- Continued:
  - Specific heat is (usually) heat capacity per gram (J K^{-1} g^{-1}).
- Molar heat capacity (once the path has been specified) can be treated as a state function characteristic of the particular substance.
  - It depends on the energy spectrum of the substance.
- The convention of the text is to use uppercase letters for extensive quantities and lower case for the molar quantities.
  - U is internal energy.
  - u is the molar internal energy. (Other texts use $\overline{U}$ for molar internal energy.)
- Consider a constant pressure experiment in which the fluid is allowed to expand.

- Work, w_p, is negative since work is done on the surroundings.
- Therefore adding a given quantity of energy to the system causes a smaller internal energy change than in the case when the volume is held constant and no work is done on the surroundings.
  - In the constant volume case, all the heat added to the system is used to increase the internal energy of the system.
- Thus for the same value of q, $(\Delta U)_p < (\Delta U)_V$, $(\Delta T)_p < (\Delta T)_V$, and $C_p > C_V$.
- For a constant volume process $(dU)_V = C_V dT$.
- From the first law in differential form:

$$(dU)_p = C_p \, dT - p \, dV$$

- This describes a reversible constant pressure process of a system that can do only pV work.
  - This can be rewritten as $C_p dT = (dU + pdV)_p$.
  - This in turn suggests a new thermodynamic variable, H, or enthalpy:

$$H \equiv U + pV$$

- The differential of H at constant p:

$$(dH)_p = (dU + pdV)_p = C_p dT$$

and thus

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

- The heat transferred in a constant pressure process is:

$$q_p = (\Delta H)_p$$

- Because U and pV are also state functions, H is a state function.
- Enthalpy is convenient as a state function to describe processes carried out at constant pressure.
- Enthalpy along paths other than constant p many be considered.
    - For example for constant V,

$$(dH)_V = (dU)_V + d(pV)_V = C_V dT + V dp$$

- Enthalpy is usually determined with a calorimeter.
    - Calorimetry can also be used to determine heat capacity.

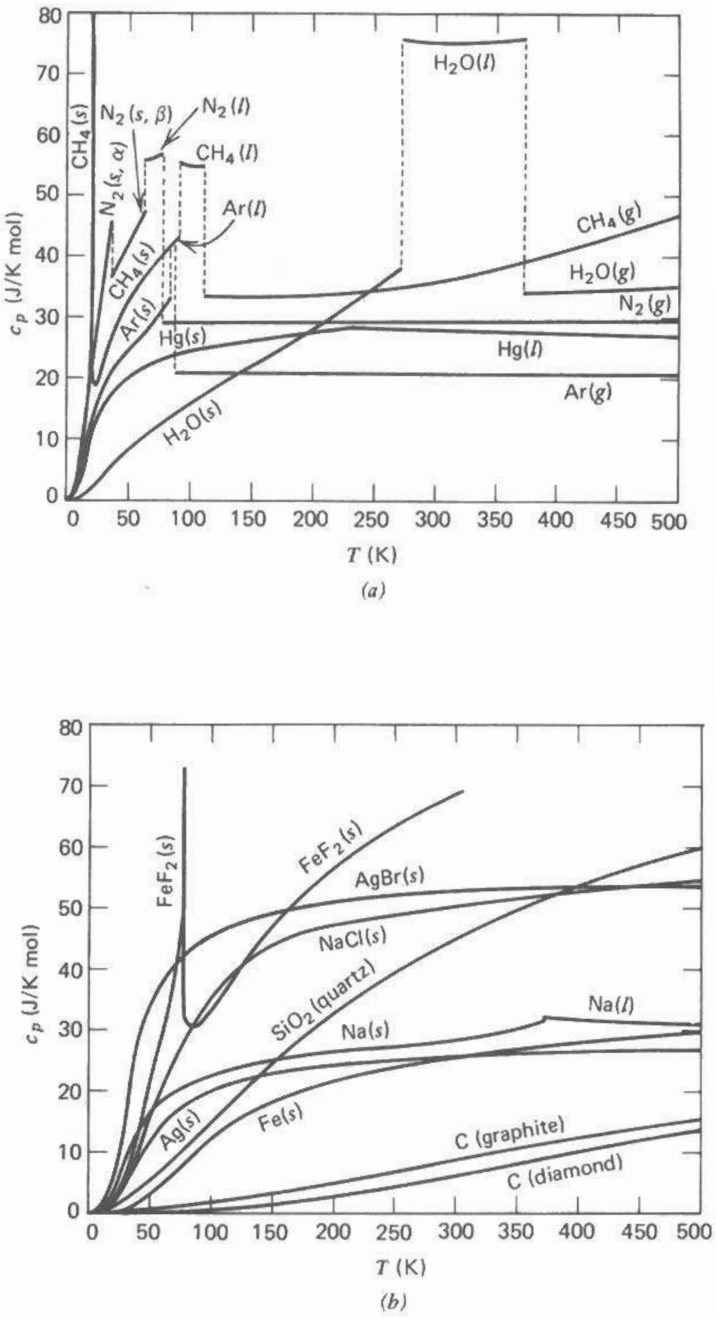

Figure 14.1 Temperature dependence of the heat capacity for various substances. (*a*) Room-temperature gases and liquids. (*b*) Room-temperature solids.

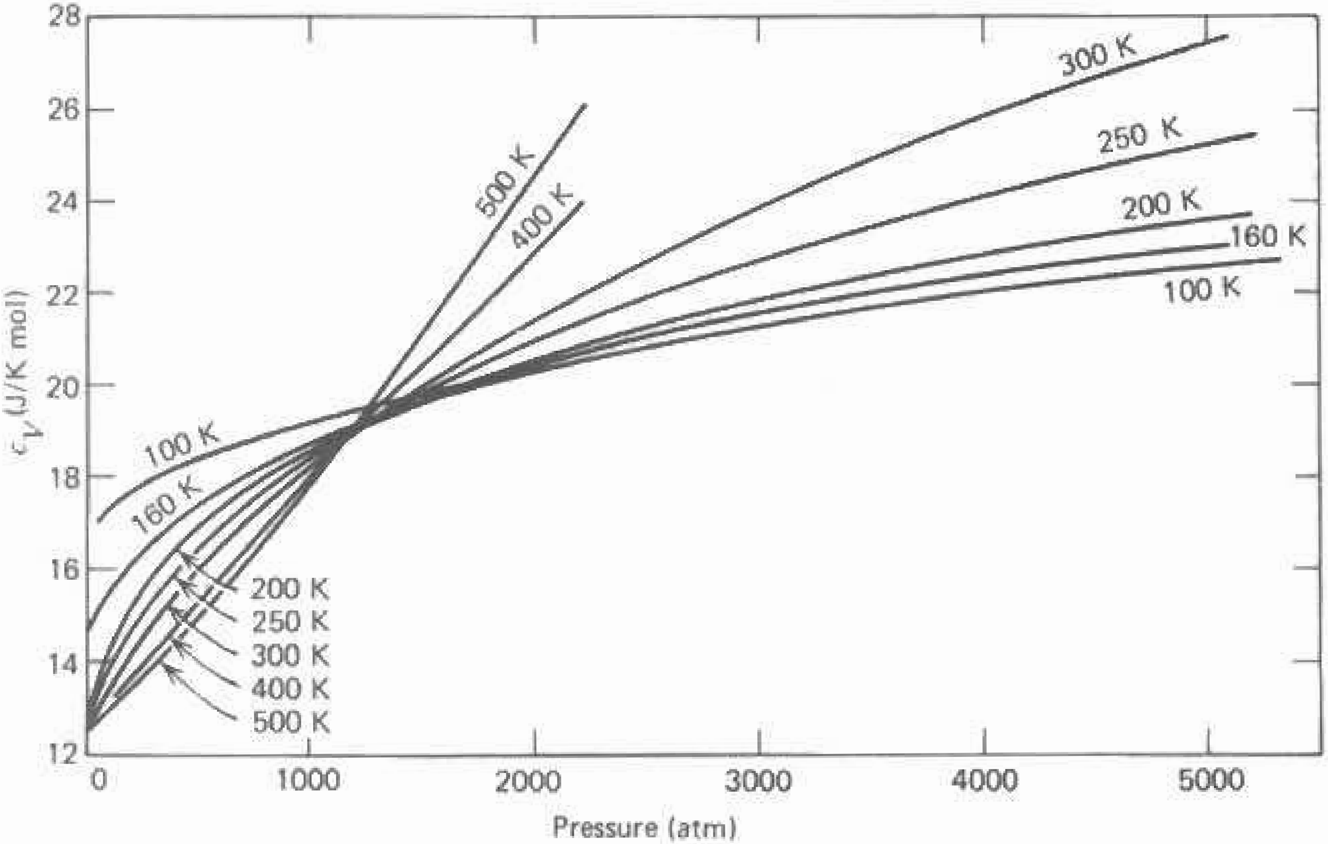

Figure 14.2 Constant-volume heat capacity of gaseous argon as a function of pressure and temperature. From F. Din (Ed.), *Thermodynamic Functions of Gases,* Vol. 2 (Butterworths, London, 1962).

- C_p and C_V are usually determined as functions of temperature and pressure over the ranges of interest.
- C_p and C_V are related to each other.
- For a perfect gas:

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left[\frac{\partial(U + pV)}{\partial T}\right]_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left[\frac{\partial(pV)}{\partial T}\right]_P = \left[\frac{\partial(nRT)}{\partial T}\right]_P = nR$$

- In the gas phase, $C_p - C_V$ can be significant.

- In condensed phases, pV is much smaller than nRT, so C_p and C_V are similar.
- $C_p - C_V$ will be explored further in Chapter 17.
- Heat capacities are usually dependent on temperature and are expressed in the form:

$$c_P = a + bT + cT^2$$

  for the phase of interest.

Energy and Enthalpy Changes in Chemical Reactions

- Consider a general chemical reaction of the form:
  $$\mathrm{aA} + \mathrm{bB} + \cdots = \mathrm{lL} + \mathrm{mM} + \cdots$$
- This may be rewritten as:
  $$\mathrm{lL} + \mathrm{mM} + \cdots - \mathrm{aA} - \mathrm{bB} - \cdots = \sum_{i=1}^{r} \nu_i X_i = 0$$

- X_i represents the species and ν_i represents the stoichiometric coefficients.
- By convention $\nu_i < 0$ for reactants and $\nu_i > 0$ for products. Thus for

$$\frac{1}{2}\ \mathrm{H}_2 + \frac{1}{2}\ \mathrm{Cl}_2 = \mathrm{HCl}$$

  - $\nu_{\mathrm{HCl}} = 1$
  - $\nu_{\mathrm{H}_2} = -\frac{1}{2}$
  - $\nu_{\mathrm{Cl}_2} = -\frac{1}{2}$
- In terms of this notation, the condition of conservation of mass becomes:

$$\Delta M = \sum_{i=1}^{r} \nu_i M_i = 0$$

where M_i is the molar mass of substance i.

- Consider now internal energy U and enthalpy H

$$\Delta U = \sum_{i=1}^{r} \nu_i u_i$$

$$\Delta H = \sum_{i=1}^{r} \nu_i h_i$$

  where u_i and h_i are the internal energy and enthalpy per mole of component i.
  - Note now that ΔU and ΔH are with respect to the stoichiometry of the reaction.
- The text then goes on to connect this to Hess's Law.

Thermochemistry of Physical Processes

- Consider the changes in U and H for a fluid initially in equilibrium at p_1, V_1, T_1 moving to a new equilibrium at p_2, V_2, T_2.
  - U and H are state functions, therefore the values of ΔU and ΔH are independent of the path between the initial and final state.
- Consider a path from the initial state and the final state that consists of two steps:
  - An isochor: the fluid is heated or cooled at constant V to T_2.
  - An isotherm: the fluid is held at constant temperature T_2 and the volume is changed until V_2 is reached.
- ΔU may be calculated on this path.

