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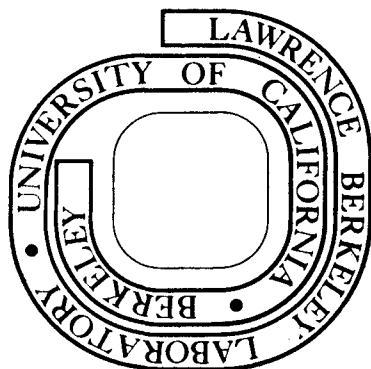
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The law of microscopic reversibility is a fundamental principle that is extremely useful in both the qualitative and quantitative analysis and understanding of rate and equilibrium phenomena. Reference to this principle is made as early as the freshman year, and it and its consequences are frequently cited or invoked in subsequent undergraduate and graduate instruction. In recent years it has seen increasing use as a criterion of validity for approximate theories of rate processes, and as a device by which measurements of rate constants for reactions in one direction may be used to obtain the rate constants for the experimentally inaccessible reverse directions (1,2).

Despite the importance of the principle of microscopic reversibility, most chemists are rather uncertain about its origin, nature, and limitations. In part, this is because the basis of the principle is usually treated in physics textbooks in terms of rather formal quantum mechanics. In addition, a certain amount of confusion results from the fact that the term "detailed balance" is often encountered in the same context as is microscopic reversibility. According to some authors, microscopic reversibility refers only to mechanical quantities such as transition probabilities,

trajectories, and cross sections, whereas detailed balance
pertains to statistical mechanical concepts such as rate
constants and equilibrium. Unfortunately, usage is not
uniform, and what is microscopic reversibility to one may be
detailed balance to another, and vice versa, while still
others prefer to draw no distinction. Informative discussions
of microscopic reversibility and detailed balance exist (3-8),
but are largely confined to the monograph and advanced
textbook literature. In what follows, we will present a
discussion of these principles in terms that are appropriate
for undergraduate and early graduate instruction.

Mechanics and Microreversibility

The principle of microscopic reversibility is a consequence
of the invariance of the mechanical equations of motion under
the operation of time reversal. What is meant by time
reversal? Suppose we start a system at $t = 0$ with the
initial coordinates $r(0)$ and velocities $v(0)$ and let it
evolve for a period t_1. The trajectory which represents
this evolution is shown in Figure 1a. Now at time t_1, we
instantaneously reverse the direction of all velocity components,
leave the coordinates unmolested, and allow the system to
evolve for another time period t_1. If at the end of this
time the system has the same coordinates and the exactly
reversed velocities it had at $t = 0$, it is said to obey time
reversal invariance. The reason for this description is
indicated qualitatively in Figure 1b. The "reversed" trajectory

can be thought of as beginning at a time $-t_1$, and evolving as time goes _forward_ to $t = 0$.

It is possible to determine whether a system is invariant under time reversal by examining the behavior of the applicable equation of motion under the transformation

$$t = -t$$
$$\underset{\sim}{r}(t) = r(-t) \qquad\qquad (1)$$
$$\underset{\sim}{v}(t) = -\underset{\sim}{v}(-t).$$

If the equation of motion is invariant under this transformation, for every solution that describes a trajectory that starts with $\underset{\sim}{r}(0)$, $\underset{\sim}{v}(0)$, and ends with $\underset{\sim}{r}(t_1)$, $\underset{\sim}{v}(t_1)$, there will be an equally acceptable solution that starts with $\underset{\sim}{r}(-t_1)$, $-\underset{\sim}{v}(-t_1)$, and leads to $\underset{\sim}{r}(0)$, $-\underset{\sim}{v}(0)$. For systems which are felt to obey classical mechanics sufficiently exactly, an appropriate equation to examine is Newton's second law:

$$F = m\, \frac{d^2\underset{\sim}{r}(t)}{dt} = m\, \frac{d\underset{\sim}{v}(t)}{dt}. \qquad\qquad (2)$$

We assume for the moment that the force F is a function only of the coordinates, and make the transformation indicated above. We get

$$F = m\, \frac{d^2\underset{\sim}{r}(-t)}{[d(-t)]^2} = -m\, \frac{d\underset{\sim}{v}(-t)}{d(-t)}. \qquad\qquad (3)$$

When the obvious equalities $[d(-t)]^2 = dt$, $d(-t) = -dt$ are executed, eqns. (2) and (3) are the same, except that $\underset{\sim}{r}(t)$, $\underset{\sim}{v}(t)$ have become $\underset{\sim}{r}(-t)$, $\underset{\sim}{v}(-t)$ in eqns. (3). Thus along each

classical trajectory, the motion is reversible.

