

Some Comments about Thermodynamics

- Thermodynamics deals with relationships among the macroscopic properties of matter.
 - Equilibrium thermodynamics deals with relationships among macroscopic properties of matters at equilibrium.
- The laws of thermodynamics allow these relationships to be derived.
- The laws of thermodynamics are postulates.
 - These postulates conform with our observations of the world.
 - These postulates apply to systems containing a large number of molecules, i.e. a macroscopic system.

- Thermodynamics also permits us to interpret spontaneous processes.
 - Also aids in the understanding of “time’s arrow” and irreversible processes.
- The laws of thermodynamics make no assumptions about the microscopic structure of matter.
- The laws of thermodynamics allow the construction of a logically complete and internally self consistent theory.
 - The properties of real matter appear in the theory, but thermodynamics is only concerned about the relationships among these quantities.
 - These properties of real matter have the values that they do because of the microscopic interactions of the molecules.

- For example, the pressure of a gas may be given as a virial equation (or power series) in n , the number density:

$$P = a_0 + a_1n + a_2n^2 + a_3n^3 + \dots$$

where a_i are experimentally determined.

- From thermodynamics, relationships between pressure and other thermodynamic quantities such as internal energy, entropy, enthalpy, and free energy are known.
 - Thus these quantities may be determined in terms of the values of a_i .
 - The values of a_i depend on the interactions of the molecules.
 - If the molecular interaction potential is known, then a_i may be determined using the methods of statistical mechanics.

- Continued:
 - In principle, the interaction potential can be determined from quantum mechanics.
- The development of the principles of thermodynamics depends on some basic concepts.
- One of these basic concepts is the system.
 - A system is that part of the world under consideration.
 - Everything else is the surroundings.
- Systems may be classified according to their relationship to the surroundings.
 - An open system can exchange matter and energy with the surroundings.
 - A closed system can exchange energy but not matter with the surroundings.

- Continued:
 - An isolated system exchanges neither energy nor matter with the surroundings.
- A thermodynamic system is described by a set of macroscopic variables or “coordinates”.
 - p , V , and T are already familiar.
- These macroscopic variables apply to measurements made for large number of molecules over a time period sufficiently long for many interactions of the molecules and at energies larger than individual quanta.
- The thermodynamic properties of the system can be completely describe by the set of macroscopic coordinates (p, V, T) .

- A macroscopic coordinate can be a constraint on the system when it is fixed in value by the boundary conditions that define the system.
 - A system can have constraints other than macroscopic coordinates.
- Classical thermodynamics deals with the properties of a system at equilibrium.
 - At equilibrium, none of the macroscopic coordinates changes with time.
- At equilibrium there is no net energy or matter flow through the system.
- The condition of equilibrium depends upon the constraints on the system.
 - For a specified set of constraints, there is only one true equilibrium state.

- Metastable states can be observed not to change during the time of observation.
 - This is because the process that would take the system to equilibrium is so slow relative to the time of observation.
 - Nonequilibrium thermodynamics is a growing field.
- A complete set of thermodynamic coordinates uniquely determines the thermodynamic state.
 - If the mass is known, a complete set of thermodynamic coordinates is made up of those variables that can be independently specified.
 - For a one component system of fixed mass, two thermodynamic coordinates are needed.
 - For comparison, a microscopic system of N particles would need $6N - 6$ microscopic coordinates.

- The number of thermodynamic coordinates needed varies with the number of components and the number of phases in the system.
- Consider a fluid which assumes the shape of its container such as a liquid or a gas.
- The properties of a fluid are independent of its shape.
- For a pure fluid (i.e. only one component) the thermodynamic state can be completely specified by just pressure and volume.
- This means that any additional thermodynamic coordinates cannot be independent of the pressure and volume.
 - The relationship among pressure, volume, and thermodynamic coordinate X (or T) is the equation of state: $f(p, V, X) = 0$.

- The definition of the thermodynamic coordinate of temperature will be developed only in terms of those variables required to define the state of thermodynamic system, i.e. p and V or related quantities.
 - Temperature θ may be defined by an equation of the form:

$$f(p, \rho, \theta) = 0$$

where ρ is the density.

- Note that density is related to the volume, but is intensive rather than extensive.
- What properties should θ have?
 - Mathematically convenient and well-behaved in that it is finite, continuous, and single-valued.
 - Have some relationship to intuitive notions of temperature.

- Many mathematical functions satisfy these conditions such as

$$\theta = p/\rho$$

$$\theta = (p/\rho)^2$$

$$\theta = \log (p/\rho)$$

or multiples thereof.

- To select an appropriate function, express this as a generality:

$$g(\theta) = \varphi(p, \rho)$$

- Now some concepts about temperature scales must be considered.
- Consider systems 1 and 2.
 - The systems consists of the same pure fluid.

- Continued:
 - Initially, the systems are isolated from each other and are separately at equilibrium at different temperatures, i.e.

$$\varphi(p_1, \rho_1) \neq \varphi(p_2, \rho_2)$$

- The two systems are brought together so that they are isolated from the surroundings, but separated from each other by a rigid barrier B .
- B is an adiabatic wall if the systems do not change from their initial states.
 - An adiabatic wall does not allow energy to cross.
 - Isolated systems are surrounded by adiabatic walls.
- Suppose barrier B is rigid (so no work is done), but does allow energy to cross, i.e. it is diathermal.

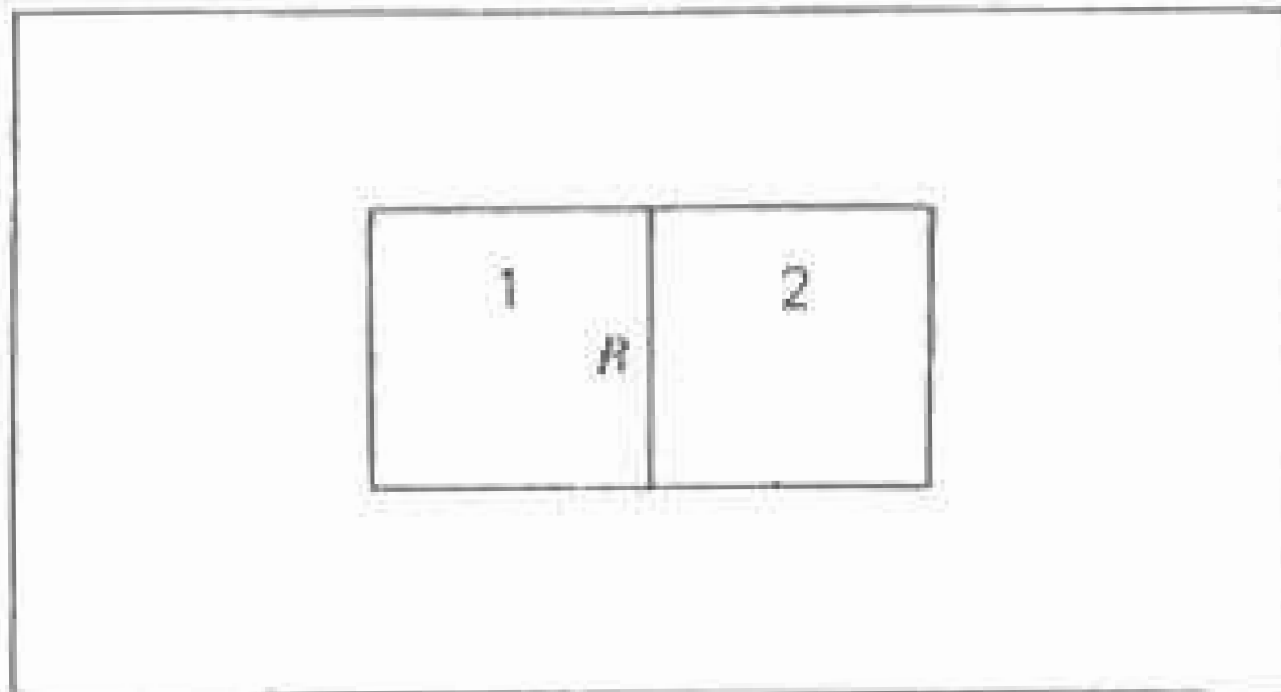


Figure 12.5 The two systems labeled 1 and 2 are separated by a rigid wall B . Both systems are isolated from the remainder of the universe.