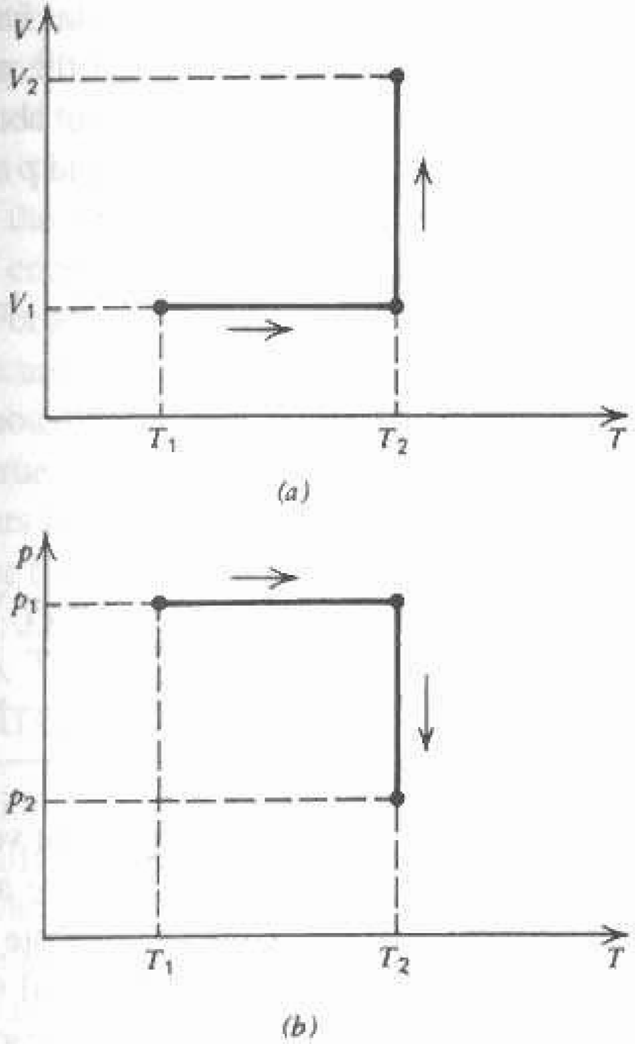

Figure 14.3 Two-step analysis of the change of state of a fluid: (*a*) constant-volume process followed by constant-temperature process, for calculating ΔU; (*b*) constant-pressure process followed by constant-temperature process, for calculating ΔH. In both cases the change is from the initial state p_1, V_1, T_1 to the final state p_2, V_2, T_2.

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- An infinitesimal change in U is given by:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

  where dT and dV are the infinitesimal changes in T and V.

- ΔU can be determined by integrating over this path:

$$\Delta U = U(T_2, V_2) - U(T_1, V_1)$$

$$= \int_{T_1,V_1}^{T_2,V_1} \left(\frac{\partial U}{\partial T}\right)_V dT + \int_{T_2,V_1}^{T_2,V_2} \left(\frac{\partial U}{\partial V}\right)_T dV$$

- The first step takes place at constant V. Therefore:

$$\Delta U_{\text{first step}} = \int_{T_1,V_1}^{T_2,V_1} \left(\frac{\partial U}{\partial T}\right)_V dT = \int_{T_1,V_1}^{T_2,V_1} C_V dT$$

- The second step takes place at constant T. Therefore:

$$\Delta U_{\text{second step}} = \int_{T_2,V_1}^{T_2,V_2} \left(\frac{\partial U}{\partial V}\right)_T dV$$

    - To evaluate this, $(\partial U/\partial V)_T$ needs to be determined.

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

- Thus for the total internal energy change:

$$\Delta U = \int_{T_1,V_1}^{T_2,V_1} \left(\frac{\partial U}{\partial T}\right)_V dT = \int_{T_1,V_1}^{T_2,V_1} C_V dT$$

$$+ \int_{T_2,V_1}^{T_2,V_2} \left\{ T \left(\frac{\partial p(T,V)}{\partial T}\right)_V - p(V,T) \right\} dV$$

- This can be evaluated if the heat capacity C_V and the equation of state are known.
- If the equation of state is not known, then measurements of p and T at constant V may be used to evaluate $(\partial U/\partial V)_T$.
- To determine the enthalpy change, a different two step path is more convenient.

- Continued:
  - An isobar: the fluid is heated or cooled at constant p to T$_2$.
  - An isotherm: the fluid is held at constant temperature and the pressure is changed until p_2 is reached.
- An infinitesimal change in H is given by:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

- It can be shown that:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

- Thus the total enthalpy change, ΔH, may be determined:

$$\Delta H = H(T_2, p_2) - H(T_1, p_1)$$

$$= \int_{T_1,p_1}^{T_2,p_1} \left(\frac{\partial H}{\partial T}\right)_p dT + \int_{T_2,p_1}^{T_2,p_2} \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$= \int_{T_1,p_1}^{T_2,p_1} C_p dT$$

$$+ \int_{T_2,p_1}^{T_2,p_2} \left\{ V(p,T) - T\left(\frac{\partial V(T,p)}{\partial T}\right)_p \right\} dp$$

- When work other than pV work is involved:

$$dU = đq + đw_{pV} + đw_X$$

$$dH = (đq)_p + đw_X$$

- Hess's Law applies to the heat capacities, C_p and C_V.

Introduction to Phase Changes

- This section will be omitted (for now).

Standard States

- This section is to be reviewed, but not in class.

Thermochemistry of Solutions

- This section is to be reviewed, but not in class.

Molecular Interpretation of Physical Processes

- This section is to be reviewed, but not in class.

Bond Energies

- This section is to be reviewed, but not in class.

Some Energy Effects in Molecular Structures

- This section is to be reviewed, but not in class.

Lattice Energies of Ionic Crystals

- This section is to be reviewed, but not in class.

involves a phase change corresponds to a path crossing one

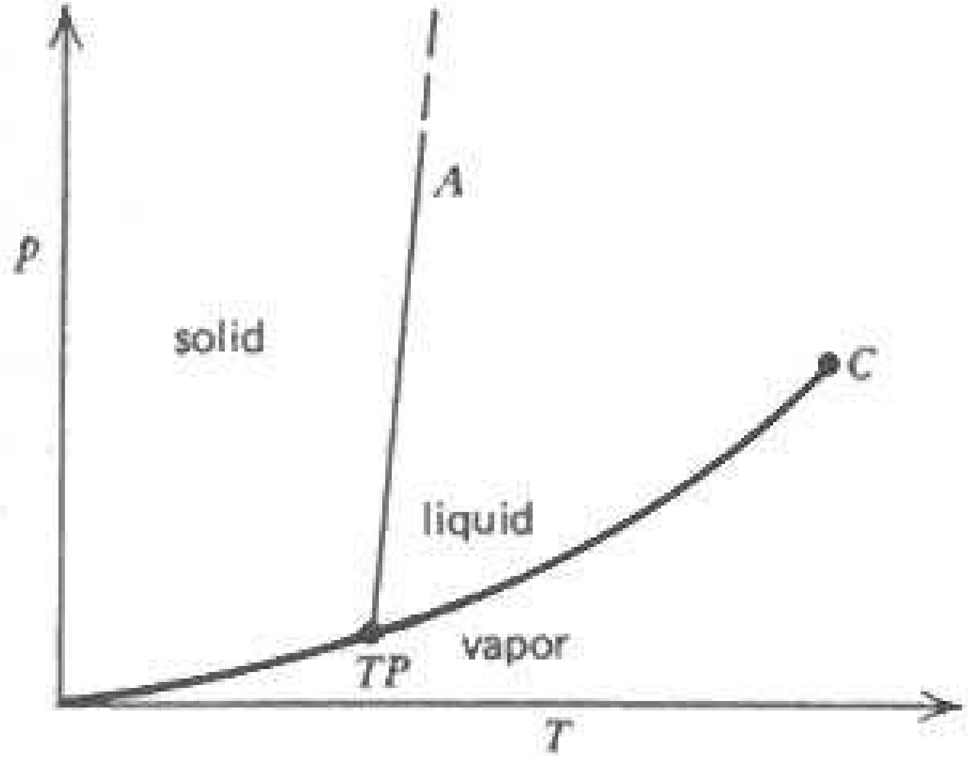

Figure 14.4 A typical phase diagram for a simple substance. The lines represent the locus of pressure and temperature for which two phases can coexist, for example liquid and vapor along the line *TP-C*. The points *TP* and *C* are, respectively, the triple point and the critical point for the substance (see Chapter 24).

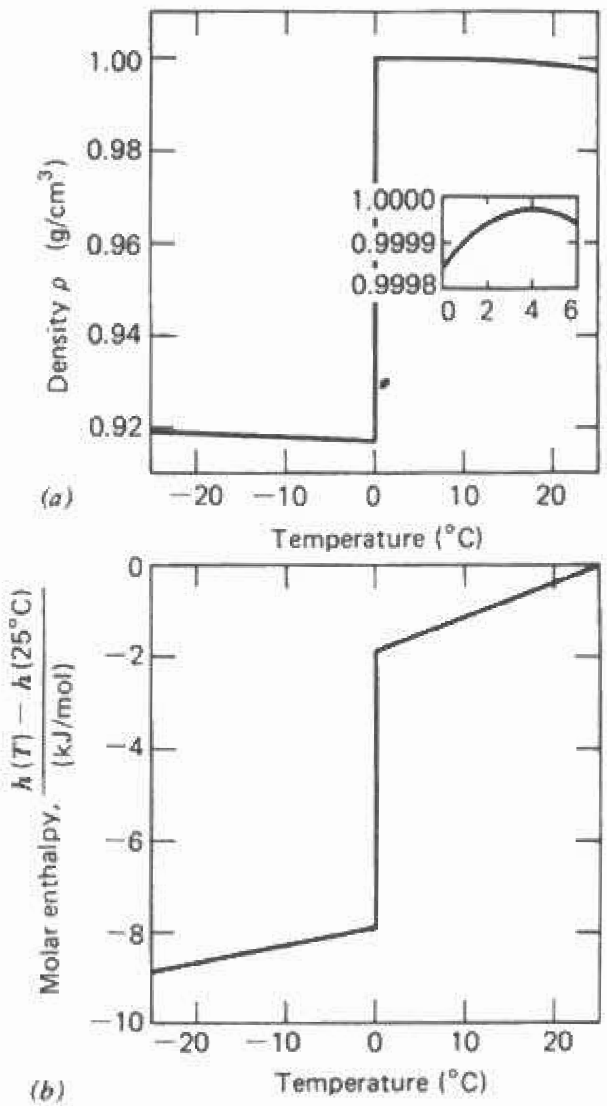

Figure 14.5 Solid-liquid phase transition for water at 1 atm: (*a*) density; (*b*) molar enthalpy (relative to 25°C). The inset in (*a*) shows the anomalous density behavior between 0 and 4°C. Note in (*b*) that the heat capacity $[c_p = (\partial h/\partial T)_p]$ of liquid water is approximately twice that of ice.

The integral heat of solution is thus fairly independent of

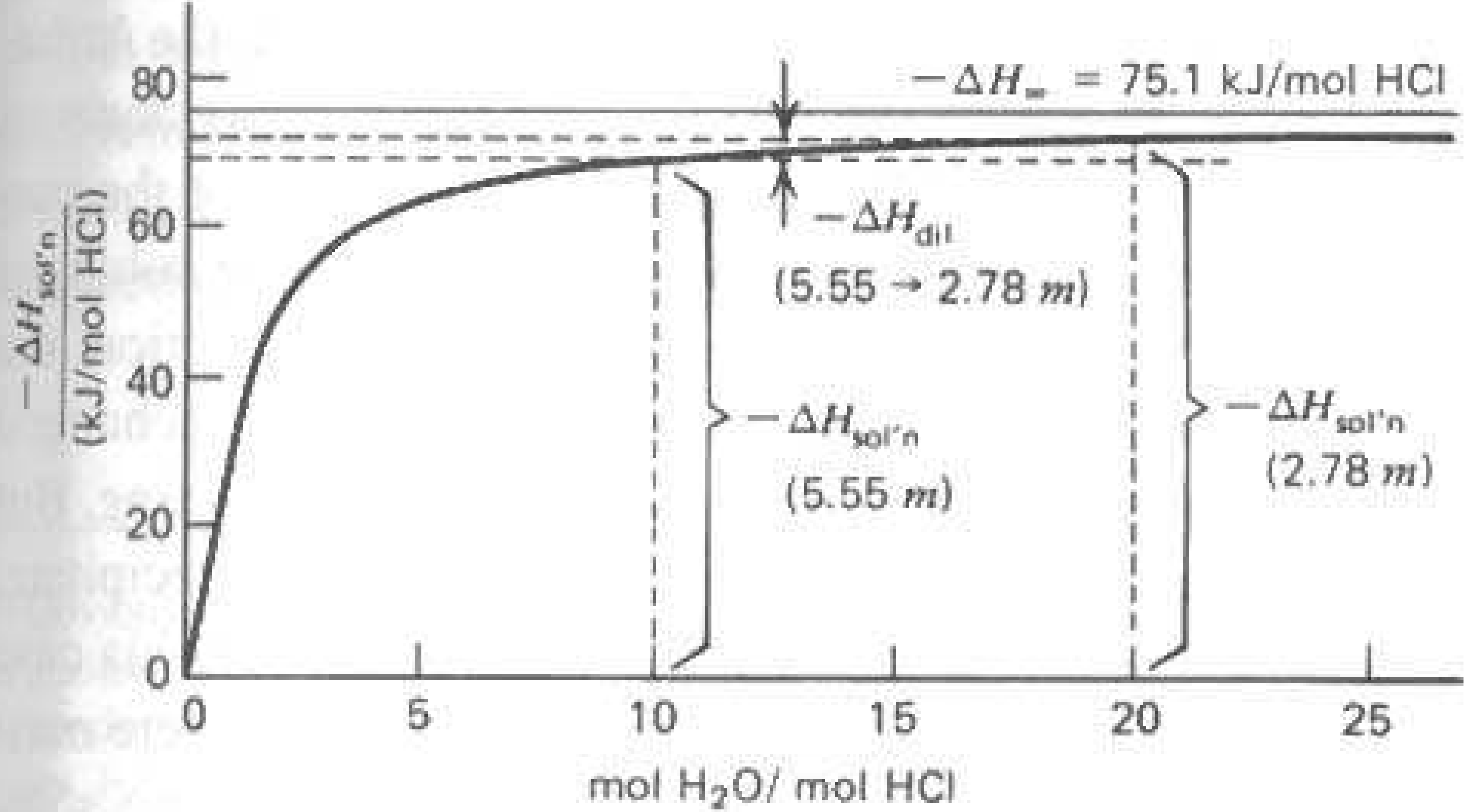

Figure 14.6 Heat of solution of HCl in water.