This deduction was made under the assumption that the force F was a function of position only, and therefore was unchanged under the transformation. While this condition is ordinarily met, there are forces which do depend on odd powers of the particle velocity: the magnetic force on a charged particle and the usual representation of frictional forces are the two most obvious examples. Time reversal invariance will not be obeyed in these cases, at least not superficially. However, if care is taken to reverse the trajectories of the charged particles which produce the magnetic fields, and of the submicroscopic displacements which give rise to friction, time reversal invariance will be obeyed in these systems also.

Microreversibility and Collision Cross Sections

Having explored the general mechanical expression of time reversal invariance, we now seek a way in which this idea can be applied to rate processes. To do this, we first define and then work with the differential scattering cross section associated with a process, since this is the essential link between mechanics and rate phenomena.

To this end, consider the experimental arrangement diagrammed in Figure 2. A collimated beam of projectiles moves toward a collection of stationary target molecules. A few of the projectiles experience a collision with the target, and are scattered. Some of these enter a detector which subtends a

differential solid angle $d^2\Omega$. It is possible to do precisely
this experiment if the target is a solid, and the projectiles
are high velocity particles. If the target is a gas in the
form of a collimated molecular beam, it is still possible to
describe a scattering experiment in this manner by adopting
a coordinate system whose origin moves with the target molecules.
Then, as in the truly stationary target case, the projectile
velocity is to be thought of as its velocity _relative_ to the
target.

Suppose that the magnitude of the initial relative momentum
of the projectile is p_1. Inevitably, there will be a small
momentum spread which we can recognize by saying that the
momentum p_1 lies in the differential element d^3p_1. After
the collision, the scattered product particle has a relative
momentum p_2 in a differential element d^3p_2. Three possi-
bilities exist: if the collision is elastic, the magnitudes
of the initial and final relative momenta are equal; if the
collision is inelastic, $|p_2| \neq |p_1|$ but chemical identity is
maintained; if a chemical reaction occurs, the masses and
momenta of the projectile and detected particle will in general
be different. The following arguments encompass all these
possibilities. Let it be clear that in each case, the
"reactants" and "products" have definitely known internal
quantum states before and after the collision.

What is the rate at which product particles are registered
at the detector? It is easy to agree that N_2, the number of
particles in state 2 detected per second, is proportional to

the beam flux F_1 (in molecules/cm^2 sec), the number of target molecules intercepted by the beam N_t, and the angular acceptance of the detector $d^2\Omega$. Thus

$$N_2 = N_t \ F_1 \ \sigma_{12} \ d^2\Omega \tag{4}$$

where σ_{12} is the proportionality constant defined by the equality. Its units here are cm^2/steradian, and consequently σ_{12} is known as the differential cross section for the process. It is a function of the scattering angle, the initial relative translational energy of the collision, and of the particular change in internal quantum states that occurs. The magnitude of σ_{12} is thus determined by the basic mechanics of the collision process.

Now consider the exact reverse process in which a beam of "product" (or state 2) molecules of momentum $-\underset{\sim}{p}_2$ impinges on the appropriate target and is converted to scattered reactant (state 1) molecules with momentum $-\underset{\sim}{p}_1$. The rate at which these "reactant" molecules are detected is

$$N_{\bar{1}} = N_t' \ F_{\bar{2}} \ \sigma_{\bar{2}\bar{1}} \ d^2\Omega \tag{5}$$

where $\sigma_{\bar{2}\bar{1}}$ is the differential scattering cross section for this reverse process. The bars have been placed over the subscripts to emphasize that the directions of the momenta have been reversed. The law of mechanical microscopic reversibility can be expected to provide a relation between σ_{12} and $\sigma_{\bar{2}\bar{1}}$.