- The two systems will equilibrate to the same temperature, i.e. they will come into thermal equilibrium eventually.
- If the original isolated systems are separately in equilibrium, the constraint of isolation defines the equilibrium.
- If the constraint is altered, in this case by replacing the adiabatic wall with a diathermal wall, the system will move to a new equilibrium.
- If two systems have reached thermal equilibrium with each other, the state of one system cannot be changed without changing the other.
 - The overall equilibrium is described by a single relationship of the independent thermodynamics coordinates of each system: $F_{12}(p_1, \rho_1, p_2, \rho_2) = 0$

- Continued:
 - The exact form of F_{12} depends on the nature of the fluids making up the systems and their individual equations of states.

The Zeroth Law of Thermodynamics

- Two systems, each separately in thermal equilibrium with a third system, are in thermal equilibrium with each other.
 - The third system is a thermometer.
 - This allows us to develop a universal definition of temperature.
 - This definition will be in terms of some property possessed by all objects “at the same temperature”.

- Consider fluids 1, 2, and 3, each described by their only independent variables, p and ρ .
- Fluids 1 and 2 are in mutual equilibrium and are described by:

$$F_{12}(p_1, \rho_1, p_2, \rho_2) = 0$$

- Fluids 1 and 3 are in mutual equilibrium and are described by:

$$F_{13}(p_1, \rho_1, p_3, \rho_3) = 0$$

- Both equations may be solved for p_1 yielding functions w_{12} and w_{13} :

$$p_1 = w_{12}(\rho_1, p_2, \rho_2) \text{ and } p_1 = w_{13}(\rho_1, p_3, \rho_3)$$

- Therefore: $w_{12}(\rho_1, p_2, \rho_2) = w_{13}(\rho_1, p_3, \rho_3)$.

- But the Zeroth Law requires that if systems 1 and 2 are in thermal equilibrium and system 2 and 3 are in thermal equilibrium, then systems 1 and 3 are in thermal equilibrium.

- Therefore there must exist some F_{23} such that:

$$F_{23}(p_2, \rho_2, p_3, \rho_3) = 0$$

which completely describes the equilibrium between systems 2 and 3.

- If this equation and $w_{12}(\rho_1, p_2, \rho_2) = w_{13}(\rho_1, p_3, \rho_3)$ is true, then the variable ρ_1 must disappear from w_{12} and w_{13} .
 - Therefore $w_2(p_2, \rho_2) = w_3(p_3, \rho_3)$, i.e. w_i depends only on the properties of system i .
 - Thus: $w_1(p_1, \rho_1) = w_2(p_2, \rho_2) = w_3(p_3, \rho_3)$

- Given the Zeroth Law, there exists a set of functions w_i which depend only on the state of fluid i and which have the same value of any number of fluids in equilibrium.
 - w_i must depend on some single property that all i systems have in equilibrium, regardless of the nature of the systems.
 - This single property is the thermodynamic temperature.
 - $w_i(p_i, \rho_i)$ is equivalent to $\varphi(p, \rho)$.
 - This means that $g(\theta)$ may be defined in terms of a property that all systems in thermal equilibrium have in common.
 - Thus a universal temperature scale may be constructed.

- Consider a particular system as the standard.
- Select one of the system's temperature functions, $g(\theta)$.
- Define a numerical value of $g(\theta)$ as the temperature θ .
- This standard system is the thermometer.
- The function used to define the system is the thermometric property.

The Perfect Gas Temperature Scale

- How does this all relate to a usable temperature scale?
- Any property of a system that is “well-behaved” can be used to define the temperature scale.
 - The choice is arbitrary and is based on convenience.

- Since the choice of thermic properties is arbitrary, it is convenient that significant changes in the property can be measured accurately in small systems, i.e. the thermometer can come into equilibrium with the system without significantly changing the system.
 - Many thermometers are based on the volume of a liquid.
 - The expansion of the liquid is measured in a narrow tube attached to a reservoir.
 - Some thermometers are based on electrical resistance.
 - Thermocouples are based on the differential properties of bimetal strip as measured by electromotive force at the junction.

- Continued:
 - Pyrometers measure the intensity of radiation.
 - It is assumed that the emitted radiation follows the blackbody distribution.
- All of these are calibrated against a thermodynamic temperature scale.
- A thermodynamic temperature scale can be based on the properties of a very dilute gas.
 - Pressure and volume (or density) are easily measured.
 - The scale can be defined as proportional to the pressure or proportional to the volume.
 - Both thermometers (constant volume or constant pressure) converge to the same low pressure limit.

- The temperature scale needs a reference point.
 - The triple point of water is such a reference point.
 - Solid, liquid, and vapour coexist at a unique point in p , ρ , and temperature.
 - Consider a system in equilibrium with pure water at the triple point.
 - This system has pressure p_3 and temperature θ_3 .
 - A constant volume temperature scale may be defined for this system in other conditions.

$$\theta(p) = \frac{p}{p_3} \theta_3$$

- θ_3 is an arbitrary constant. By convention, θ_3 is 273.16 K.

- A constant pressure scale may also be defined with respect to the triple point.

$$\theta(V) = \frac{V}{V_3} \theta_3$$

- The actual empirical scales depend on the quantity and nature of the gas.
- In the limit of small quantity, both scales approach the same limiting temperature:

$$\lim_{p \rightarrow 0} \theta(p) = \lim_{V \rightarrow \infty} \theta(V) = \theta^*$$

- θ^* is the perfect gas temperature.

- Thermometers are calibrated with respect easily reproduced phase equilibria.
- Both the constant volume and the constant pressure temperature scales converge to the same limiting value.
 - This may be expressed as:

$$\lim_{p \rightarrow 0} \frac{pV}{n} = \beta \theta^*$$

where $\beta(\theta^*)$ is a function only of θ^*

- Limits at two different temperatures are proportional to the perfect gas temperature.

$$\frac{\beta(\theta_1^*)}{\beta(\theta_2^*)} = \frac{\theta_1^*}{\theta_2^*}$$

- Temperature scales had formerly been defined in terms of two fixed points.
 - The Celsius scale had been defined in terms of the freezing and boiling points of water at a pressure of 1 atm.
 - The Fahrenheit scale had been defined in terms of the freezing point of a saturated NaCl solution and the boiling point of pure water at a pressure of 1 atm.
- These scales can be related to the perfect gas scale.
 - For a constant volume thermometer, the Celsius temperature t^* may be defined by:

$$t^* = \lim_{p_0 \rightarrow 0} \frac{100(p - p_0)}{p_{100} - p_0}$$

- This can be related to the absolute temperature, θ^* by:

$$\theta^* = t^* + \theta_0^*$$

where θ_0^* is the ice-point temperature, 273.15 K.