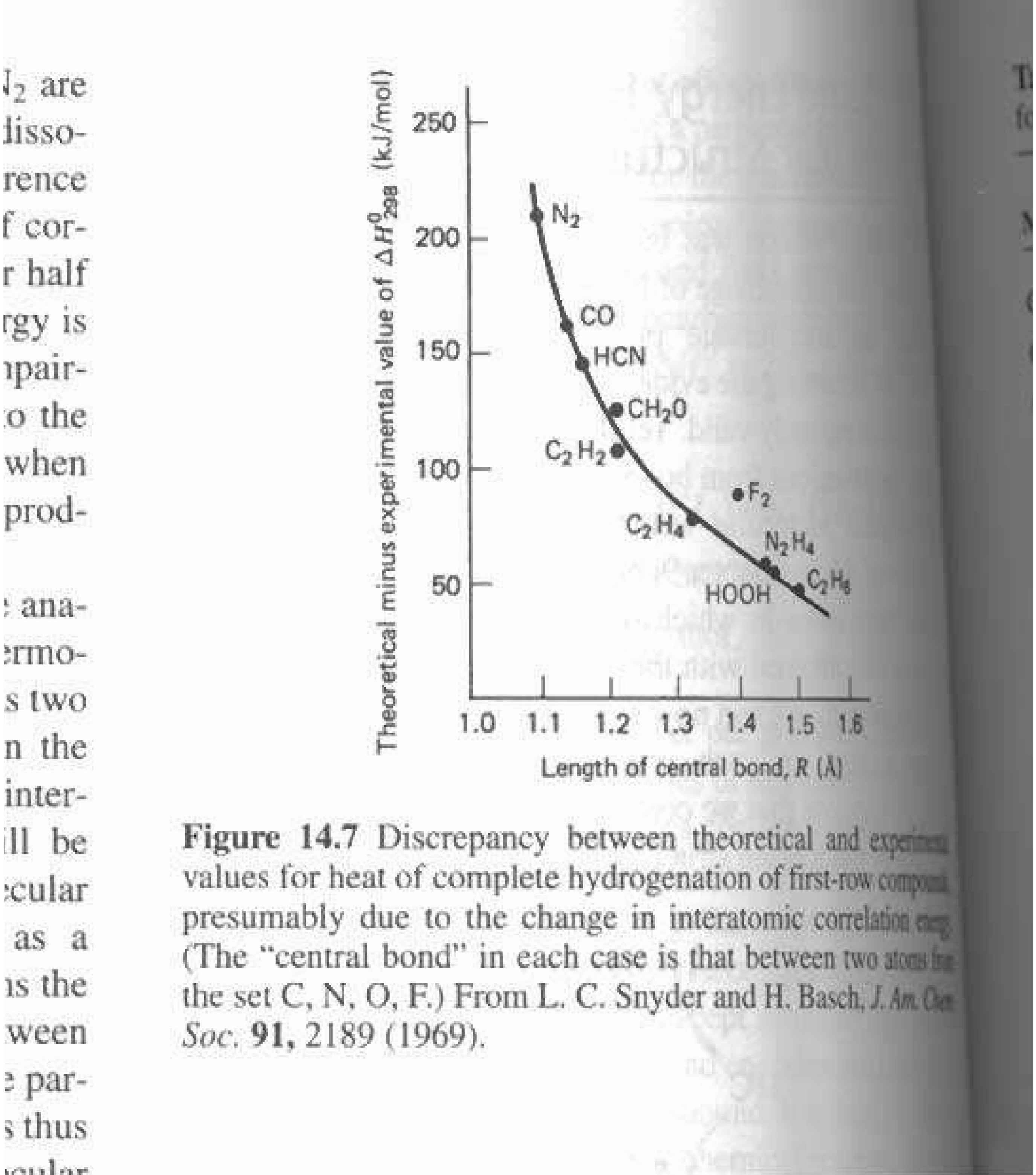

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Figure 14.7 Discrepancy between theoretical and experimental values for heat of complete hydrogenation of first-row compounds presumably due to the change in interatomic correlation energy. (The "central bond" in each case is that between two atoms from the set C, N, O, F.) From L. C. Snyder and H. Basch, *J. Am. Chem. Soc.* **91,** 2189 (1969).

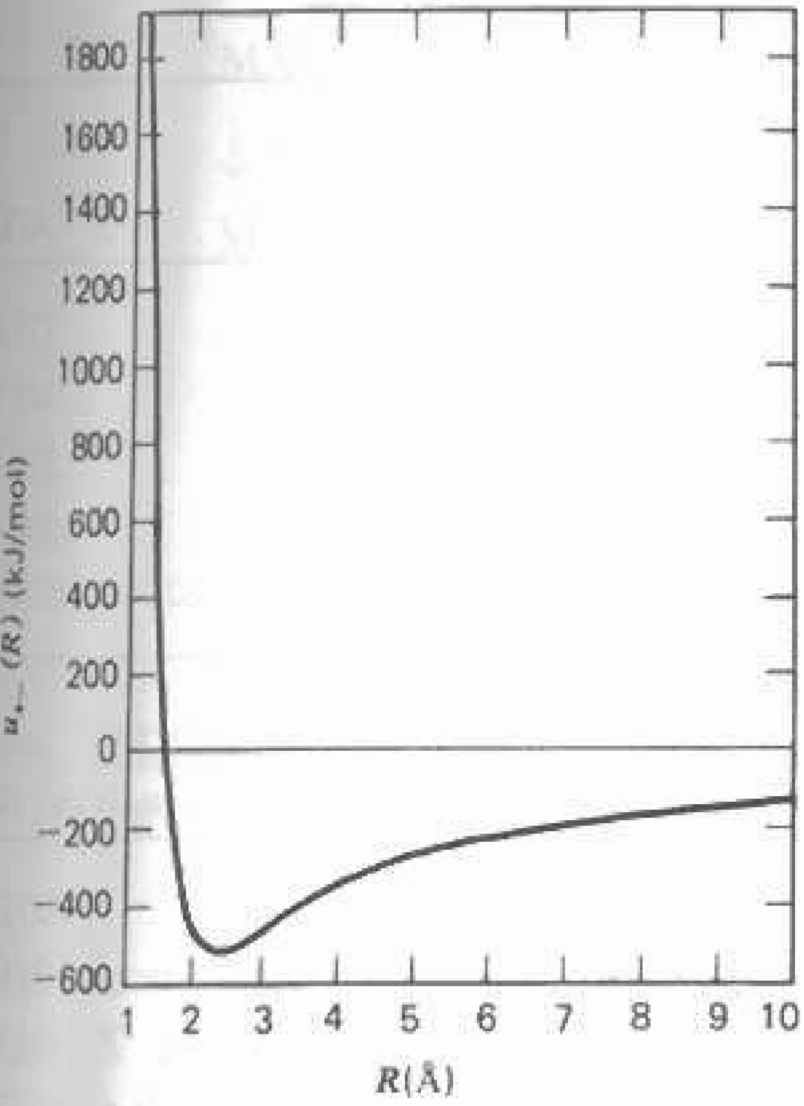

Figure 14.8 The Born–Mayer pair potential for the ionic crystal NaCl.

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The Concept of Entropy: Relationship to the Energy Level Spectrum of a System

- The first law of thermodynamics allows the definition of heat and work in terms of energy changes.
- The first law of thermodynamics also restricts the class of possible processes to those that conserve energy.
- But processes that conserve energy do not necessarily occur.
- The first law does not predict whether a process will actually occur.
- For example, consider a box with two compartments.
  - Each compartment is filled with a different gas.
  - A valve is opened between the compartments.
  - The gases mix and energy is conserved.

- But demixing of the gases is also consistent with the first law.
  - Yet it is never observed.
- Consider an adiabatic bomb calorimeter filled with H_2 and O_2.
  - By the first law, energy is conserved since energy is unable to leave the system as work or heat.
  - The reaction:
    $$\mathrm{H_2} + \tfrac{1}{2}\,\mathrm{O_2} = \mathrm{H_2O}$$
    is vigorously exothermic and can be initiated with a slight perturbation (such as a spark).
  - The first law is unable to predict whether this reaction will occur in a given set of conditions.
- Consider two systems in contact through a diathermal wall, but otherwise isolated.

- Such systems are observed to spontaneously reach a common temperature.
- Although it is consistent with the first law, it is never observed that the systems spontaneously change such that the warmer system becomes hotter and the cooler system cools further.
- Knowing the energy change of the system associated with a process is insufficient to predict the direction of the process.
- There are many spontaneous processes that are either exothermic or endothermic.
  - Mixing of water with sulfuric acid is exothermic.
  - Mixing of water with ammonia is endothermic.
- Criteria in addition to the first law is required to predict spontaneity.

- The thermodynamic function of entropy is needed.
- The second law of thermodynamics describes equilibrium in terms of entropy.
- Derivatives of entropy with respect to the parameters that describe the constraints of the system determine the stability of equilibrium.
- If the energy is constant, entropy determines whether or not a process is spontaneous.
- The second law of thermodynamics can be considered from two points of view.
  - One approach will be with respect to the redistribution of a population of molecules over energy levels as energy enters or leaves the system as heat.

- How much information about the microscopic states of a system is contained by the specification of the macroscopic parameters will be considered.
- Also considered will be degeneracy of the energy spectrum. (Degeneracy is related the number of distributions that have the same energy.)
- Statistical mechanics deals with the most probable distributions that are consistent with a particular energy.
- Statistical mechanics shows that in most cases the most probable distribution is sharply peaked.
- It also shows that the macroscopic properties are somewhat insensitive to the details of the energy spectrum.
- The second law will then be considered from a macroscopic perspective.

The Relationship between Average Properties and Molecular Motion in an N-Molecule System: Time Averages and Ensemble Averages

- Macroscopic properties have been related to averages of microscopic properties.
- Three questions arise:
  - Why is averaging used?
  - Which type of average is correct?
  - Do different averaging processes give the same description of the system?
- Averaging is used because a thermodynamic system of many molecules is described by a few macroscopic variables.
  - The thermodynamic description is consistent with some type of averaging.

- The thermodynamic description is coarser than the microscopic description.
- To discern the type of averaging to be used and whether the type of average affects the result requires careful consideration of how measurements are made.
- Already considered have been:
  - The treatment of all molecules as independent particles.
  - The momentum transferred by one molecule per unit area per unit time.
  - The sum of the contributions all molecules moving in the appropriate direction to momentum transport per unit time per unit area.
    - To do this, the distribution function $f(\mathbf{v})$ is assumed to be independent of time.

- Assuming that the distribution function $f(\mathbf{v})$ is independent of time is equivalent to following the trajectory of a single molecule for a very long time and averaging the momentum transported across the plane each time it crosses the plane.
- But, what exactly does this type of equivalency mean?
- Successive crossings of the plane by different molecules are not uniform in time.
  - Instantaneous rates of momentum vary with time.
  - But at equilibrium, the average rate of crossing the plane must be independent of time.
- Consider the time average of momentum transfers occurring in some long time interval $\Im$.