To find this relation, we must compare eqns. (4) and (5) after they have been reduced to the description of single trajectories. To do this, we first divide by the number of target molecules in each case to give us the rate of product collection per target molecule. Also, eqns. (4) and (5) refer to "bundles" of trajectories that <u>end</u> in respectively d^3p_2 and $d^3p_{\bar{1}} = d^3p_1$. Therefore, we must divide eqn. (4) by

$$d^3p_2 = p_2^2 \, dp_2 \, d^2\Omega$$

and eqn. (5) by

$$d^3p_1 = p_1^2 \, dp_1 \, d^2\Omega.$$

When this is done, we may equate the quantities

$$\frac{N_2}{d^3p_2 N_t} = \frac{N_{\bar{1}}}{d^3p_1 N_t'} \tag{6}$$

by virtue of mechanical microreversibility. The left side of eqn. (6) gives the specific rate at which products are formed by individual trajectories in the forward direction, while the right side gives the same quantity for the reverse direction. Since for each forward trajectory there is a reverse, the two expressions must be equal. Note that we have not divided N_2 or $N_{\bar{1}}$ by the corresponding fluxes since these fluxes are not independent of each other. That is, F_1 and the molecular mechanics determines F_2, so the two factors are related by microscopic reversibility.

As a consequence of eqn. (6) we can write

$$\frac{F_1 \sigma_{12}}{p_2^2 dp_2} = \frac{F_2 \sigma_{\bar{2}\bar{1}}}{p_1^2 dp_1} . \tag{7}$$

Now the fluxes can be expressed as the ratio of the appropriate velocity a fixed volume V, i.e., $F_i = v_i/V$. Also, differentiation of the conservation of energy expression

$$\frac{p_1^2}{2\mu_1} = \frac{p_2^2}{2\mu_2} + \Delta E_{21}$$

where $\Delta E_{21} = E_2 - E_1$ is the internal energy change for the process considered, gives $v_1 dp_1 = v_2 dp_2$. This, combined with the expression for the fluxes, reduces eqn. (7) to

$$p_1^2 \sigma_{12} = p_2^2 \sigma_{\bar{2}\bar{1}} \tag{8}$$

which is the fundamental expression of microscopic reversibility as it applies to collision processes. Although our arguments have been couched in the language of classical trajectories, eqn. (8) is more commonly derived (5) using formal quantum mechanics.

It is important to note that eqn. (8) is of purely mechanical (as opposed to statistical mechanical or thermodynamic) origin. As derived, it pertains to definite internal states of reactants and products. However, often cross sections $\bar{\sigma}$ are measured which are really the average of the individual cross sections for the degenerate reactant states, and which sum over

the formation of products in degenerate final states. The appropriate version of eqn. (8) is then (5)

$$p_1^2 \ g_1 \ \bar{\sigma}_{12} = p_2 \ g_2 \ \bar{\sigma}_{\bar{2}\bar{1}} \tag{9}$$

where the g_i are the total degeneracies of the internal reactant and product states.

A comment is in order on why N_1 and N_2 were divided by volume elements in momentum space rather than velocity space. According to Liouville's theorem it is the volume element in phase (coordinate-<u>momentum</u>) space that is conserved as members of a group of representative points move along their trajectories. Consequently, to reduce N_1 and N_2 to a single trajectory basis, division by $d^3r \ d^3p$ is not only appropriate, but essential if processes involving changes of mass are considered. The volume element in coordinate space can be integrated to give the volume of the box in which the events occur. Since this is the same for forward and reverse process, it need not appear in eqn. (6).

Microreversibility and Detailed Balance

While microscopic reversibility is a mechanical relation between cross sections, detailed balance has to do with the relation between rate constants at equilibrium. Detailed balance can be derived (6) from microscopic reversibility by making use of the connection between cross sections and rate constants:

$$k_{12} = \int_{p_1} \int_{\Omega} v_1\sigma_{12} \, f(p_1) \, d^3p_1 \, d^2\Omega. \tag{10}$$

Here for simplicity of notation we have considered non-degenerate reactant and product states. In eqn. (10), integration over the product scattering angle $d^2\Omega$ converts the differential scattering cross section into a total cross section, and thereby includes all possible contributions to k_{12} that occur for a fixed initial translational momentum p_1. Integration over p_1 includes the possible contributions from all initial relative momenta that occur. The distribution function for initial relative momenta is given by the Maxwell-Boltzmann expression

$$f(p) = (2\pi\mu kT)^{-3/2} \exp\left(-\frac{p^2}{2\mu kT}\right) \tag{11}$$

and

$$d^3p = p^2 \, dp \, d^2\omega$$

where the solid angle ω locates the direction of the initial relative momentum.