- The triple point temperature θ_3^* is by definition 273.16 K.
 - As a result the boiling point of water is 373.146 K.
(This supersedes the previous definition of Celsius temperature.)
- There are other ways to establish thermodynamic temperature scales that do not depend on the properties of a substance.
 - It can be shown that these scales are equivalent to the perfect gas scale.

- T will be used to represent the perfect gas temperature.
 - The thermodynamic temperature T is equal to the perfect gas temperature θ .

Pressure Units

- The SI unit is the Pascal. $1 \text{ Pa} = 1 \text{ N m}^{-2}$.
- Other units are:
 - In cgs (centimeter gram second), $1 \text{ dyne cm}^{-2} = 0.1 \text{ Pa}$.
 - Common in meteorology is the bar, $1 \text{ bar} = 10^5 \text{ Pa}$.
 - Widely used is atm. By definition, $1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$.
 - The torr is defined as $1/760 \text{ atm}$ or 1 mmHg .

- The perfect gas equation of state is:

$$pV = nRT$$

where n is number of moles of gas in volume V .

- The universal gas constant is evaluated by:

$$R = \lim_{p \rightarrow 0} \frac{pV}{nT}$$

- R is related to the Boltzmann constant k_B :

$$k_B = \frac{R}{N_A}$$

where N_A is Avogadro's number.

- The perfect gas equation of state may be written:

$$pV = Nk_B T$$

where N is the number of molecules in volume V .

- Molar mass, M , may be determined by measuring p , ρ , and T

$$M = RT \lim_{p \rightarrow 0} \frac{\rho}{p}$$

Microscopic and Macroscopic Approaches

- What are the essential features of each?
- What is general and what is specific to each approach?
- How are the two approaches to a perfect gas related?

The microscopic approach to the perfect gas

- The perfect gas is defined entirely in terms of the properties of the individual molecules that make up the gas.
- Already considered has been the case of monoatomic molecules which collide elastically with the walls.
 - What about polyatomic molecules?
 - What about molecules that interact with one another?
 - Statistical mechanics involves the adoption of a model of the molecular interactions.
 - Thus the results are specific to that model.

The macroscopic (or thermodynamic) approach to the perfect gas

- This is based on the properties of real gas in the limit of low pressure.
- No assumptions are necessary about the nature of the interactions of molecules with each other.
- This thermodynamic approach is tied directly to experiment.

How are the two approaches related?

- The microscopic approach and kinetic theory leads to

$$p = \frac{2}{3} \frac{U}{V}$$

where U is the total kinetic energy.

- The macroscopic approach involves only measurable variables:

$$p = \frac{nRT}{V}$$

- Combining these gives:

$$U = \frac{3}{2}nRT = \frac{3}{2}Nk_B T$$

and the molecular kinetic energy per mole is proportional to absolute temperature.

- This can be shown to be generally true for real gases.
- The microscopic perfect gas has properties chosen to match those of the thermodynamic perfect gas.

- This basic approach is applicable to other systems.
- For a given mass of any fluid, two of p , V and T are independent.
 - That is, there exists an equation of state such that $f(p, V, T) = 0$.
- The corresponding molecular model must involve p , V and the molecular energy.
 - Intramolecular energy (vibrational, rotational, and electronic) as well as kinetic energy.
- Equations of state may be obtained by:
 - Direct measurement.
 - Extrapolation from a hypothetical system.
 - From statistical mechanics.

- Thermodynamics deals with relationships between the equation of state and measurable quantities and thermodynamic functions.
 - These relationships are general and apply regardless of the equation of state.
 - It can be shown that:

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

is true for all systems, but its actual value depends on the equation of state.

The First Law of Thermodynamics

- What do
 - Energy
 - Work
 - Heatmean in thermodynamics?
- From a microscopic view energy is defined in terms of quantum mechanics.
- Both microscopic and macroscopic views of the perfect gas will be considered.
- Also considered are:
 - Nature of intensive and extensive variables.
 - Quasi-static and reversible processes.
 - Nature of constraints.

Microscopic and Macroscopic Energy in a Perfect Gas

- The First Law of Thermodynamics may be expressed in terms of conservation of energy.
- Consistent with the treatment of energy conservation in classical and quantum mechanics.
- The kinetic energy of a single particle is $\frac{1}{2}mv^2$.
- The potential energy is defined in terms of intermolecular potential.
- Total energy is conserved throughout the system.
 - NOT the energy of the individual particles.
- But thermodynamics is concerned with macroscopic properties of the system.

- What does “energy” mean in the context of thermodynamics.
 - How is energy related to p , ρ , and T ?
 - How do mechanical and thermodynamic concepts of energy relate to each other?
- Consider the mechanical description of a system:
 - The positions and velocities of the particles can be controlled by the manipulation of forces.
 - The work associated with moving a particle can be determined by controlling movement of that particle and all other particles in the system.
 - The motion of the individual particles is followed as closely as possible.
- In contrast, consider the thermodynamic description:

- Only macroscopic variables, such as volume, are controlled.
- Work is performed when the systems boundaries are displaced.
 - Positions and velocities of individual molecules can change freely so long as the average properties of the system are consistent with the macroscopic properties.
- These uncontrolled molecular motions account for the differences between thermodynamic and mechanical energy.
 - But there is a connection between the thermodynamic and mechanical quantities.
 - The thermodynamic quantities are related to the averages over large number of molecules (or over a long time) of the mechanical quantities.

- Continued:
 - Recall the relationship between the temperature and kinetic energy of molecules.
- Consider a monatomic gas from a quantum mechanical perspective:
 - Consider a system of N noninteracting particles in cubic box of volume V .
 - This is a closed system.
 - The possible energies of the particles in the box are quantized.
- The energy spectrum for a particle in a 3-D cubic box is given by:

$$\epsilon_{n_1, n_2, n_3} = \frac{\pi^2 \hbar^2}{2mV^{2/3}} (n_1^2 + n_2^2 + n_3^2)$$

where n_1^2 , n_2^2 , and n_3^2 are the quantum numbers for the x , y , and z axes of the cube.

- The larger the cube is, the more closely spaced are the energy levels.
- The total energy of the system is the number of particles in each energy state, summed over all states.

$$E = \sum_{n_1, n_2, n_3} N_{n_1, n_2, n_3} \epsilon_{n_1, n_2, n_3}$$

- Now consider a change in the size of the box such that it is still a cube.
 - How does this change the energy?

$$d\epsilon_{n_1, n_2, n_3} = -\frac{\pi^2 h^2}{3mV^{5/3}} (n_1^2 + n_2^2 + n_3^2) dV$$

$$= -\frac{2\epsilon_{n_1, n_2, n_3}}{3V} dV$$

- This means that increasing the volume makes the spacing of the energy levels smaller.
- The energy spectrum changes when the macroscopic coordinate of V is altered.
- But does changing the volume of the system change its energy?
- Whether or not changing the volume changes the energy of the system depends on how the change is made.
 - A perturbation of the wall of the system will lead to transitions among the energy levels of the system.