- Continued:
  - If $\Im$ is short (i.e. the interval between crossing is comparable to $\Im$, then averages over that time interval will fluctuate with that time scale.
  - If $\Im$ is large (i.e. the interval between crossings is small relative to $\Im$), then the average over $\Im$ is independent of $\Im$.
- Now consider following the trajectory of a single molecule in a gas.
  - If it is followed long enough, it will approach arbitrarily close to each point within the volume.
  - It will also approach arbitrarily close to each velocity in the velocity distribution.
  - This is the quasi-ergodic hypothesis.

- If the gas is dilute, collisions between molecules are so infrequent that they may be ignored.
    - In this case it is feasible to follow the trajectory of a particular molecule sufficiently long to compute the time average of a mechanical quantity.
    - The distance that the molecule travels in time t grows linearly with t.
    - The contributions to momentum transport across a plane could be summed and then divided by t.
    - Then taking the limit as t goes to infinity becomes the equivalent to averaging over a distribution function.
- If the gas is not dilute, then the molecule is almost always within the force field of another molecule.
- The trajectory is very complicated.

- In such cases, calculation of the trajectory is computationally impossible.
- An alternative method is needed to relate molecular properties to macroscopic properties.
- The alternative approach was proposed independently by Gibbs and by Einstein.
- Recall that for a given macroscopic state of the system, there are many microscopic states that are consistent with the macroscopic state.
- Instead of one system in a microscopic state consistent with the macroscopic state, many such systems in different microstates are constructed.
    - This collection of systems encompasses the entire distribution of microstates that match the macrostate.

- Continued:
  - Each member system of the collection is a replica system.
  - The entire collection is called an *ensemble*.
- Averages may be calculated by considering the quantity of interest for each of the replicas, then averaging over the entire ensemble.
- Statistical mechanics takes as a postulate that the ensemble average is equal to the time average in the limit of infinitely long time.
- Ensemble averages are easier to calculate than are time averages.
- This postulate follows from the quasi-ergodic hypothesis.

- To understand the quasi-ergodic hypothesis, consider a geometric visualization of molecular dynamics.
  - Classical mechanics will be used.
  - Assume that the molecules have no internal structure.
  - Consider a many dimensional coordinate system that describes the position and momentum of N particles in volume V.
    - $6N$ axes are required.
    - There are $3N$ position coordinates $x_1, y_1, z_1, \ldots, x_N, y_N, z_N$.
    - There are $3N$ momentum coordinates $p_{x_1}, p_{y_1}, p_{z_1}, \ldots, p_{x_N}, p_{y_N}, p_{z_N}$.
    - This space is called the *phase space* of the N molecule system.

- Phase space is assumed to be Cartesian with distances between two points given by:

  $$D(w, w^*) = \left[\sum_{j=1}^{6N} (w_j - w_j^*)^2 \right]^{1/2}$$

  where w_j and w_j^* are the j elements of the vector of coordinates and momentum describing point w or w^* in $6N$ dimensional phase space.
- For a given value of energy, the possible values of coordinates and momentum will describe a surface in phase space.
  - For a perfect gas, energy depends only on the momenta of the particles.

- The total energy is:

  $$E = \frac{(p_{x_1}^2 + \ldots p_{z_N}^2)}{2m}$$

  which describes a sphere in $3N$ dimensions.
- If the molecules interact, then the energy depends also on the instantaneous positions.
  - The total energy expression still describes a surface, but that surface is much more complicated.
  - If a trajectory on an isolated system is considered, then the trajectory moves on the surface in phase space that is defined by energy conservation.
- Consider the difference between time averaging and ensemble averaging.

- The trajectory moving over the surface defined by energy conservation will sample coordinates and momenta consistent with the total energy.
    - The time average will average over these.
- For an ensemble, each replica system has the same value of E, V and N.
- Therefore the momenta and coordinates will be a representative point on the same surface considered for the time averaging.
- Different replicas will will have different representative points, but all points lie on the same surface.
- The possible points will densely cover the surface.
- Unless the time average covers this surface in the same way as the ensemble, the averages will be different.

- There exist conditions for which they are equivalent.
- The ensemble average is the fundamental concept in the description of equilibrium.
  - By definition, a macroscopic property of a system is to be identified with the ensemble average of the corresponding microscopic dynamical property.
  - This definition can be justified by the comparison of theory and observation.
- Ergodic theory as applied to statistical mechanics explores the equivalence of time and ensemble averages.
- The ergodic hypothesis as originally formulated by Boltzmann is incorrect.
  - Boltzmann postulated that a trajectory representing the time evolution of the system would pass through every point on the energy surface.

- This cannot occur because:
    - A solution to an equation in mechanics has a unique solution which never crosses itself.
    - The trajectory is of lower dimensionality than the surface and so can thus never fill the higher dimensional energy system.
- The quasi-ergodic hypothesis makes a weaker statement about the trajectory on the energy surface.
- Birkhoff (1931) proved that if a boundary on an energy surface could not be constructed such that a trajectory originating from a representative point would lie entirely on one side of the boundary then the trajectory will pass arbitrarily close to every point on the energy surface.
- The quasi-ergodic hypothesis is valid only in classical mechanics.

- The quasiergodic hypothesis cannot be rigorously proven,
- There are other difficulties in basing a description of equilibrium on ergodicity.
  - Any microscopic description of a system moving to equilibrium should have a time-independent description of the equilibrium state.
- That a system is quasi-ergodic is necessary, but not sufficient, to give a time independent average.
  - A quasi-ergodic trajectory can also be quasi-periodic, such as in the case of couples oscillators with an irrational ratio of frequencies.
- Two trajectories can start at points close together on the energy surface.
  - As the trajectories evolve, they remain close together.

- The distance between them grows smoothly with time.
- If reversibility is to be avoided, more turbulent trajectories are needed.
- These turbulent trajectories are associated with $mixing$ and diverge exponentially with time.
  - The trajectory is chaotic and does not return to the initial state.
  - Thus mixing implies quasi-ergodicity.
  - Simulation studies have demonstrated mixing and quasi-ergodicity.
  - For general mechanical systems, there exist energy regions which exhibit dynamical chaos.
  - In the limit of thermodynamic size ($N \approx 10^{23}$), ensemble averages satisfactorily describe equilibrium properties.

- To use ensemble averages in place of time averages, a number of issues must be considered.
  - The mixing property has been established only for classical mechanics.
  - Quantum ergodic theory is not well developed.
  - The use of ensemble averages is valid both quantally and classically.
  - Equilibrium is defined as being invariant with time.
    - This neglects fluctuations about equilibrium.
    - Ensemble averages permit the study of these fluctuations.
  - The type of the equilibrium that exists depends on the constraints.
    - Constraints are more easily implemented in ensembles than in trajectories.

Ensembles and Probability Distributions

- Consider tossing a coin:
    - It can land either head or tails.
    - Which it will be cannot be predicted with certainty.
    - If the coin is balanced, then head and tails have equal probability.
    - For a large number of tosses, the number of heads should be approximately equal to the number of tails.
    - But other outcomes are possible, although not as likely.
- For a single toss of the balanced coin, the probability of heads is $\frac{1}{2}$.
- The probability of tails is also $\frac{1}{2}$.

- Consider n tosses.
  - The probability that n_1 will be heads is:

$$\frac{n!}{n_1!(n-n_1)!}\left(\frac{1}{2^n}\right)$$

  where $n!/n_1!(n-n_1)!$ is the number of ways that n_1 heads could occur regardless of order and 2^n is the number of possible sequences of heads and tails.
- For 4 tosses this predicts:
  - 1/16 will be all heads and 1/16 will be all tails.
  - 4/16 will be 3 heads and 1 tail and 4/16 will be 1 head and 3 tails.
  - 6/16 will be 2 heads and 2 tails
- For 400 tosses, the probability that 200 will be heads is 5×10^{22} more likely than 100 of 400 tosses being heads.

- Now consider this in the context of molecules in a gas.
  - Molecules of a gas are in motion.
  - The number of molecules in a fixed volume element will vary from one moment to the next.
  - Consider a perfect gas of N molecules in a volume V.
  - Now consider some volume element ω within the container.
  - ω/V is the fraction of the total volume occupied by ω.
  - Assume that the gas is uniformly distributed.
  - The probability of finding a particular molecule within ω is ω/V
  - The probability of all N molecules being within ω is $(\omega/V)^N$.

- If ω is small with linear dimensions comparable to molecular separations, then the number of molecules in ω would most likely be 0,1, or 2.
- If ω was 0.1 of the total volume, then $N/10$ molecules (with small fluctuations) would be most likely to be found within ω.
- $P(N_1)$ is the probability distribution that describes the probability of finding N_1 in ω and $N - N_1$ in $V - \omega$.

$$P(N_1) = \frac{N!}{(N-N_1)!N!}\left(\frac{\omega}{V}\right)^{N_1}\left(\frac{V-\omega}{V}\right)^{N-N_1}$$

- The relative fluctuation in the number of molecules in ω decreases as ω increases and is given by $(N\omega/V)^2$.
  - The relative deviation is a volume of 1 mm^3 is of the order of 10^{-8} at room temperature and pressure.

- The relationship between an ensemble and the probability distribution must be considered.
- Macroscopic density does not vary perceptibly from point to point in a gas at equilibrium.
- In applying probability to the study of molecules the following must be considered:
    - The relationship between the definition of the probability distribution and the class of events being described.
    - The relationship between the probability and the fundamental classical or quantum description of the system.
- An ensemble is a collection of replica systems.
- The following must be specified:
    - The nature of the collection.

- Continued:
    - The set of possible states for the objects composing the collection
    - Any other relevant details.
- The probability of finding a characteristic is the fraction of replicas that possess the characteristic.
- The probability depends on the nature of the ensemble.
- Replicas composing the ensemble are consistent with the constraints.
- Consider an ensemble composed of pennies:
    - Whether they are heads up or tails up does not need to be specified since they are included in the properties of a penny.
- Consider an ensemble of containers of gas having rigid adiabatic walls and the same density of molecules.

- It is not necessary to state whether the pressures in all containers are the same.
- There is a relationship between the external constraints defining a macroscopic system and the nature of the corresponding ensemble.
  - This allows the establishment of correspondence between macroscopic and microscopic approaches to the behaviour of matter.
- Consider the number of replicas $\mathcal{N}$ within the ensemble to be sufficiently large that that the limit $\mathcal{N} \rightarrow \infty$ may be taken.
  - This means that the probability distribution function may be treated as continuous and may be considered in terms of a probability density.
    - For a discrete probability function, the probability of x occurring is considered.

- For a continuous probability function, the probability that x is between a and b is considered.
- This probability is expressed in terms of an integral over a probability density, $\mathcal{P}(x)$:

$$P(x_1 \leq x \leq x_2) = \int_{x_1}^{x_2} \mathcal{P}(x)dx$$

- If $x_2 = x_1 + dx$ then:

$$P(x_1 \leq x \leq x_1 + dx) = \mathcal{P}(x)dx$$

    - Note that $P(x)$ is dimensionless, but $\mathcal{P}$ has units x^{-1}.
- It is possible to relate this to a discrete distribution by dividing x into arbitrarily small intervals Δ and labelling each with an index i.

- Then:

$$P(x_i) = \mathcal{P}(x_i)\Delta$$

  This is valid as long as Δ is small enough for $\mathcal{P}$ to be treated as a constant over the interval.

