Lecture 6: Irreversible Processes

Thermodynamics generally deals with measurable properties of materials, formulated on the basis of equilibrium. Thus, properties such as entropy and free energy are, on an appropriate scale, static and time–invariant during equilibrium. There are other parameters not relevant to the discussion of equilibrium: thermal conductivity, diffusivity and viscosity, but which 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 thermodynamics of irreversible processes deals with systems which are not at equilibrium but are nevertheless *stationary.* The theory in effect uses thermodynamics to deal with *kinetic* phenomena. There is nevertheless, a distinction between the thermodynamics of irreversible processes and kinetics (Denbigh). The former applies strictly to the steady–state, whereas there is no such restriction on kinetic theory.

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 revert to its original state.

On the other hand, if there is friction during the motion of the piston, 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 thermodynamics 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 approximating relationships even though the system is not at equilibrium.

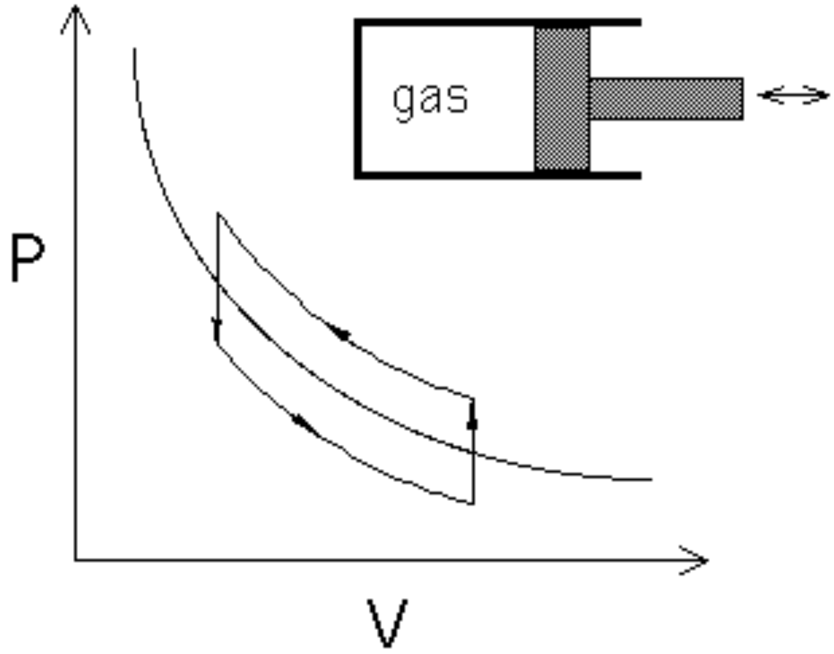

Fig. 1: The curve represents the variation in pressure within the cylinder as the volume of the ideal gas is altered by positioning the frictionless piston. The cycle represents the dissipation of energy when the motion of the piston causes friction.

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:

$$T\sigma = JX \tag{1}$$

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

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

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.

Multiple Irreversible Processes

There are many circumstances in which 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

Force	Flux
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
Stress	Strain rate

Table 1: Examples of forces and their conjugate fluxes. z is distance, ϕ is the electrical potential in Volts, and μ is a chemical potential. "e.m.f." stands for electromotive force.

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)†. Electromigration involves diffusion driven by an electromotive force. When there is more then one dissipative process, the total energy dissipation rate can still be written

$$T\sigma = \sum_i J_i X_i. \tag{2}$$

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

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† 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.

conjugate force X_i, but also is related linearly to all other forces present. Thus,

$$J_i = M_{ij} X_j \tag{3}$$

with $i,\ j = 1, 2, 3 \ldots$. 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 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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