- Continued:
 - If the perturbation is carried out infinitely slowly, then the process is adiabatic and no transitions will take place.
 - Such a process is adiabatic.
- In an adiabatic process, same number of particles are in each energy level before and after the volume change.
 - But the spacing of the energy levels has changed.

$$\begin{aligned}
 dE &= \sum_{n_1, n_2, n_3} N_{n_1, n_2, n_3} d\epsilon_{n_1, n_2, n_3} \\
 &= -\frac{2}{3V} \left[\sum_{n_1, n_2, n_3} N_{n_1, n_2, n_3} \epsilon_{n_1, n_2, n_3} \right] dV = -\frac{2}{3} \frac{E}{V} dV
 \end{aligned}$$

- The only way the particles in the box can have energy is as kinetic energy.
- If the occupation number (N_{n_1, n_2, n_3}) does not change, but the energy of the level does change as the volume changes, then the total kinetic energy of the system changes.
 - This means that there will be a temperature change in the gas.
- The change in the volume does not have to be carried out in such a way that no transitions in the energy of individual particles occurs.
 - Since the molecules are indistinguishable, all that is necessary is the average population of the energy levels remains unchanged.
 - Populations of the energy levels fluctuate around their average values.

- Equilibrium thermodynamics can be used at any point on the path if the fluctuations are small.
- The adiabatic process carried out very slowly is referred to as reversible and “quasi-static”.
 - The system never deviates significantly from equilibrium at any point in the process.
- The First Law of Thermodynamics requires that energy be conserved.
- Therefore if the energy of the system changes, then the energy of the surroundings must change in such a way as to conserve energy.
 - Energy in some form is transferred to or from the particles from or to the surroundings.
 - Work is one of the ways that this energy transfer can occur.

- To compress a box, an external force must be applied to it.
 - By definition, work is force times distance.
 - The applied pressure times the area is the force.
- The inward displacement of the container is the distance. This distance may be obtained by dividing the volume by the area to which the force has been applied.
- Therefore:

$$\text{Work} = -p_{app}A\frac{dV}{A} = -p_{app}dV$$

- This work represents the energy transferred from the surroundings in the case of compression ($dV < 0$).

- Continued:
 - In the case of expansion ($dV > 0$), energy is transferred to the surroundings as work.
- Is this energy change in the surroundings the same size as the energy change in the system?
- In the case of particles in the box, the box imposes the boundary conditions at which the wave function vanishes.
 - This is how quantum mechanics describes particles being inside the box, but not outside.
- If the volume of the box is changed, then this is a change in the boundary conditions for the wavefunctions describing the particles.
- This means that the energy levels change.

- Therefore energy crosses the walls of the system in the form of work.
- The walls are adiabatic so work is the only way of changing the energy of the system.
- How do real systems differ from the ideal system?
 - The walls of a real system are made up of molecules.
 - These molecules can vibrate.
 - Energy can be transferred across the walls to the gas molecules on the other side without doing work.
 - This energy is transferred across the walls as heat.
 - Such walls are diathermal.
- Thermodynamics answers the question of how much energy is transferred as heat and how much energy is transferred as work.

- Mechanics uses the trajectories of the individual particles to figure out how much energy is transferred as work.
- Thermodynamics considers work in terms of the energy that crosses the boundaries of a system and describes it in terms of the surroundings.

Description of Thermodynamic States

- In order to develop thermodynamic definitions of work and heat, a thermodynamic state must be described precisely.
- Two thermodynamic states are identical if they are described by sets of macroscopic variables that have the same values for each state.
 - How are relevant thermodynamic variables chosen?
 - How many can be constrained or fixed?

- Only variables that can be independently chosen can be selected as constraints.
- A thermodynamic state is uniquely defined by specifying a complete set of thermodynamic variables.
 - Each set of values for such variables corresponds to a distinct state of the system.
- Consider an equation of state for a pure substance.
 - p and v (specific volume) would be a set of independent variables in that the temperature T would be determined once their values were chosen.
 - Any two of p , v and T can be chosen independently and constrain the value of the third coordinate.
 - Geometrically, the equation of state defines a surface in p, v, T space.

- The surface can be defined by:

$$p = f_1(v, T) \text{ or } v = f_2(p, T) \text{ or } T = f_3(p, v)$$

where the forms of the function are determined by the equation of state.

- The surface is illustrated in Figures 13.1 and 13.2.
- Fixing one of the thermodynamic coordinates is equivalent to taking a cut through the surface parallel to appropriate axis.
- All points on the surface correspond to an equilibrium thermodynamic state.
- All points in p, v, T space that do not lie on the surface are nonequilibrium states of the system.
- A nonequilibrium state of the system requires more than p, v, T to describe it fully.

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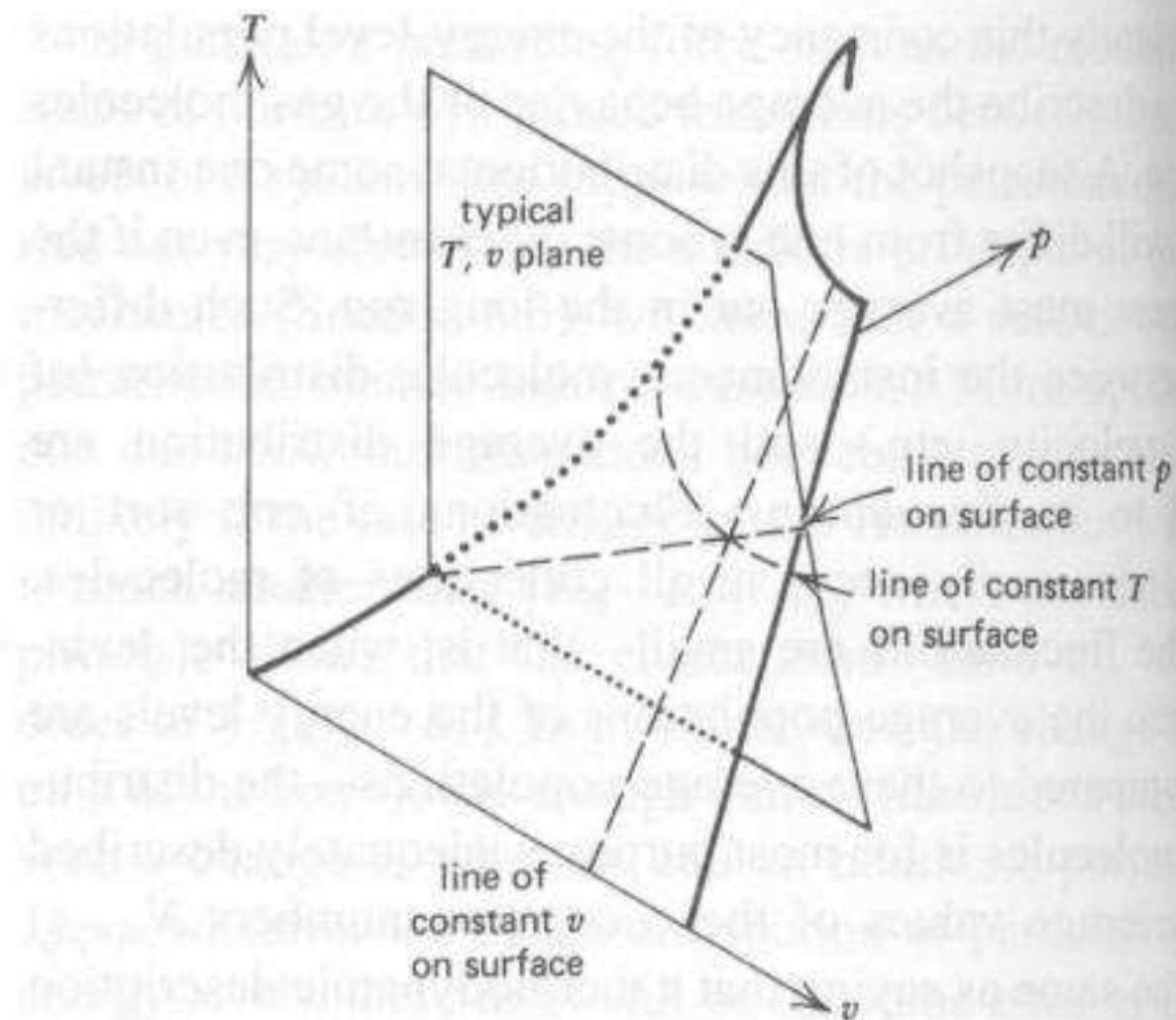
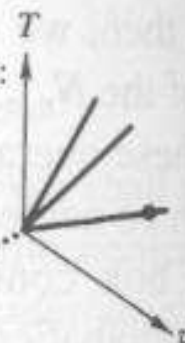


Figure 13.1 Part of a surface representing the equation of state in (p, v, T) space. The particular surface shown is for the perfect gas, with the equation of state $p v = R T$. The lines of constant p , T , and v on the surface are the loci of the intersections of the surface with typical (T, v) , (p, v) , and (T, p) planes, respectively. A typical (T, v) plane is shown; the others are omitted for clarity.