- Analogously to continuous distribution functions, averages can be determined using discrete probability functions.
- Let x be a discrete variable from the set $x_1, \ldots, x_n$ with probabilities $P(x_1), \ldots, P(x_N)$.
- The average value of x (also known as the arithmetic average or the mean or expectation value) is:

$$\langle x \rangle = \frac{x_1 P(x_1) + x_2 P(x_2) + \cdots x_N P(x_N)}{P(x_1) + P(x_2) + \cdots P(x_N)} = \frac{\sum_i x_i P(x_i)}{\sum_i P(x_i)}$$

- The mean value of $f(x)$ is:

$$\langle f(x)\rangle = \frac{\sum_i f(x_i)P(x_i)}{\sum_i P(x_i)}$$

- If $(f(x) = x^n$, the $\langle f(x)\rangle$ is the nth moment of $P(x)$
- For a continuous variable x and continuous $f(x)$, the equations become:

$$\langle x\rangle = \frac{\int x\mathcal{P}(x)dx}{\int \mathcal{P}(x)dx}$$

$$\langle f(x)\rangle = \frac{\int f(x)\mathcal{P}(x)dx}{\int \mathcal{P}(x)dx}$$

- From this follows relations:

$$\langle f(x) + g(x) \rangle = \langle f(x) \rangle + \langle g(x) \rangle$$

$$\langle c f(x) \rangle = c \langle f(x) \rangle$$

- Probability distributions are often normalized:

$$\sum_i P(x_i) = 1$$

$$\int \mathcal{P}(x) dx = 1$$

  - Normalization is not necessary if only relative probabilities are of interest.
- The spread of a probability density distribution $\mathcal{P}(x)$ is given by $\langle x^2 \rangle - \langle x \rangle^2$

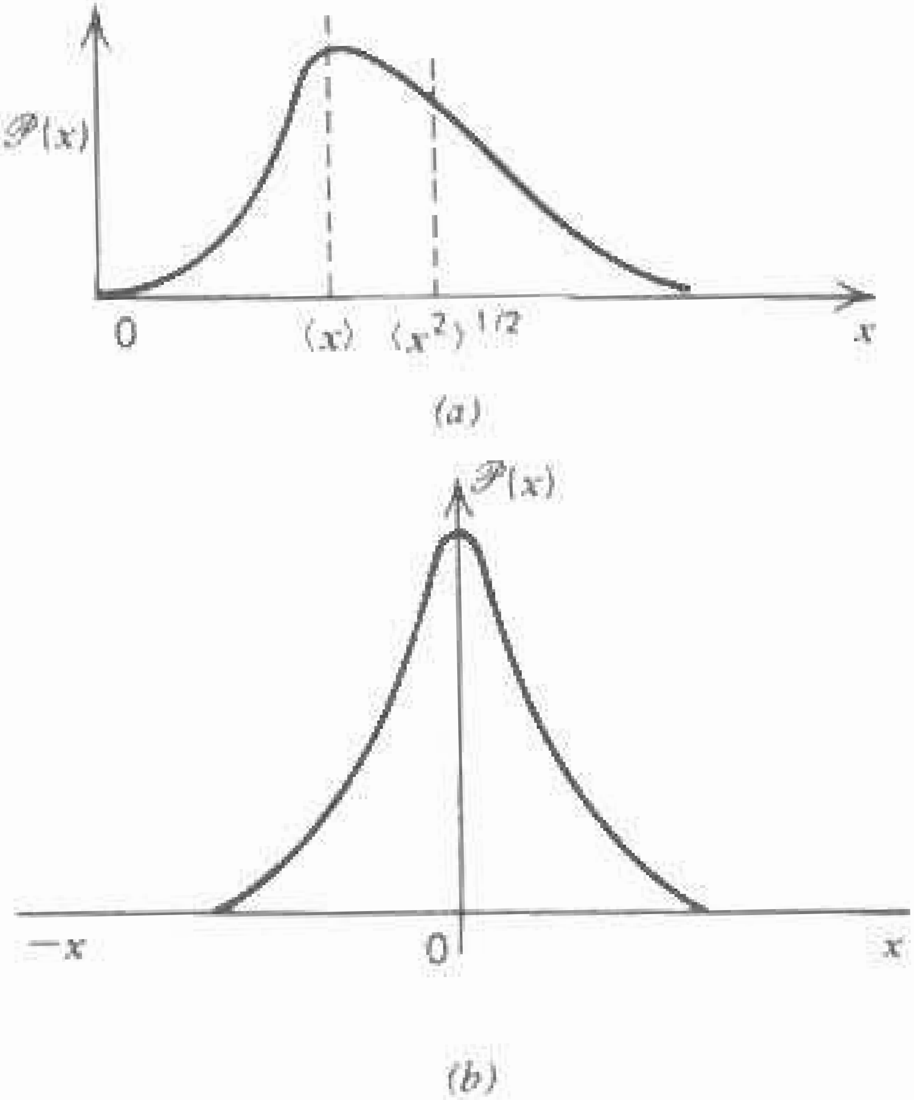

Figure 15.1 (*a*) A typical probability density distribution with $\langle x \rangle \neq 0$. (*b*) A typical symmetric probability density distribution with $\langle x \rangle = 0$.

- Except when $\mathcal{P}(x)$ is a delta function, $\langle x^2 \rangle > \langle x \rangle^2$ where $\langle x^2 \rangle = \int x^2 \mathcal{P}(x) dx$
- One implication of a distribution having width is the possibility of fluctuations.
  - There is a nonzero probability of finding a value of x that differs from the average value of x.
  - The probability of a fluctuation depends on its deviation from the mean value.
  - These fluctuations show up in fluctuations of the macroscopic variables.
- Another property of probability distributions that is important is the concept of joint probability.
  - Consider two variables, x and y, with probability density distributions $\mathcal{P}_1(x)$ and $\mathcal{P}_2(y)$ respectively.

- The joint probability distribution is $\mathcal{P}(x,y)dxdy = \mathcal{P}_1(x)\mathcal{P}_2(y)dxdy$
- This gives the probability of finding x between x and $x+dx$ and y between y and $y+dy$ if $\mathcal{P}_1(x)$ and $\mathcal{P}_2(y)$ are independent of each other.
- If $\mathcal{P}_1(x)$ and $\mathcal{P}_2(y)$ are not independent but rather are correlated, then the joint probability includes a correlation function:

$$\mathcal{P}(x,y)dxdy = \mathcal{P}_1(x)\mathcal{P}_2(y)g(x,y)dxdy$$

$$\text{or } \mathcal{P}(x,y)dxdy = \mathcal{P}_1(x)\mathcal{P}_2(y)[1+h(x,y)]dxdy$$

  where $g(x,y)$ and $h(x,y)$ are the correlation functions.
  - When x and y are independent, $g(x,y)=1$ and $h(x,y)=0$

Some Properties of a System with Many Degrees of Freedom: Elements of the Statistical Theory of Matter at Equilibrium

- Consider a sample containing a large number of molecules, N, in volume V.
- The energy of the system is between E and $E + dE$ with $dE/E << 1$.
- An energy spectrum exists for the system.
    - The details of the spectrum do not need to be known.
- There are an enormous number of quantum states consistent with the macroscopic constraints of E, V, N.
- There are many distributions over the energy levels that are consistent with E, V, N.

- The equations of motion for N molecules cannot be solved exactly (classically or quantally).
  - Therefore the exact mechanical behaviour of the system is not determined and is not available for a macroscopic system.
  - This is not of interest in macroscopic thermodynamics.
- $\Omega(E, V, N)$ is the number of states with energy between E and $E + dE$.
  - Each solution of the N molecule Schrödinger equation gives a small number of the $\Omega(E, V, N)$ states.
  - The properties of the macroscopic variables depend only on $\Omega(E, V, N)$, not the microscopic details.

- The fundamental postulate of equilibrium statistical mechanics is:
  “All possible quantum states of an isolated system consistent with a given set of macroscopic parameters of constraint are to be considered as equally probable”.
  - This is also known as the postulate of *equal a priori* probability.
  - This is an assumption which has been validated by the success of statistical mechanics in producing results consistent with observations.
- To apply this postulate an ensemble of systems is considered.
- A large number of replica systems is constructed, each consistent with the macroscopic variables E, V, N.
- All other properties are allowed to vary freely.

- Suppose that all possible quantum states consistent with the definition of the ensemble are represented in the ensemble.
    - The relative frequency definition of probability is in agreement with the assumption of equal $a\ priori$ probability of all quantum states consistent with E, V, N.
    - Therefore the probability of a random choice of a replica from the ensemble being the same as an arbitrarily chosen member of the ensemble is $1/\mathcal{N}$ when there are $\mathcal{N}$ replicas in the ensemble.
- Consider the constraints used to define the ensemble.
- The equilibrium macroscopic properties of an isolated system are independent of time.
- Therefore the distribution over the energy levels is independent of time.

- Constants of motion include total energy, total linear momentum, and total angular momentum of the system.
- In an isolated system, no energy is transferred across the borders and thus no forces act upon the system.
  - Therefore there is no change in either linear or angular momentum.
- The constraints make it possible to define an appropriate probability distribution.
- Often it is sufficient to use only one of the constants of motion, typically the total energy (since it is used to define the ensemble).
  - The other constants of motion are allowed to vary freely.
- Consider an ensemble of replica systems, each with volume V and number of molecules N.

- The ensemble is specified by the requirement that the energy be between E and $E + dE$.
    - The number of quantum states with energy less than E is $\Gamma(E, V, N)$.
    - Therefore the number of quantum states with energy between E and $E + dE$ is:

$$\Omega(E, dE, V, N) = \Gamma(E + dE, V, N) - \Gamma(E, V, N)$$

- $\Omega(E, dE, V, N)$ describes the energy spectrum including degeneracy and dependence on volume.
    - The dependence on V is due to the effect of the boundary conditions on the energy spectrum of the isolated system.
- In large systems, the dependence of Ω on the energy interval dE is insignificant.

- In large systems, the dependence of Ω on the energy interval dE is insignificant.
  - As the system becomes larger the dependence of Ω on dE is increasingly insignificant.
  - This is a consequence of the Schrödinger equation, the solution of which depends on the form of the potential and the boundary conditions.
- The solutions to the Schrödinger equation for particles in a box are of the form $\sin kx$ and $\cos kx$.
  - The boundary conditions assume that the walls of the box are infinitely repulsive (there is zero probability of the particle being outside the box).
  - These boundary conditions force k and consequently the energy to have finite values.
  - The larger the box, the greater number of finite energies allowed in the spectrum.

- In the limit of an infinite box (i.e. a free particle), the allowed values of k become continuous and the energy spectrum becomes a continuum.
- The fact that a macroscopic system contain a large number of molecules allows the analysis to be simplified.
- Divide the energy scale into intervals of dE with $dE << E$
  - For a large system the interval dE contains many energy levels.
  - The number of states between E and $E + dE$ is $\Omega(E)$.
  - $\Omega(E)$ varies with E and obeys the relation:

$$\Omega(E) = \left(\frac{\partial \Gamma}{\partial E}\right) dE = \omega(E) dE$$

- $\omega(E)$ is the density of states and is characteristic of the system.
- The sensitivity of $\Omega(E)$ and $\omega(E)$ to the energy E of the system will now be considered.
- It can be shown that $\Omega(E)$ is insensitive to the details of the nature of the energy spectrum in the limit of a large system.
    - This is a characteristic of a macroscopic parameter.
    - $\Omega(E)$ connects the microscopic properties of the system to the macroscopic system.
- ν quantum numbers describe a system of energy E.
- The energy per degree of freedom is:

$$\epsilon = \frac{E}{\nu}$$

- For a perfect gas with $3N$ degrees of freedom:

$$\epsilon_{\text{perfect gas}} = \frac{1}{2} k_B T$$

- In classical mechanics, the total energy is divided among the degrees of freedom such that the average energy per degree of freedom is $\frac{1}{2} k_B T$.
- In quantum mechanics, this is true if $k_B T$ is large relative to the energy spacings, but not when $k_B T$ is small relative to the energy spacings.
    - For real molecules at room temperature, $k_B T$ is often small relative to the spacing of vibrational levels.
- The equipartition of energy ($\epsilon = E/\nu$) will be used as an approximation to further explore the properties of $\Omega(E)$ for an arbitrary system with ν degrees of freedom.

- Consider $\Gamma(E)$, the total number of quantum states with energy less than E.
  - The energy is separable into contributions from ν degrees of freedom.
  - Each of the possible contributions contributes a state to $\Gamma(E)$.
  - E_i is the energy of the ith degree of freedom.
  - $\Gamma(E_i)$ is the number of states of the ith degree of freedom with energy less than E_i.
  - Then $\prod_{i=1}^{\nu} \Gamma_i(E_i)$ is the total number of states with energy less than E for a particular subdivision of energy.
  - For all possible subdivisions of E, the total number of states with energy less than E is:

$$\Gamma(E) = \sum_{E_i} \prod_{i=1}^{\nu} \Gamma_i(E_i)$$

where $E = \sum_i E_i$.

- Note that the summation over E_i is over all possible ways of subdividing the energy that are consistent with the constraint of conservation of energy.
- To estimate $\Gamma(E)$ require that each of the E_i be the average energy ϵ.
  - This is equivalent to choosing the one term in the sum over all the subdivisions of energy that has uniform distribution of energy over all the degrees of freedom.
  - This gives:

$$\Gamma(E) = \prod_{i=1}^{\nu} \Gamma_i(\epsilon) = [\Gamma_1(\epsilon)]^{\nu}$$

- Although crude, this can give an adequate order of magnitude estimate.
- It is assumed that all degrees of freedom are sufficiently alike that the same average behaviour may be ascribed to them.
- Expansion in a Taylor series gives:

$$\Omega(E) = \frac{\partial \Gamma}{\partial E} dE = \frac{\partial}{\partial E} \left\{ [\Gamma_1(\epsilon)]^{\nu} \right\}$$

$$= \nu \Gamma_1^{\nu-1} \frac{\partial \Gamma_1}{\partial(\nu\epsilon)} dE = \Gamma_1^{\nu-1} \frac{\partial \Gamma_1}{\partial \epsilon} dE$$

- $\Gamma_1(\epsilon)$ increases as E increases.
  - Since ν is very large in a macroscopic system, $\Omega(E)$ increases rapidly with E.
  - The rate of increase is evident when $\Omega(E)$ is rewritten as:

$$\ln \Omega(E) = (\nu - 1) \ln \Gamma_1(\epsilon) + \ln \left(\frac{\partial \Gamma_1}{\partial \epsilon} dE \right)$$

  - Recall that dE is much larger than the separation of the energy levels.
  - This means that $\ln \left(\partial \Gamma_1 / \partial \epsilon \right) dE$ is negligible relative to the first term of the expression.
    - Since $\Gamma_1(\epsilon)$ is proportional to ϵ, $(\partial \Gamma_1 / \partial \epsilon)$ is $\Gamma_1(\epsilon)/\epsilon$.