The procedure now is to start with

$$k_{12} = \frac{4\pi}{(2\pi\mu_1 kT)^{3/2}} \int \int v_1\sigma_{12} \, e^{-p_1^2/(2\mu_1 kT)} \, p_1^2 \, dp_1 \, d^2\Omega \tag{12}$$

and convert the right side to an expression involving k_{21}. We have already integrated over $d^2\omega$, since the initial direction of the relative motion is immaterial. The necessary

substitutions are quite straightforward. The microscopic reversibility relation eqn. (8) converts $p_1^2 \sigma_{12}$ to $p_2^2 \sigma_{\bar{2}\bar{1}}$, the conservation of energy relation can be used to replace $p_1^2/2\mu$ by $p_2^2/2\mu + \Delta E_{21}$ in the exponent, and the same relation allows us to replace $v_1 dp_1$ with $v_2 dp_2$. The result is

$$k_{12} = \frac{4\pi}{(2\pi\mu_1 kT)^{3/2}} e^{-\Delta E_{21}/kT} \int \int v_2 \sigma_{\bar{2}\bar{1}} e^{-p_2^2/(2\mu_2 kT)} p_2^2 \, dp_2 \, d^2\Omega. \quad (13)$$

Comparison with eqn. (12) shows that the right side of eqn. (13) is very nearly what we would have written down directly for k_{21}, the rate constant for the reverse process. By recognizing this, it is a simple matter to proceed to

$$k_{12} = k_{21} \left(\frac{\mu_2}{\mu_1}\right)^{3/2} e^{-\Delta E_{21}/kT}. \quad (14)$$

Equation (14) is the mathematical expression of detailed balance. If the process considered is a simple inelastic event in which the reduced mass is unchanged, eqn. (14) reduces to the familiar expression that the ratio of the rate constants for the forward and reverse processes is just the appropriate Boltzmann factor. It is important to realize, however, that for reactive events in which the reduced mass changes, the indicated reduced mass ratio must appear raised to the three-halves power. This factor in eqn. 14 could also be represented by Q_2^t/Q_1^t, the ratio of the translational partition functions for initial and final relative motion, since these partition functions are the normalizing factors for the distribution of eqn. (11).

It is important to realize that while an equilibrium Maxwell-Boltzmann distribution of translational energies has been assumed, no assumption has been made that the _internal_ states 1 and 2 are at equilibrium. Thus eqn. (14) applies, for example, to the rate constants for vibrational excitation and de-excitation of a gas whose vibrational state distribution has been thrown far out of equilibrium by a pulse of light, but whose translational energy distribution remains of the Maxwell-Boltzmann form. Thus statements often encountered in textbooks to the effect that expressions akin to eqn. (14) hold only at complete chemical equilibrium are overly restrictive.

It is of interest to find an expression for the total rate constant for conversion of all reactant states to products. If i designates any reactant state, and f any product state, then the desired quantity is just

$$\vec{k} = \sum_i \sum_f k_{if} \, x_i \qquad (15)$$

where x_i is the fraction of the reactants in state i. Equation (15) says that the total chemical conversion rate constant is found by adding up the rate constants for each individual type of transition, weighting each by the probability that the system will start in that initial state. Similarly, the total rate constant for the reverse process is

$$\overleftarrow{k} = \sum_i \sum_f k_{fi} \, x_f \qquad (16)$$

where x_f is the fraction of "products" in state f.