(a) T, p plane:



(b) T, v plane:



(c) p, v plane:

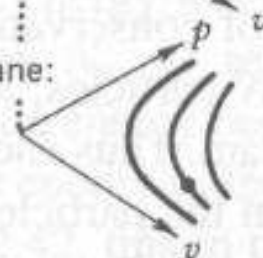


Figure 13.2 Intersections of the perfect gas surface of Fig. 13.1 with planes on which v , p , or T is constant. (a) (T, P) plane—each line in this plane is the locus of the intersection of the p, v, T surface and a plane on which v is constant. (b) (T, v) plane—each line in this plane is the locus of the intersection of the p, v, T surface and a plane on which p is constant. (c) (p, v) plane—each curve (hyperbola) in this plane is the locus of the intersection of the p, v, T surface and a plane on which T is constant.

- Some examples of nonequilibrium systems are:
 - A one component, one phase system that is spatially inhomogeneous.
 - A system with a nonequilibrium velocity distribution.
 - A system in which a chemical reaction is occurring.
 - A steady state system through which energy or mass is flowing.
 - Any system in which a change is being carried out at a perceptible rate.
- A quasi-static and reversible process is carried out so slowly that all points on the path lie on (or very near) the surface described by the equation of state.

The Concept of Work in Thermodynamics

- Consider the mechanical definition of work:

$$dw = \mathbf{F} \cdot d\mathbf{s} = F_s ds$$

where:

- \mathbf{F} is force.
- s is the displacement
- F_s is the component of \mathbf{F} in the direction of ds .
- If the object is displaced from point 1 to point 2, the work done is determined by evaluating the line integral:

$$w_{12} = \int_1^2 \mathbf{F} \cdot d\mathbf{s} = \int_1^2 F_s ds$$

- The value of a line integral depends on the path taken between point 1 and point 2.

- Line integrals are also known as path integrals.
- Therefore if different paths are taken between point 1 and point 2, different amounts of work are involved.
- Work is defined only with respect to motion.
 - It is a process variable that passes between systems.
- An object does not contain work.
 - That is the system does not contain one amount of work at the beginning of the process and another amount at the end.
- There are some important distinctions between mechanical and thermodynamic work.
- In mechanical work, force is typically related to the interaction potential and $\mathbf{F} \cdot d\mathbf{s} = F_x dx + F_y dy + F_z dz$ is an exact differential.

- This means that the cross derivatives are equal:

$$\left(\frac{\partial F_y}{\partial x}\right) = \left(\frac{\partial F_x}{\partial y}\right), \quad \left(\frac{\partial F_z}{\partial y}\right) = \left(\frac{\partial F_y}{\partial z}\right), \quad \left(\frac{\partial F_x}{\partial z}\right) = \left(\frac{\partial F_z}{\partial x}\right)$$

- If this condition is met, the mechanical system is conservative and the mechanical work can be determined just from the initial and final positions.
- If this condition is not met, then the mechanical system is dissipative.
- A typical thermodynamic system is dissipative.
- It is possible to define thermodynamics potentials that are related to the work that a thermodynamic system can do under specific conditions.
- Thermodynamic work involved in the expansion or compression of a fluid.

- Consider a volume of fluid in a container with movable walls.
- This fluid exerts pressure p on the walls.
- The pressure applied to the walls from the surroundings is p_{app} .
 - p_{app} can be any force applied to the container.
- When the system is at equilibrium $p = p_{app}$.
- If p_{app} is increased then the volume of the fluid must decrease.
- Consider a small element of the surface of the container with area dA which moves inward by infinitesimal distance dx_i .

- The work done on the system as the result of the force exerted on the i th element of area is

$$\vec{d}w_i = F_i dx_i = (p_{app})_i dA_i dx_i = (p_{app})_i dV_i$$

where $dV_i = dA_i dx_i$ is the change in volume of the system.

- This summed over the entire surface area of the container will give the work done on the system.
- The sign convention for work:
 - $w > 0$ when $dV < 0$.
 - $w < 0$ when $dV > 0$.
 - This is expressed as

$$\vec{d}w = -p_{app}dV$$

- The total work done on a system for a finite volume change is:

$$w = - \int_{V_1}^{V_2} p_{app} dV$$

where V_1 and V_2 are the initial and final volumes respectively and p_{app} is the effective pressure exerted by the surroundings.

- If work is to be done at a measurable rate (i.e. not quasi-statically), then p_{app} must differ from p .
 - Either p or p_{app} can be varied independently of the volume.
 - For example, p_{app} can be varied by changing the weight placed on a piston.
 - p could be altered by changing the temperature.

- There are an infinite number of paths between state 1 and state 2.
 - Therefore work cannot be determined unless the path is specified.
 - Work cannot be determined solely by the initial and final point of the path.
 - This is why the differential of work is represented by δw . (δ denotes an **inexact** differential.)

Some properties of inexact differentials:

- Consider

$$\int_1^2 \delta X$$

- There exists no function X of which δX is the differential and which has a unique value in either the initial or final state.

- Therefore a thermodynamic system does not contain work.
- Work cannot be defined as a function of the variables that determine the state of a thermodynamic system.
 - Only state functions can be expressed in terms of state variables (p, v, T) .
- Work is a **path** function.
- Work has many forms:
 - Mechanical $w = \int_{x_1}^{x_2} F dx$
 - Pressure-volume work $w = - \int_{V_1}^{V_2} p_{app} dV$
 - Electrical work to charge a capacitor $w = \int_{Q_1}^{Q_2} \mathcal{E} dQ$
- A general definition of work that can be applied in principle is: “The performance of work is equivalent to the lifting of a mass in a gravitational field.”