- For simple model systems, $\Gamma_1(\epsilon)$ is proportional to ϵ^{α} where α is small.
  - For a harmonic oscillator, $\alpha = 1$
  - For a particle in a box, $\alpha = 1/2$.
- This means that $\ln\left(\partial\Gamma_1/\partial\epsilon\right)dE$ is a factor of ν smaller than $(\nu - 1)\ln\Gamma_1(\epsilon)$
- The magnitude of $(\nu - 1)\ln\Gamma_1(\epsilon)$ can be estimated.
  - Δ is the average spacing between energy levels.
  - Therefore $\Gamma_1(\epsilon)$ is of the order of ϵ/Δ and

$$\ln\Omega(E) = \nu\ln\Gamma_1(\epsilon)$$

  - This means that Ω is of order magnitude of ν or better for E well above the ground state.

The Influence of Constraints on the Density of States

- The role of constraints in defining the density of states $\omega(E)$ or the number of states $\Omega(E)$ between E and $E + dE$ is now examined.
- Consider a perfect gas, described as N particles in a cubical box of volume $V = a^3$
  - The wave function for a single particle in a cubical box is:

    $$\Psi_j = A \sin \frac{n_{jx}\pi x}{a} \sin \frac{n_{jy}\pi y}{a} \sin \frac{n_{jx}\pi z}{a}$$

    for $0 < x < a$, $0 < y < a$,$0 < z < a$, where
    - $j = 1, \ldots, N$ labels the particles,
    - A is the normalization constant.

- The quantum numbers n_{jx}, n_{jy}, n_{jz} satisfy:

$$n_{jx}^2 + n_{jy}^2 + n_{jz}^2 = \frac{2m\epsilon_j}{\pi^2\hbar^2}a^2$$

  where ϵ_j is the energy of particle j.
    - The values of n_{jx}, n_{jy}, n_{jz} are positive.
- The total energy of N particles is:

$$E = \sum_{j=1}^{N} \epsilon_j$$

- This may be rewritten as:

$$\sum_{j=1}^{N}(n_{jx}^2 + n_{jy}^2 + n_{jz}^2) = \frac{2mE}{\pi^2\hbar^2}a^2$$

- The total number of states with energy below E can be determined by the number of states with integer coordinates lying within the $3N$ dimensional hyperspherical surface with radius R_s of $(2mEa^2/\pi^2\hbar^2)^{1/2}$
  - The dimensionality of $3N$ comes from the allowed values of the quantum numbers n_{jl} where $j = 1, \dots, N$ and $l = x, y, z$.
- When the box is large, the spacing between energy levels is small and the volume enclosed by the hyperspherical surface is:

$$\frac{\pi^{3N/2}}{(3N/2)!} R_s^{3N} = \frac{\pi^{3N/2}}{(3N/2)!} \left(\frac{2mEa^2}{\pi^2\hbar^2} \right)^{3N/2}$$

- Since only positive values of n_{jl} are allowed, the volume of interest is the positive orthant which is $(\frac{1}{2})^{3N}$ of the total volume. Therefore:

$$\Gamma(E) = \frac{1}{(3N/2)!}\left(\frac{mEa^2}{2\pi\hbar^2}\right)^{3N/2}$$

- The number of states between E and $E + dE$ is:

$$\Omega(E) = \left[\frac{\partial\Gamma(E)}{\partial E}\right] dE = \frac{E^{3N/2-1}}{((3N/2)-1)!}\left(\frac{ma^2}{2\pi\hbar^2}\right)^{3N/2} dE$$

- Therefore, the density of states is:

$$\omega(E) = \frac{E^{3N/2-1}}{((3N/2)-1)!}\left(\frac{ma^2}{2\pi\hbar^2}\right)^{3N/2}$$

- Note that $(a^2)^{3N/2}$ is V^N and it is the boundary condition that defines the energy spectrum.
- In more general cases, other macroscopic variables (besides V) can affect the energy spectrum.
- Consider a macroscopic system described by the set of variable:

  $$y_1 = \alpha_1, y_2 = \alpha_2, \ldots, y_n = \alpha_n$$

  - There exists a corresponding dependence of the energy level spectrum on these variables.
- In this case, the number of states between E and $E + dE$ is:

  $$\Omega = \Omega(E, y_1, y_2, \ldots, y_n)$$

  when y_i is between y_i and $y_i + dy_i$

- If a constraint is removed, then the number of states is increased:

$$\Omega(E, y_1, y_2, \ldots, y_{n-1}) > \Omega(E, y_1, y_2, \ldots, y_n)$$

- In most physical processes, constraints are altered instead of being removed.
  - How does $\Omega(E, y)$ change in such cases?
  - Consider N particles in a box. The constraint is the volume of the box.
  - By definition, relaxation of a constraint always leads to:

$$\Omega_f(E, y) > \Omega_i(E, y)$$

  - Consider an isolated system at equilibrium with a particular set of constraints.
    - This system has Ω_i equally accessible states.

- Some constraints are removed or relaxed by an external change involving no work.
- The new system thus created has Ω_f equally accessible states.
- Therefore:

$$\Omega_f \geq \Omega_i$$

  .
- Consider an ensemble of systems that are in equilibrium with the constraints.
    - All Ω_i accessible states are equally probable.
- Let one constraint be relaxed or removed.
    - At the instant that the constraint is changed, the system is still in one of the Ω_i states.

- The system is not at equilibrium.
- The approach to equilibrium requires that the Ω_f states be occupied with equal probability.
- The system changes until a new equilibrium is achieved, consistent with the remaining constraints.
- Now consider the case in which an additional constraint is imposed.
- The system cannot go to an equilibrium consistent with these constraints unless work is done on the system.
- Consider the particle in a box model of the perfect gas.
- As shown in Figure 15.2(a), the gas occupies half the volume of an isolated system.
  - The system is separated into two equal volumes with the other half of the system is evacuated.

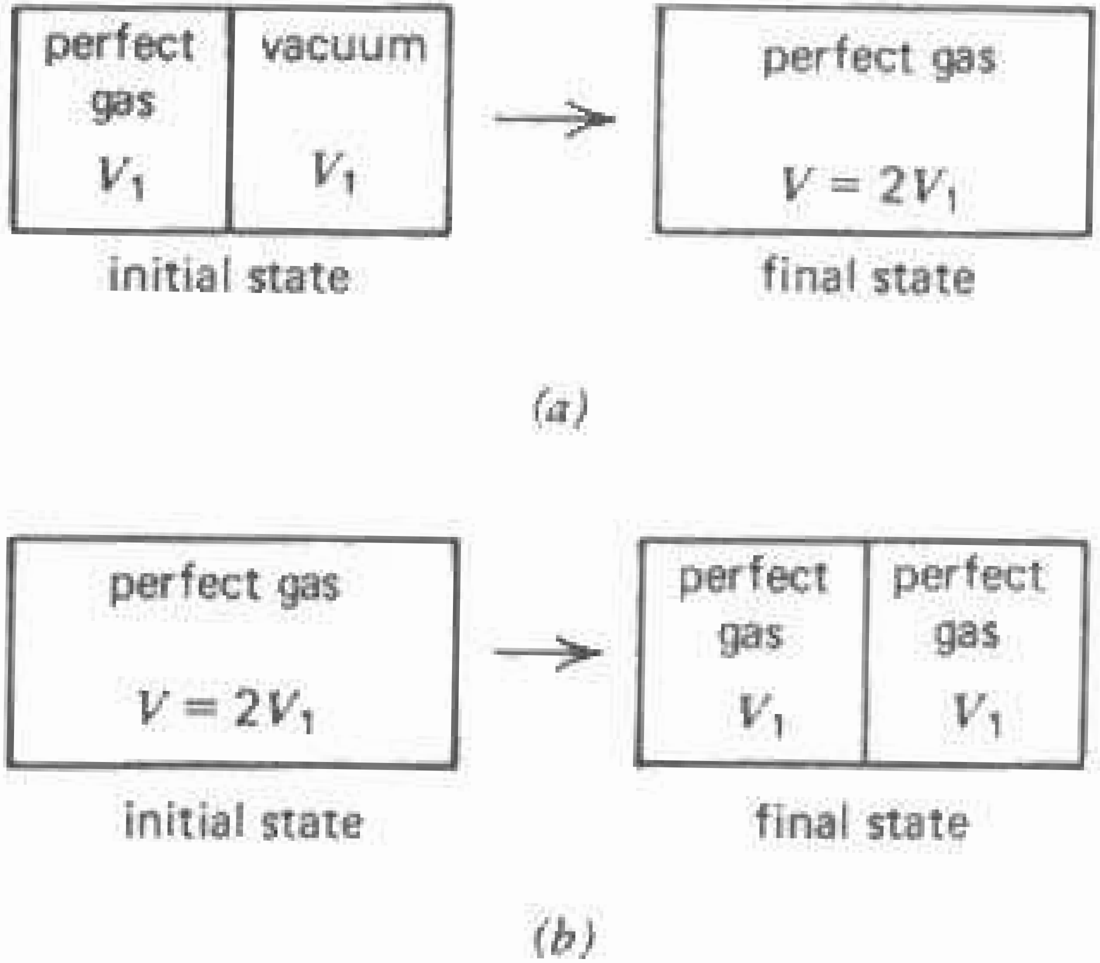

Figure 15.2 Schematic illustration demonstrating that restoration of a previously relaxed constraint without execution of work does not regenerate the initial state of the system.

- The barrier is removed by the expenditure of a negligibly small amount of work.
- The gas expands to fill the entire volume $V = 2V_i$.
- For this process:

$$\Omega_f \geq \Omega_i$$

- Now consider reinsertion of the barrier.
- The system does not return spontaneously to its initial state.
- In this case the relationship between Ω_f and Ω_i is not the inverse foe the previous case.
- Recall:

$$\Omega = \left[\frac{\partial \Gamma(E)}{\partial E}\right] dE = \frac{E^{3N/2-1}}{((3N/2)-1)!}\left(\frac{ma^2}{2\pi\hbar^2}\right)^{3N/2} dE$$

- Therefore

$$\Omega(E, V, N) = CV^N \left(\frac{E}{N}\right)^{3N/2} dE$$

  where C is a constant independent of E and V.
- This was derived using the Stirling Approximation.

$$N! \approx N^N \exp(-N)$$

- For the initial state for 15.2b, the particles are anywhere within volume V.
- For the final state for 15.2, $N/2$ particles are in each of the two subvolumes $V/2$.
- The energy per particle has not changed in this process.

- There are $[N!/(N/2)!(N/2)!]$ ways that $N/2$ particles can each be placed in the subvolumes.
- Therefore:

$$\Omega_f(E,V,N) =$$

$$C\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}\left(\frac{V}{2}\right)^{N/2}\left(\frac{E/2}{N/2}\right)^{3N/4}\left(\frac{V}{2}\right)^{N/2}\left(\frac{E/2}{N/2}\right)^{3N/4} dE$$

$$= CV^N\left(\frac{E}{N}\right)^{3N/2} dE$$

- This means that $\Omega_f = \Omega_i$ and the insertion of the barrier has not changed the system.
- To restore the system to the initial state given in 15.2a, the gas must be removed from one of the compartments.
  - Compress the gas into a subvolume by a sliding wall.

- This would involve energy being put into the system as work and would result in a temperature change.
- There is no way to get back to the original state of 15.2a without transferring work or heat across the boundary of the system.
- Once the barrier is removed and the molecules distribute themselves over the Ω_f states, the reimposition of the boundary condition does not cause the system to spontaneously return to the initial state.
    - This is an irreversible process.
- The groundwork has now been laid for the comparison of statistical mechanical and the thermodynamic descriptions of a spontaneous process.
- Consider a process in an isolated system that takes the system from an initial to a final state.