A particularly interesting situation occurs when x_i and x_f are given by the expressions which hold at thermal equilibrium:

$$x_i = \frac{e^{-E_i/kT}}{Q_r^{int}} \qquad (17)$$

$$x_f = \frac{e^{-E_f/kT}}{Q_p^{int}} . \qquad (18)$$

Here Q_r^{int} and Q_p^{int} are the usual internal partition functions of reactants and products, and the E_i and E_f are the energy eigenvalues of the reactant and product states measured relative to their individual energy zeros. We now substitute eqn. (17) into eqn. (15) and get

$$\vec{k} = \frac{1}{Q_r^{int}} \sum_i \sum_f k_{if}\, e^{-E_i/kT} .$$

Then we use the detailed balance relation, eqn. (14), in the form

$$k_{if} = \frac{Q_p^t}{Q_r^t} k_{fi}\, e^{-(E_f - E_i + \Delta E_o)/kT}$$

where the Q's are the translational partition functions, and ΔE_o is the difference in the lowest energies of products and reactants. The result is

$$\vec{k} = \frac{Q_p^t e^{-\Delta E_o/kT}}{Q_r^t Q_r^{int}} \sum_i \sum_f k_{fi}\, e^{-E_f/kT} . \qquad (19)$$

The summed quantity is nearly what we would write for the total reverse rate constant $\overleftarrow{k}$. Inserting a factor of Q_p^{int} in the numerator and denominator, we get

$$\frac{\overrightarrow{k}}{\overleftarrow{k}} = \frac{Q_p}{Q_r} e^{-\Delta E_o/kT} = K(T). \tag{20}$$

That is, the ratio of the total rate constants for the forward and reverse reactions is a constant which depends only on temperature. Since the Q's in eqn. (20) are to total partition functions (the product of translational and internal factors), we have found the standard statistical mechanical expression for the equilibrium constant.

If we express the equilibrium constant for the bimolecular reaction

$$A + B = C + D$$
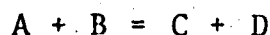
in the usual way

$$\frac{[C]_e [D]_e}{[A]_e [B]_e} = K(T)$$

we see that eqn. (20) leads to

$$\overrightarrow{k} [A]_e [B]_e = \overleftarrow{k} [C]_e [D]_e \tag{21}$$

where the subscripts indicate equilibrium concentrations. In eqn. (21) we have one of the more common statements of detailed balance: at equilibrium, the rate of an elementary process and of its reverse are equal. The consequences of this observation have been pointed out in a number of undergraduate textbooks (9-12).

The derivation of eqn. 20 sheds some light on the
question of whether, in order to obtain a rate constant for
a reverse reaction, it is legitimate to use an equilibrium
constant together with a rate constant for the forward
reaction which has been measured with the system far from
chemical equilibrium. It is clear that such a procedure is
legitimate if the measured forward reaction is proceeding
slowly enough so that the translational and internal states
of the reactants have very nearly their Boltzmann equilibrium
population. This condition is almost always met for bi-
molecular reactions, and is verily the standard equilibrium
assumption of chemical kinetics, upon which conventional
absolute rate theory and collision theory are based. There
are instances, such as collision induced dissociation and
recombination reactions, when the populations of internal
reactant or product states deviate considerably from the
equilibrium Boltzmann values. Even then, it can be argued (8)
that in some cases a relation of the type of eqn. (20)
holds between the measured rate constants for the forward
and reverse reactions.

Concluding Remarks

The microscopic reversibility of classical and quantum
mechanics has consequences for molecular dynamics that can be
interpreted at various levels of specificity. There is a
connection, eqn. (8), between the cross section of the
collisional process which converts one specific reactant