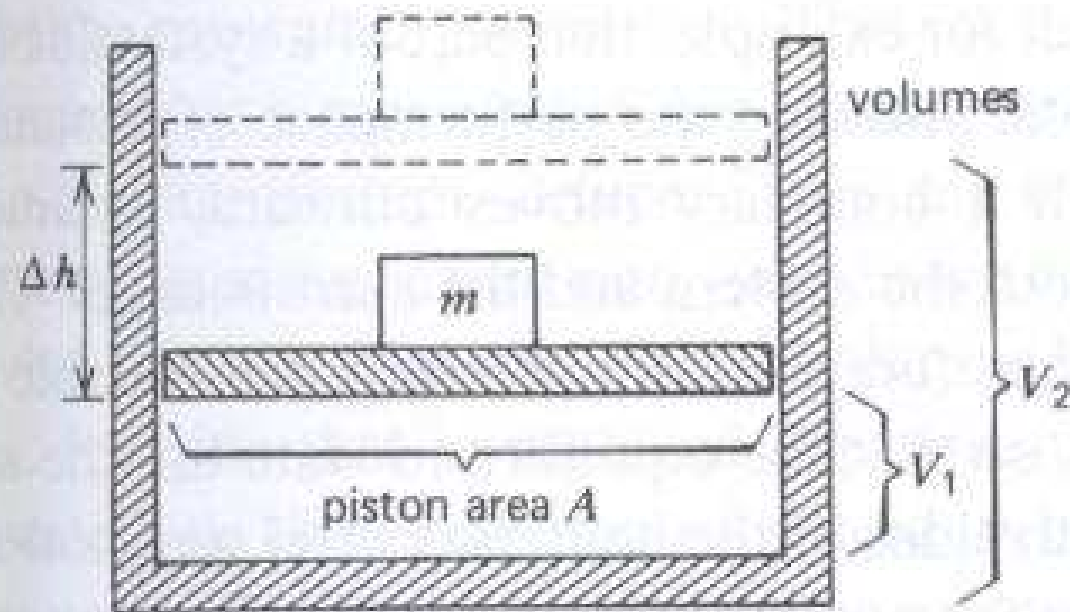


Figure 13.3 Equivalence of work with lifting a mass in a gravitational field. The system is a fluid in a cylindrical container with rigid walls, except for a movable piston atop the container. The piston itself is weightless and frictionless, but is held in place by a mass m . The fluid expands in volume from V_1 to V_2 by upward motion of the piston, thereby lifting the mass m through a vertical distance Δh . (See text for computation of work.)

- Applied to pressure-volume work this gives:

$$-w = \int_1^2 p_{app} dV = \int_1^2 \left(\frac{mg}{A} \right) (A dh) = mg \int_1^2 dh$$

- All of this **assumes** that work is a form of energy and that energy can be converted in form.
 - Work has the units of energy.
- What is the difference between mechanical and thermodynamic work?
- Thermodynamic work deals with a wider range of variables.
- Mechanical work is concerned with the trajectories of the individual particles that make up the system.
- Thermodynamic work is concerned with what crosses the boundaries of the system.

- In principle, this thermodynamic work can be converted into lifting a mass.
- Thermodynamics is not concerned with what is happening with that energy before or after it crosses the boundary of the system.
- It is concerned with how much of that energy is work.

Intensive and Extensive Variables

- Intensive variables are independent of the mass of the system.
 - Some examples of intensive variables are T and p .
- Extensive variables depend on the mass of the system.
 - Internal energy and volume are examples of extensive variables.

- Consider intensive and extensive variables in the context of two identical systems.
 - The two systems are combined by removing a barrier between them.
 - The intensive variables, p and T , do not change.
 - The extensive variables such as U or V do change, to twice their initial values.
- Work is expressed in terms of an intensive variable and an extensive variable.
 - These pairs of variables are conjugate variables.
 - What they are depends on what type of work is involved.
 - When the members of these conjugate pairs are multiplied together, the result has units of energy.

- Generally:

$$\delta w = X dY$$

where X is an intensive variable that has the same value inside and outside the system and Y is the conjugate extensive variable such that an infinitesimal change dY does work δw .

- There are many such pairs of variables (see Table 13.1).
- Pairs of conjugate variables also appear in mechanics as generalized coordinates and generalized forces.
 - The potential energy of the mechanical system can often be expressed as a function of the generalized coordinates i.e. $U = U(q_1, q_2, \dots, q_n)$.

- If this is true of the potential then:
 - The generalized force Q_i conjugate to the particular generalized coordinate q_i is the negative partial derivative of the potential with respect to that generalized coordinate:

$$Q_i = - \left(\frac{\partial U}{\partial q_i} \right)$$

- The differential work is $\dot{d}w = \sum_i Q_i q_i$.
- Thus $X = -(\partial U / \partial Y)$ where X and Y are conjugate variables.
- Note that the product of the conjugate variables has dimensions of energy.
- The boundaries of the system determine whether or not work can be performed.

- If the boundary is movable, expansion work may be done.
- If the boundary is rigid, then no expansion work can be done.
- If the boundary is conducting, then electrical work may be done.
- If the boundary is insulating, then no electrical work may be done.
- Work of a given type is always associated with a change in the extensive variable until the intensive variable has the same value on both sides of the boundary i.e. when the system attains equilibrium with the surroundings.
- Consider a system where a portion of the boundary is displaceable.
 - When the boundary moves outward, the volume changes in both the system and the surroundings.

- The moving boundary may be thought of as “transmitting” pressure, since the change occurs until the pressure (the variable conjugate to volume) is the same in both the system and the surroundings.
- If the boundary is rigid, then pressure volume-work cannot be performed.
 - When the system attains equilibrium, the pressure (intensive variable) can have different values in the system and the surroundings.
- If a system at equilibrium is to undergo a change in state, energy must be able to cross its boundaries as either heat or work.

Quasi-static and Reversible Processes

- The path by which a change in state occurs must be carefully considered.

- The change in the state function depends on the initial and final states and not the path.
- The path by which the change in state occurs determines how much heat or work is transferred by the process.
- Two categories of paths will be considered:
 - reversible
 - irreversible
- Consider a reversible path followed by a system between the initial and final states.
 - Every point of the path can be described by the equation of state.
 - But a system at equilibrium cannot change with time.
 - Any real process that occurs at a measurable rate is not a reversible process.

- The reversible process represents the limiting case of a real change in state carried out at an infinitesimal rate of change.
- The process carried out at an infinitesimal rate of change is carried out quasi-statically.
- A given change of state can be carried out quasi-statically by infinitely many routes.
- Not all quasi-static processes are reversible.
 - The limiting behaviour depends on the conditions or constraints.
- Consider a reversible quasi-static processes.
 - In the limit of an infinitely slow process, a system undergoing a reversible, quasi-static process moves through a continuous sequence of equilibrium states.
 - But is this of any practical use?

- Many real processes have characteristics so close to that of a reversible process, that the process may be assumed to be reversible for the purposes of calculating useful quantities.
- This implies that any deviation from equilibrium tends to zero more rapidly than the rate of change.
- Consider an irreversible path between initial and final states.
 - It is possible to calculate work if the relationship between p_{app} and the volume is known.
- Consider the expansion of a perfect gas from V_1 to V_2 .
 - This may be carried out quasi-statically with a frictionless piston.
 - Initially the pressure p_{app} is equal to the internal pressure p .

- The pressure is changed by a small amount Δp and the gas expands.
- Maintaining the relationship $p_{app} = p - \Delta p$, the process continues until the final volume is reached.
- Now consider repeating the process with a smaller Δp .
 - Since Δp is smaller, the force will be less and the process will occur more slowly.
 - In the limit $\Delta p \rightarrow 0$, the rate is infinitesimal with $p_{app} = p$ throughout (i.e. reversible expansion).
 - If this is the case and the gas is perfect, then:

$$w = - \int_{V_1}^{V_2} p_{app} dV = - \int_{V_1}^{V_2} p dV$$

$$= - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

- Work may be thought of as the area under the curve in (p, V) space as illustrated in Fig. 13.4.
- It is to be noted in this case that:
 - expansion work is performed.
 - The intensive variable associated with this work, pressure, has the same value on both sides of the barrier during this reversible process.
- The complete definition of a reversible process is:
 - It takes place at an infinitesimal (quasi-static) rate.
 - It passes through a continuous sequence of equilibrium states.
 - At every point in the process, the intensive variable corresponding to the type of work involved is continuous in value.