- If this final state is such that the imposition or relaxation of constraints without the requirement of external work cannot recreate the initial state, the process is irreversible.
- If the imposition or relaxation of constraints without external work recreates the initial state, the process is reversible.
- For processes at constant energy and constant volume.
  - If some of the constraints defining an isolated system are relaxed, $\Omega_f \geq \Omega_i$
  - If $\Omega_f = \Omega_i$, the systems of the ensemble are distributed over the same accessible states before and after the constraint is relaxed.
  - The system is in equilibrium at all steps of the process and the transition $i \rightarrow f$ is reversible.

- If $\Omega_f > \Omega_i$, the transition $i \rightarrow f$ is irreversible.
- In Chapter 13, a reversible process was defined in terms of intensive variables being continuous across the boundary of the system.
  - This involves the system being in contact with some reservoirs.
  - How is a reversible process defined for an isolated system, which by definition is not in contact with any reservoirs?
- Consider the system illustrated in Figure 13.3.
  - The system is subdivided into two subsystems, separated by a movable piston upon which weights rest confining subsystem 1.
  - The weights can be moved by a pulley arrangement between the piston and a ledge at the same height.

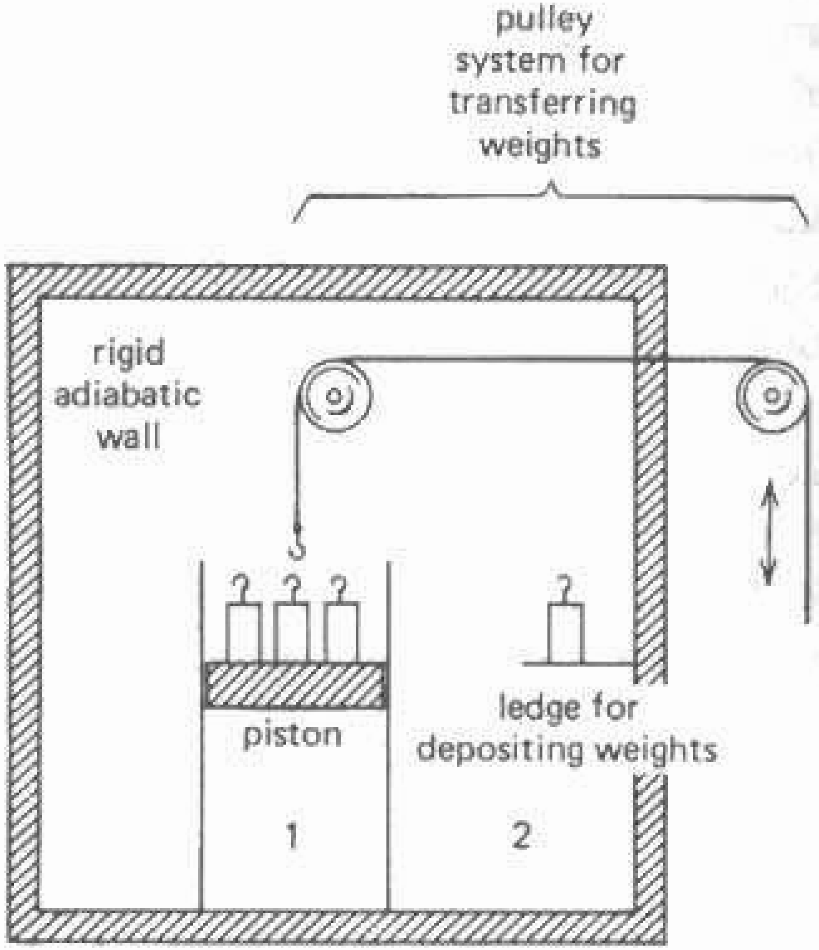

Figure 15.3 Schematic illustration of how a reversible process in an isolated system can be made to occur.

- Therefore moving the weight involves no net work.
- The pulley arrangement is therefore a device to change constraints inside an otherwise isolated system.
- If the weights are infinitesimally small, the pressure will be continuous across the piston as subsystem 1 expands and subsystem 2 is compressed.
    - Subsystem 2 may be considered the surroundings of subsystem 1.
- The thermodynamic definition of a reversible process requires that every point on the path be infinitesimally close to an equilibrium state of the system.
    - At every point along the path, the relevant intensive variables are continuous across the boundary of the system.

- Therefore the extensive variables of the system must also be infinitesimally close in value in two states that are infinitesimally close.
- This is equivalent to $\Omega_f = \Omega_i$ since the extensive variables usually describe the constraints or boundary conditions defining Ω.

The Entropy: A Potential Function for the Equilibrium State

- Consider the properties of the number of accessible states for a composite system.
  - The total energy may be distributed over parts of the system.
  - The most probable distribution of the total energy over the system will be shown to be equivalent to systems in equilibrium having equal temperatures.

- This will be the basis of the definition of entropy.
  - It will be shown that it is related to work and internal energy.
  - Entropy may be considered as providing a relationship between microscopic and macroscopic descriptions of the system.
- Consider two macroscopic systems, A and B with energies E_A and E_B respectively.
- Let $\Omega_A(E_A)$ and $\Omega_B(E_B)$ be the number of states between E_A and $E_A + dE_A$ and between E_B and $E_B + dE_B$ respectively.
- N_A and N_B are the numbers of A and B molecules and are fixed.
- The ensemble is specified by the requirement that $E_T = E_A + E_B$ is constant.

- The ensemble consists of pairs of systems, with the replicas having different distributions of E_T between A and B.
- The volumes V_A and V_B are independently varied as are any other constraints.
- The ensemble is defined by the value of E_T.
- If system A of a replica pair has energy E_A, then system B has an energy of $E_T - E_A$.
- When system A has energy E_A it can be in any one $\Omega_A(E_A)$ equally likely state while system B can simultaneously be in any one of $\Omega_B(E_T - E_B)$ states.
- Every possible state of A can be combined with every possible state of B, so the total number of states is:

$$\Omega_T(E_T, E_A) = \Omega_A(E_A)\Omega_B(E_T - E_B)$$

- Since E_T is constant, $\Omega(E_T, E_A)$ is a function of E_A.
- Now consider the contribution to $\Omega_T(E_A) = \Omega_T(E_T, E_A)$ from different subdivisions of E_T between A and B.
- The probability of finding $A + B$ with the energy of A between E_A and $E_A + dE_A$ is:

$$\frac{\Omega_T(E_A)}{\sum_{E_A} \Omega_T(E_A)}$$

  where $\Omega_T(E_A)$ is the total number of states accessible to the total system for a given E_A taken over all possible values of E_A.
- Let

$$\sum_{E_A} \Omega_T(E_A) \equiv C^{-1}$$

- Therefore the probability of finding $A + B$ in a state with energy between E_A and $E_A + dE_A$ is:

$$P(E_A) = C\Omega_A(E_A)\Omega_B(E_T - E_B)$$

- As E_A increases, $\Gamma_A(E_A)$ increases but $\Gamma_B(E_T - E_A)$ decreases.
- However $P(E_A$ has a maximum at some E_A^*.
  - Because $\Gamma_A(E_A)$ and $\Gamma_B(E_T - E_A)$ are rapidly varying functions, the maximum will be sharp.
- If Γ_A and Γ_B are treated as continuous functions, then the maximum may be found by differentiation:

$$\left(\frac{\partial P(E_A)}{\partial E_A}\right)_{V,N} = 0 \qquad \text{and}$$

$$C\Omega_B(E_T - E_B)\left(\frac{\partial \Omega_A}{\partial E_A}\right) + C\Omega_A(E_A)\left(\frac{\partial \Omega_B}{\partial E_A}\right) = 0$$

- Dividing by $P(E_A)$ and using $E_A = E_T - E_B$,

$$\left(\frac{\partial \ln \Omega_A}{\partial E_A}\right)_{V,N} = \left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)_{V,N}$$

- Define

$$\beta = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}$$

- Therefore $\beta_A = \beta_B$ (which has the same properties as temperature).
  - It can be shown that $\beta = (k_B T)^{-1}$.
  - By definition $S = k_B \ln \Omega$ where S is entropy.

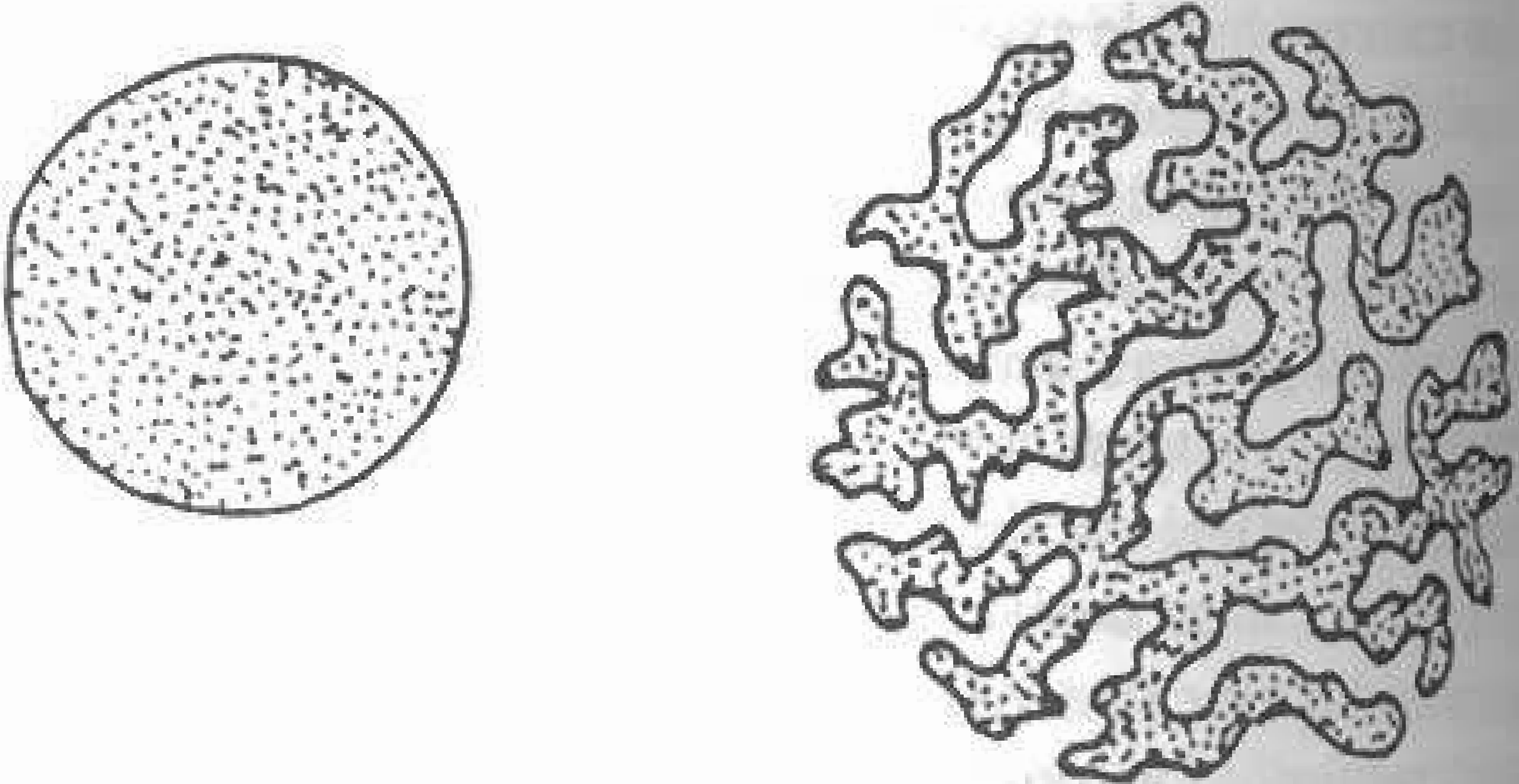

Figure 15.4 Spreading of a volume element in phase space when the dynamics is mixing.