quantum state to one specific product state, and the cross section for the exact reverse process. A closely related expression, eqn. (9), pertains to measured cross sections that are averages over degenerate initial states and sums over degenerate final states. When a Maxwell-Boltzmann distribution of translational energies enters the problem, one has the relation, eqn. (14), between rate constants for the interconversion of specific internal states. Finally, when the translational and internal states of reactants and products separately have their Boltzmann equilibrium populations, microscopic reversibility and detailed balance provide a relation, eqn. (20), between the forward and reverse reaction rate constants and the equilibrium constant.
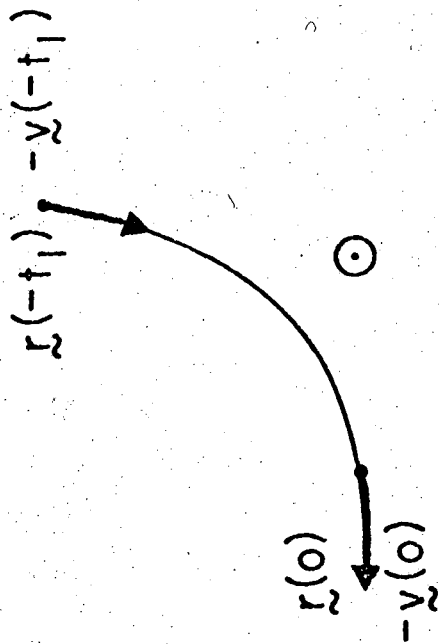
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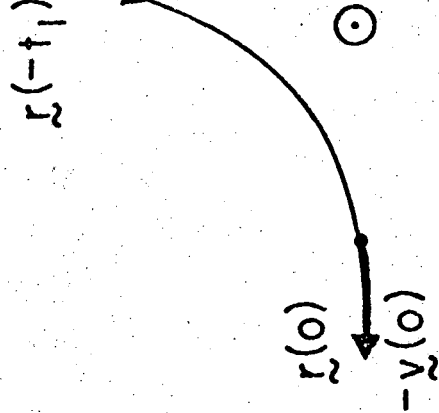   Englewood Cliffs, New Jersey, 4th ed., 1972.

FIGURE CAPTIONS

Figure 1.   A schematic representation of a forward trajectory
(a) and the corresponding reverse trajectory (b).
Note that the reverse trajectory does not restore the
system to its original state, but rather to the original
state with reversed velocities.

Figure 2.   A schematic diagram of the essentials of a
scattering experiment. A collimated beam of projectiles
of momentum p_1 impinges on N_t target molecules.
The scattered particles with momentum p_2 enter a
detector which intercepts a solid angle $d^2\Omega$ at a
rate of N_2 particles per second. The original flux
of the beam if F_1 projectiles per cm^2 per second,
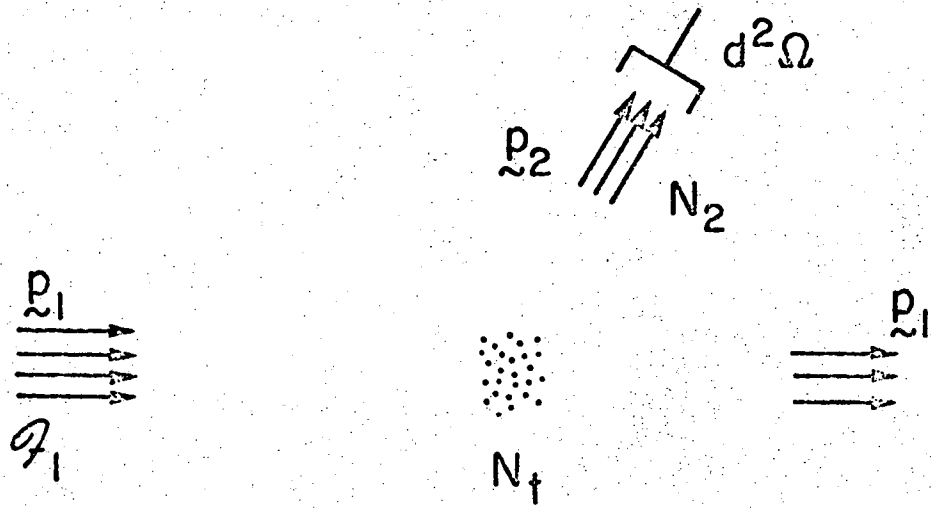and most of this is unscattered.

$\underset{\sim}{r}(t_1)$ $\underset{\sim}{v}(t_1)$

$\underset{\sim}{r}(o)$ $\underset{\sim}{v}(o)$

$\odot$

(a)

$\underset{\sim}{r}(-t_1)$ $-\underset{\sim}{v}(-t_1)$

$\underset{\sim}{r}(o)$ $-\underset{\sim}{v}(o)$

$\odot$

(b)

XBL748-7110

Fig. 1

Fig. 2

XBL 748-7111