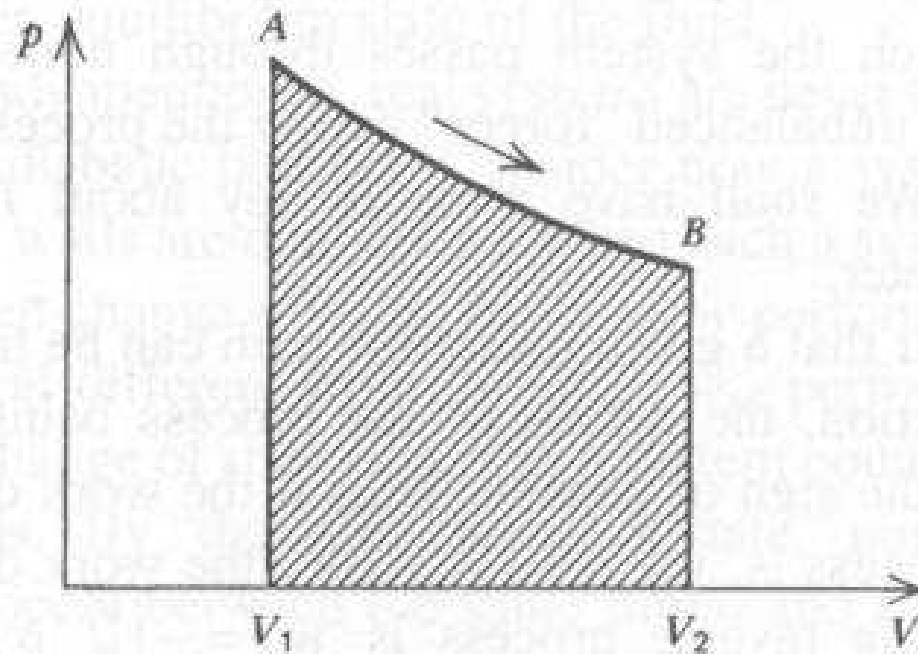


Figure 13.4 Work performed in the reversible expansion of a fluid. The heavy line AB gives the value of p as a function of V during the expansion from V_1 to V_2 ; the work performed on the fluid is then

$$w = - \int_{V_1}^{V_2} p \, dV,$$

equal to the negative of the area under the curve AB .

- A reversible path can be traversed in either direction.
 - The result is identical in magnitude but not in sign.
 - The direction of the process is determined by the direction of the infinitesimal change in the intensive variable.
 - If $p_{app} < p$, then expansion occurs.
 - if $p_{app} > p$, then compression occurs.
 - If the work done in the forward process is $w_f = - \int_{V_1}^{V_2} p dV$, then the work in the reverse process $w_r = - \int_{V_2}^{V_1} p dV = -w_f$.
 - $w_f = -w_r$ is valid only for reversible paths.
- A system undergoing a reversible quasi-static process differs from a system at equilibrium in that the latter does not exchange work or heat with the surroundings.

- Consider an irreversible process.
 - Can no longer assume that $p_{app} = p$.
 - The driving force will be $A(p_{app} - p)$ and the change will occur at a nonzero rate.
 - The work performed is not given by $w = - \int_{V_1}^{V_2} p dV$ but by $w = - \int_{V_1}^{V_2} p_{app} dV$
 - The substitution $p_{app} = nRT/V$ is not valid for an irreversible process.
 - To calculate work, the actual p_{app} must be known.
 - If p_{app} were constant, then $w = -p_{app} \int_{V_1}^{V_2} dV$
 - If p_{app} were zero, the system would expand without doing any work.
 - More about irreversible work in Chapter 16.

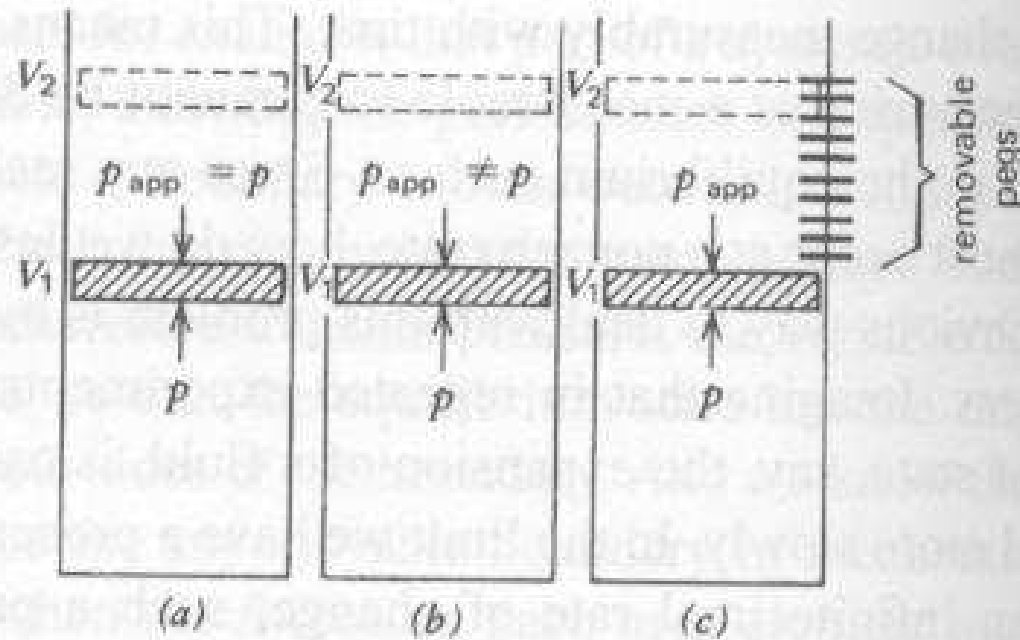


Figure 13.5 Reversible, irreversible, and quasi-static expansion of a fluid. (a) Reversible (and thus quasi-static): $p_{app} = p$ at all times, and the expansion proceeds infinitely slowly. (b) Irreversible: $p_{app} \neq p$, and the expansion proceeds at a measurable rate. (c) Quasi-static but irreversible: See text.

- A process can be quasi-static without being reversible.
- Consider Fig. 13.5c.
 - A fluid is confined by a piston held in place by a series of pegs.
 - There is a vacuum above the piston, so $p_{app} = 0$.
 - Removal of the lowest peg results in the fluid expanding irreversibly until the piston hits the next peg.
 - The process is repeated for the remaining pegs.
 - If the spacing of the pegs is made infinitesimal, then the process becomes quasi-static, but not reversible.
- Another example of quasi-static irreversible expansion involves the case of piston moving with friction.

The First Law: Internal Energy and Heat

- Consider a system with adiabatic walls.
 - Recall that all real walls have some thermal conductivity, but real systems exist which approximate this ideal system.
- The first law may be stated formally:

“If the state of an otherwise isolated system is changed from A to B by the performance of work, the amount of work required depends solely on the initial state A and the final state B , and not on the means by which the work is performed, nor the intermediate stages through which the system passes between the initial and final states.”

- Note that the initial and final states must be equilibrium states.
- The internal energy U of a system is defined by the statement:

“If an otherwise isolated system is brought from one state to another by the performance upon it of an amount of work w_{ad} , the change in the system’s internal energy in the process is defined to be the amount ΔU exactly equal to w_{ad} ”

- Note that w_{ad} is adiabatic work.
- Therefore $\Delta U = U_B - U_A = w_{ad}$ where A and B designate respectively, the initial and final states
 - $\Delta U > 0$ when work is done on the system.
 - $\Delta U < 0$ when work is done by the system.