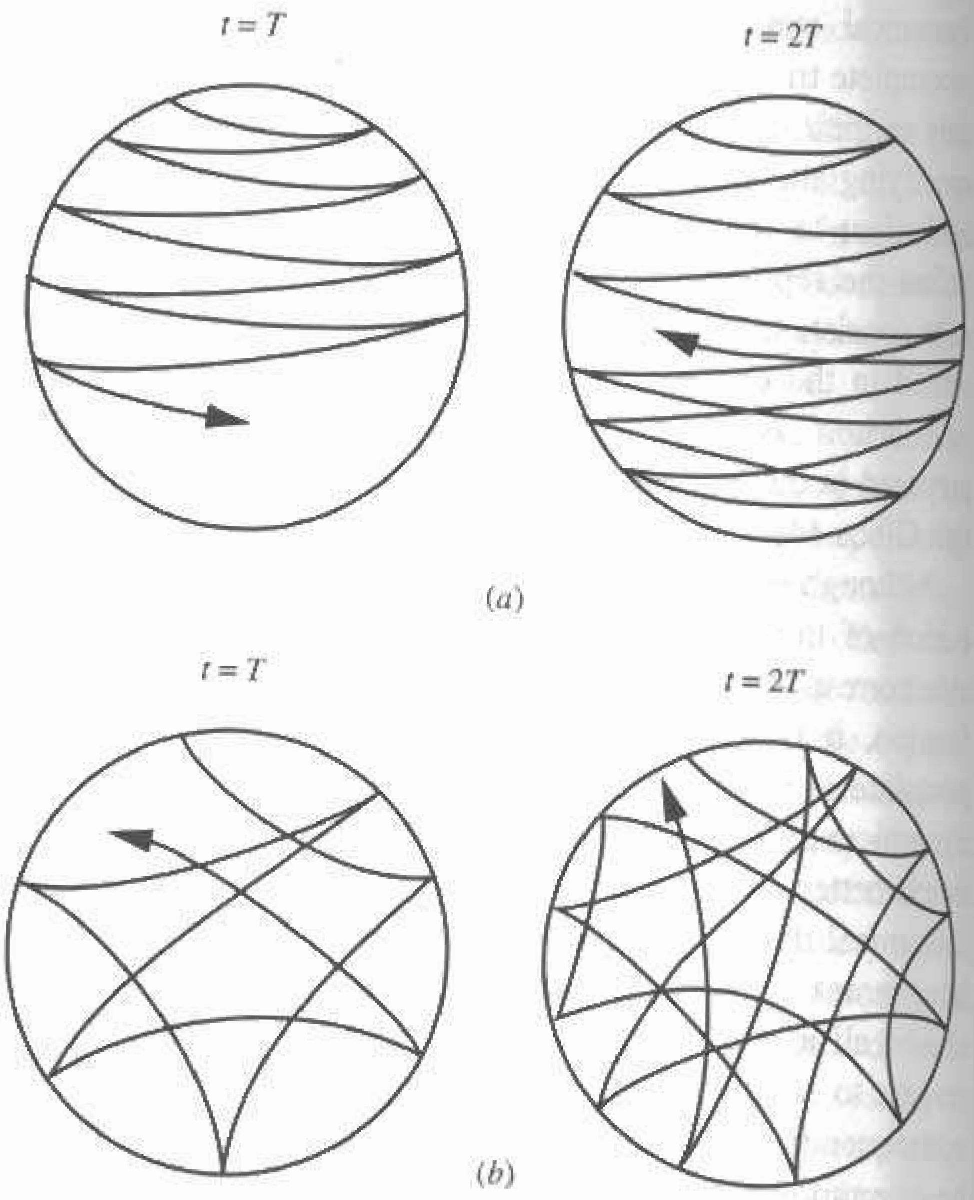

Figure 15.5 Schematic representation of the way the energy surface is covered by a trajectory when (*a*) the dynamics is ergodic and (*b*) the dynamics is mixing.

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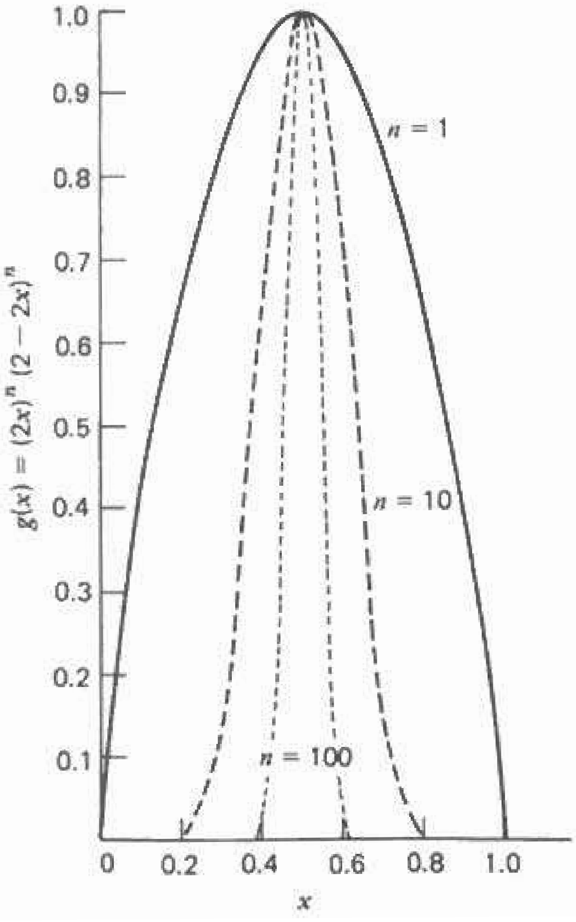
[17] We can illustrate how a sharp maximum develops in the function $P(E_A)$ by examining the simpler function $[4x(1-x)]^n$ in the range $0 \le x \le 1$. This function is the product of two factors, $(2x)^n$ and $(2-2x)^n$, which respectively increase and decrease over this range, thus corresponding to our Ω_A and Ω_B. Clearly, as n increases (corresponding to increasing the number of available states in our model), the increase and decrease of the two factors become steeper and steeper. Whatever the value of n, however, the product of these factors has a maximum value of unity at $x = \frac{1}{2}$. The peak of this function becomes steadily narrower as n increases, sharpening to an infinitely narrow spike in the limit $n \to \infty$. This behavior is illustrated in the accompanying graph.



Entropy: A Summary

- A statement of the Second Law of Thermodynamics is: “The Entropy of the Universe is increasing.”
- More formal statements include:
  - Clausius: It is impossible to devise a continuously cycling engine that transfers heat from a colder to a hotter body without doing work on the system.
  - Kelvin: It is impossible to devise a continuously cycling engine that produces no effect other than the extraction of heat from a reservoir at one temperature and the performance of an equal amount of mechanical work.
  - Caratheodory: In the neighbourhood of every equilibrium state of a closed system, there are states that cannot be reached from the first state along any adiabatic path by any spontaneous process or reversible limit of a spontaneous process.

- This means that reversible adiabats do not cross each other. (Neither do reversible isotherms.)
- The Second Law gives the condition for spontaneity of a process.
    - Spontaneous processes maximize entropy.
- In Chapter 15, entropy may be defined as:

$$S = k_B \ln \Omega$$

- Entropy may also be defined as:

$$dS = \frac{\text{đ}q_{rev}}{T}$$

- Recall that $dU = \text{đ}q + \text{đ}w$ or $\Delta U = q + w$.

- Entropy is a state function, so if the path of the process is not convenient for the calculation of the change in entropy, a convenient alternate path may be selected.
  - Any two points in pV space may be joined by a combination of up to two of the following:
    - A reversible adiabat
    - A reversible isotherm
    - A reversible isobar
    - A reversible isochor

Calculation of entropy on various paths.

- Reversible adiabat

$$đq_{rev} = 0; \quad \frac{đq_{rev}}{T} = 0; \quad dS = 0$$

- Reversible isotherm

$$đq_{rev} = dU - đw; \quad dS = \frac{dU + pdV}{T}$$

- Reversible isobar

$$đq_{rev} = C_p dT; \quad dS = \frac{C_p}{T} dT$$

- Reversible isochore

$$đq_{rev} = C_V dT; \quad dS = \frac{C_V}{T} dT$$

- The change in internal energy may be expressed in terms of entropy: $dU = TdS - pdV$ where T and S are a conjugate pair of variables. (We have previously encountered p and V as a conjugate pair).

- This equation is also known as the master equation of thermodynamics.

Thermodynamic Potentials

- There are four thermodynamic potentials:
  - U internal energy
  - H enthalpy
  - A Helmholtz free energy
  - G Gibbs free energy
- They are related through the pairs of conjugate variables.
  - $H = U + PV$; $dH = dU + pdV + Vdp = TdS + Vdp$
  - $A = U - TS$;
    $dA = dU - TdS - SdT = -SdT - pdV$
  - $G = U - TS + PV$;
    $dG = dU - TdS - SdT + pdV + Vdp = -SdT + Vdp$

- U, H, A, and G are also known as Legendre transforms.

Thermodynamic Potentials as State Functions

- State functions have exact differentials
  - This means that cross derivatives are equal
  - Consider U.

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)$$

  - But $dU = TdS - pdV$. Therefore:

$$\left(\frac{\partial U}{\partial S}\right)_V = T; \left(\frac{\partial U}{\partial V}\right)_S = -p$$

- and

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

- Similarly from the expressions for dH, dA, and dG may be shown respectively:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

- These are known as the Maxwell relations.

The Third Law

- A popular statement of the Third Law of Thermodynamics is:
  "It is impossible to reach absolute zero."
- More formal statements include:
  - In any system in internal equilibrium undergoing an isothermal process between two states, the entropy change of the process approaches zero as the temperature of the system approaches zero.
  - The entropy of any system vanishes in the state for which

$$T = \left(\frac{\partial U}{\partial S} \right)_V = 0$$

Recommended Reading

- The rest of Chapter 15
- In Chapter 16
  - Section 16.1 about statements of the Second Law
  - Section 16.2 about reversible processes and cycles
  - Section 16.3
  - Section 16.4 about the Carnot cycle.
- In Chapter 17
  - Section 17.1 about H, A and G.
  - Section 17.3 and 17.4 about calculating ΔS for reversible and irreversible processes.

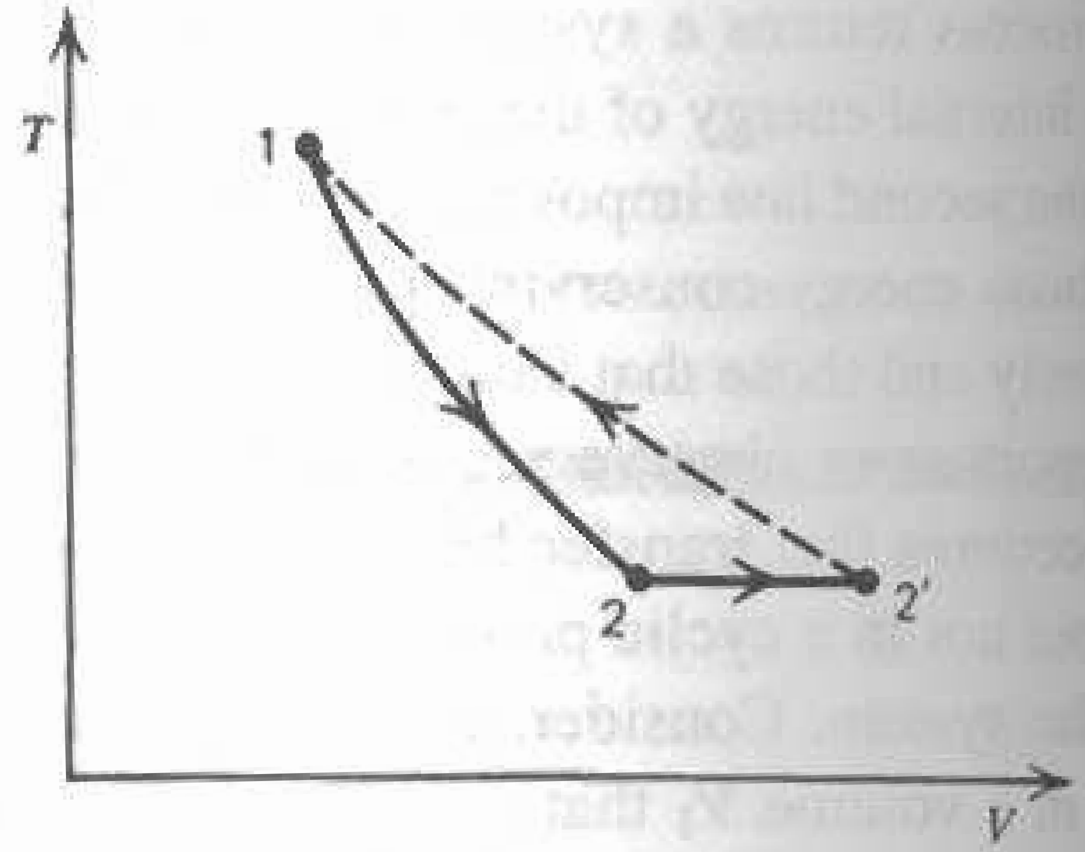


Figure 16.1 Existence of an entropy function for reversible processes: If 1 → 2 by a reversible adiabatic process, and 2 → 2′ by a reversible isothermal process, the path 2′ → 1 cannot be a reversible adiabatic path (see text).