A · 12 *The H theorem and the approach to equilibrium*

We consider in greater detail the situation described at the end of Sec. 2·3. Let us denote the approximate quantum states of an isolated system by r (or s). The most complete description of interest to us in considering this system is one which specifies at any time t the probability $P_r(t)$ of finding this system in any one of its accessible states r. This probability is understood to be properly normalized so that summation over all accessible states always yields

$$\sum_r P_r(t) = 1 \tag{A·12·1}$$

Small interactions between the particles cause transitions between the accessible approximate quantum states of the system. There exists accordingly some transition probability W_{rs} per unit time that the system originally in a state r ends up in some state s as a result of these interactions. Similarly, there exists a probability W_{sr} per unit time that the system makes an inverse transition from the state s to the state r. The laws of quantum mechanics show that the effect of small interactions can to a good approximation be described in terms of such transition probabilities per unit time, and that these satisfy the symmetry property*

$$W_{sr} = W_{rs} \tag{A·12·2}$$

The probability P_r of finding the system in a particular state r *increases* with time because the system, having originally probability P_s of being in any other state s, makes transitions to the given state r; similarly, it *decreases* because the system, having originally probability P_r of being in the given state r, makes transitions to all other states s. The change per unit time in the probability P_r can, therefore, be expressed in terms of the transition prob-

* The conditions necessary for the validity of this description in terms of transition probabilites and the symmetry property (A·12·2) are discussed more fully in connection with Eq. (15·1·3).

abilities per unit time by the relation

$$\frac{dP_r}{dt} = \sum_s P_s W_{sr} - \sum_s P_r W_{rs}$$

or

$$\frac{dP_r}{dt} = \sum_s W_{rs}(P_s - P_r) \qquad \text{(A·12·3)}$$

where we have used the symmetry property (A·12·2).*

Consider now the quantity H defined as the mean value of $\ln P_r$ over all accessible states; i.e.,

$$H \equiv \overline{\ln P_r} \equiv \sum_r P_r \ln P_r \qquad \text{(A·12·4)}$$

This quantity changes in time since the probabilities P_r vary in time. Differentiation of (A·12·4) then gives

$$\frac{dH}{dt} = \sum_r \left(\frac{dP_r}{dt} \ln P_r + \frac{dP_r}{dt}\right) = \sum_r \frac{dP_r}{dt}(\ln P_r + 1)$$

or

$$\frac{dH}{dt} = \sum_r \sum_s W_{rs}(P_s - P_r)(\ln P_r + 1) \qquad \text{(A·12·5)}$$

where we have used (A·12·3). Interchange of the summation indices r and s on the right side does not affect the sum so that (A·12·5) can equally well be written

$$\frac{dH}{dt} = \sum_r \sum_s W_{sr}(P_r - P_s)(\ln P_s + 1) \qquad \text{(A·12·6)}$$

Using the property (A·12·2), dH/dt can then be written in very symmetrical form by adding (A·12·5) and (A·12·6). Thus one gets

$$\frac{dH}{dt} = -\frac{1}{2} \sum_r \sum_s W_{rs}(P_r - P_s)(\ln P_r - \ln P_s) \qquad \text{(A·12·7)}$$

But since $\ln P_r$ is a monotonically increasing function of P_r, it follows that if $P_r > P_s$, then $\ln P_r > \ln P_s$, and vice versa. Hence

$$(P_r - P_s)(\ln P_r - \ln P_s) \geq 0 \qquad (= \text{sign only if } P_r = P_s) \qquad \text{(A·12·8)}$$

Since the probability W_{rs} is intrinsically positive, each term in the sum (A·12·7) must be positive or zero. Hence one can conclude that

▶ $$\frac{dH}{dt} \leq 0 \qquad \text{(A·12·9)}$$

where the equals sign holds only if $P_r = P_s$ for *all* states r and s between which transitions are possible (so that $W_{rs} \neq 0$), i.e., for *all* accessible states. Thus

$$\frac{dH}{dt} = 0 \qquad \text{only if } P_r = C \text{ for all accessible states} \qquad \text{(A·12·10)}$$

* Note that the relation (A·12·3) is just the "master equation" discussed in (15·1·5).

where C is some constant independent of the particular state r. The result (A · 12 · 9) is called the "H theorem" and expresses the fact that the quantity H always tends to decrease in time.*

An isolated system is not in equilibrium when any quantity, and in particular the quantity H, changes systematically in time. Now (A · 12 · 7) shows that, irrespective of the initial values of the probabilities P_r, the quantity H tends always to decrease as long as not all of these probabilities are equal. It will thus continue to decrease until H has reached its minimum possible value when $dH/dt = 0$. This final situation is, by (A · 12 · 10), characterized by the fact that the system is then equally likely to be found in any one of its accessible states. This situation is clearly one of equilibrium, since any subsequent change in the probabilities P_r could only make some probabilities again unequal and thus again increase H, a possibility ruled out by (A · 12 · 9). The final equilibrium situation is thus indeed consistent with the postulate of equal a priori probabilities.†