though the same thermo-

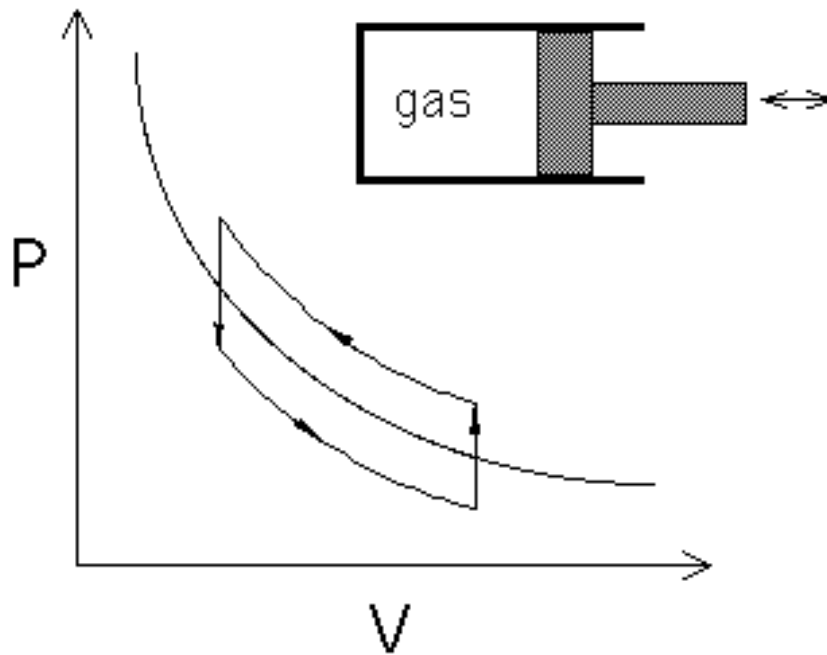


Fig. 1: The curve represents the variation in pressure within the cylinder as the volume of the ideal gas is altered by the frictionless positioning the piston. The cycle represents the dissipation of energy when the motion of the piston causes friction.

dynamics defines whether or not a process can occur spontaneously without ambiguity.

For irreversible processes the *equations* of classical thermodynamics become *inequalities*. For example, at the equilibrium melting temperature, the free energies of the liquid and solid are identical ( $G_{liquid} = G_{solid}$ ) but not so below that temperature ( $G_{liquid} > G_{solid}$ ). Such inequalities are much more difficult to deal with though they indicate the natural direction of change. For steady-

state processes however, the thermodynamic framework for irreversible processes as developed by Onsager is particularly useful in obtaining useful relationships even though the system may not be at equilibrium.

### *The Linear Laws*

At equilibrium there is no change in entropy or free energy. An irreversible process dissipates energy and entropy is created continuously. In the example illustrated in Fig. 1, the dissipation was due to friction; diffusion ahead of a moving interface is dissipative. The rate at which energy is dissipated is the product of the temperature and the rate of entropy production (*i.e.*  $T\sigma$ ) with:

$$T\sigma = JX \quad (1)$$

where  $J$  is a generalised flux of some kind, and  $X$  a generalised force. In the case of an electrical current, the heat dissipation is the product of the current ( $J$ ) and the electromotive force ( $X$ ).

As long as the flux–force sets can be expressed as in equation 1, the flux must naturally depend in some way on the force. It may then be written as a function  $J\{X\}$  of the force  $X$ . At equilibrium, the force is zero. If  $J\{X\}$  is expanded in a Taylor series about equilibrium ( $X = 0$ ), we get

$$\begin{aligned} J\{X\} &= \sum_0^{\infty} a_n X^n \\ &= \sum_0^{\infty} \frac{f^{(n)}\{0\}}{n!} X^n \\ &= J\{0\} + J'\{0\} \frac{X}{1!} + J''\{0\} \frac{X^2}{2!} \dots \end{aligned}$$

Note that  $J\{0\} = 0$  since that represents equilibrium. If the high order terms are neglected then we see that

$$J \propto X.$$

This is a key result from the theory, that the forces and their conjugate fluxes are linearly related ( $J \propto X$ ) whenever the dissipation can be written as in equation 1, at least when the deviations from equilibrium are not large. Some examples of forces and fluxes in the context of the present theory are given in Table 1.

Force	Flux
Electromotive force (e.m.f.) = $\frac{\partial\phi}{\partial z}$	Electrical Current
$-\frac{1}{T} \frac{\partial T}{\partial z}$	Heat flux
$-\frac{\partial\mu_i}{\partial z}$	Diffusion flux

Table 1: Examples of forces and their conjugate fluxes.  $z$  is distance,  $\phi$  is the electrical potential in Volts, and  $\mu$  is a chemical potential.

### *Multiple Irreversible Processes*

There are many circumstances where a number of irreversible processes occur together. In a ternary Fe–Mn–C alloy, the diffusion flux of carbon depends not only on the gradient of carbon, but also on that of manganese. Thus, a uniform distribution of carbon will tend to become inhomogeneous in the presence of a manganese concentration gradient. Similarly, the flux of heat may not depend on the temperature gradient alone; heat can be driven also by an

electromotive force (Peltier effect)<sup>†</sup>. Electromigration involves diffusion driven by an electromotive force. When there is more than one dissipative process, the total energy dissipation rate can still be written

$$T\sigma = \sum_i J_i X_i. \quad (2)$$

In general, if there is more than one irreversible process occurring, it is found *experimentally* that each flow  $J_i$  is related not only to its conjugate force  $X_i$ , but also is related linearly to all other forces present. Thus,

$$J_i = M_{ij} X_j \quad (3)$$

with  $i, j = 1, 2, 3, \dots$ . Therefore, a given flux depends on all the forces causing the dissipation of energy.

### *Onsager Reciprocal Relations*

Equilibrium in real systems is always dynamic on a microscopic scale. It seems obvious that to maintain equilibrium under these dynamic conditions, a process and its reverse must occur at the same rate on the microscopic scale. The consequence is that provided the forces and fluxes are chosen from the dissipation equation and are independent,  $M_{ij} = M_{ji}$ . This is known as the Onsager

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<sup>†</sup> In the Peltier effect, the two junctions of a thermocouple are kept at the same temperature but the passage of an electrical current causes one of the junctions to absorb heat and the other to liberate the same quantity of heat. This Peltier heat is found to be proportional to the current.

theorem, or the Onsager reciprocal relations. It applies to systems near equilibrium when the properties of interest have even parity, and assuming that the fluxes and their corresponding forces are independent. An exception occurs with magnetic fields in which case there is a sign difference  $M_{ij} = -M_{ji}$  (Miller, 1960).

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