- This relationship holds for both reversible and irreversible adiabatic processes.
- Note that the definition refers only to the change in internal energy.
 - It does not establish the zero of the energy scale.
 - The zero of the energy scale is arbitrary.
- When a given equilibrium system is used to fix the value of U_0 , then the value of U for any other equilibrium system is uniquely determined.
- ΔU is independent of the path, i.e. U is a state function.
- Therefore for a fluid:
 $U = U_1(p, v) = U_2(p, T) = U_3(v, T)$ and have the same value for any equilibrium state of the fluid (even though the functions differ in form).

- Consider a system with diathermal walls.
 - Now energy can be exchanged with the surrounding as heat and as work.
- For a given change in state in this case, w will differ from w_{ad} .
 - Diathermal work depends on the path.
 - q , the heat transferred can be defined in terms of w and w_{ad} :

$$q \equiv w_{ad} - w$$

- But $\Delta U = w_{ad}$, therefore:

$$q = \Delta U - w \text{ or } \Delta U = q + w$$

- Thus heat may be determined in terms of the change of state (i.e. change in internal energy) and the work performed on or by the system.
- As in the case of the sign convention for work, heat is positive when energy is transferred to the system as heat and negative when energy leaves the system as heat.
- Heat is anything that enters or leaves the system by a means other than work.
- Internal energy U is a state function and has exact differential dU
- Heat q and work w are path functions and have inexact differentials δq and δw and $dU = \delta q + \delta w$.
- One consequence of the definition of a state function is that $\oint dU = 0$.

- Therefore $\oint \dot{d}w + \oint \dot{d}q = 0$ but:

$$\oint \dot{d}w = 0 \text{ and } \oint \dot{d}q = 0$$

is **not** necessarily true.

- What are $\oint \dot{d}w$ and $\oint \dot{d}q$?
 - Consider first a cycle that follows a reversible path from state A to state B and then returns from state B to state A along the same reversible path.
 - $\Delta U_f = -\Delta U_r$ and $w_f = -w_r$
 - Therefore $q_f = -q_r$.
- If on the other hand, the path from state B to A is not the exact reverse of the path taken from A to B , then
 - $\Delta U_f = -\Delta U_r$ but $w_f \neq -w_r$
 - Therefore $q_f \neq -q_r$.

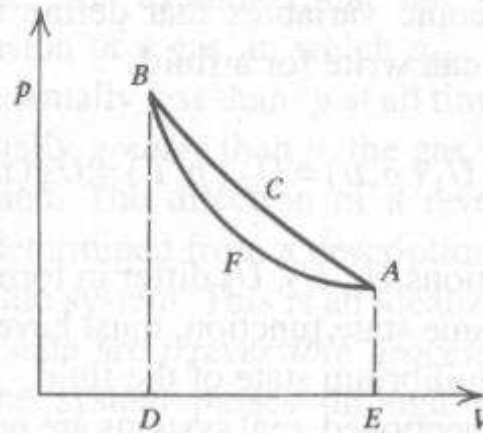


Figure 13.6 Graphical representation of internal energy, work, and heat. Consider a given change of state, in this case the reversible compression of a fluid from state $A(p_1, V_1)$ to state $B(p_2, V_2)$. Assume that ACB is the path followed when this change of state is carried out *adiabatically*. The adiabatic work w_{ad} associated with this change of state is then equal to the area $ACBDEA$, and by Eq. 13.15 this must equal the internal energy change:

$$\Delta U = U_B - U_A = w_{\text{ad}} = \text{area } ACBDEA$$

Now consider any other path AFB along which the same change of state can be carried out diathermally. The work performed on the system in the diathermal process is then equal to the area $AFBDEA$, the internal energy change is the same as in the adiabatic process, and the heat q absorbed by the system must equal the area between the two paths:

$$q = w_{\text{ad}} - w = \text{area } ACBDEA - \text{area } AFBDEA = \text{area } ACBFA$$

In this case q and w are both positive.

- Consider Fig. 13.6 and a cyclic path from A to B by adiabatic path ACB and from B back to A by path BFA .
 - The work associated with ACB , w_{ACB} , is proportional to the area enclosed by $ACBDEA$.
 - w_{ACB} is positive since the process is a compression.
 - q_{ACB} is zero because the path is adiabatic.
- Now consider BFA :
 - The work associated with BFA , w_{BFA} is proportional to the area enclosed by $BFAED$.
 - w_{BFA} is negative since the process is an expansion.
 - Due to the first law, the heat associated with this portion of the path plus the work must $U_A - U_B$:
i.e. $\Delta U_{BA} = w_{BFA} + q_{BFA}$.

- But $\Delta U_{BA} = -\Delta U_{AB} = -w_{ACB}$ and $w_{BFA} + q_{BFA} = -w_{ACB}$.
 - Therefore $q_{BFA} = -w_{ACB} - w_{BFA}$ which is proportional to the area enclosed by $ACBFA$.
 - q_{BFA} is negative because w_{ACB} is larger in magnitude than w_{BFA} .
- The net work of the cycle is $w_{ACB} + w_{BFA}$ (also the area enclosed by the cycle).
- Overall:

$$\oint dU = \oint \vec{dq} + \oint \vec{dw} = 0$$

$$\oint \vec{dw} = - \oint \vec{dq} = w_{ACB} + w_{BFA}$$

.

- If a system is undergoing **only** reversible processes, then the first law may be written in general form:

$$dU = \delta q + \sum_i X_i dY_i$$

where X_i, Y_i are the conjugate pairs of intensive and extensive variables.

- Thus X_i , the intensive variable, can be defined as:

$$X_i = \left(\frac{\partial U}{\partial Y_i} \right)_{\text{rev ad, } Y_j, j \neq i}$$

- Note that the first law applies to all processes.

Some Historical Notes

- Our understanding of the first law is ~ 200 years old.
- That work can be converted to heat was shown in many ways.
 - Rumford (1798) showed that mechanical work involved in the boring of cannons could be continuously converted to heat
 - Davy (1799) rubbed two ice cubes together and caused them to melt.
 - Mayer (1842) formulated the principles of equivalence of different kinds of energy and of conservation of total energy.
 - Joule (circa 1850s) provided the qualitative basis for the law of the conservation of energy.

- Joule produced heat from work in various ways.
 - Water was heated by the rotation of a paddle wheel in liquid with the paddle wheel driven by a fallen weight.
 - Measured heat produced by passing electrical current through a resistor.
 - Measured heat produced by rubbing bodies together.
 - Measured heat produced by expansion and contraction of air.
 - Established the value of J , the mechanical equivalent of heat:

$$w = Jq$$

- Work and heat were measured in different units (work as footpounds and heat as calories).

- A calorie was defined as the heat required to raise the temperature of 1 g of water from 14.5°C to 15.5°C and is denoted as cal_{15} .
- Joule experiments established that $1 \text{ cal}_{15} = 4.15 \text{ J}$, superseding Mayer's value of 3.6 J/cal_{15} .
- Modern measurements give $1 \text{ cal}_{15} = 4.1855 \text{ J}$.
- The thermochemical calorie is now, *by definition*, $1 \text{ cal}_{th} = 4.1840 \text{ J}$.
- Once the equivalency of heat and work was established, a thermodynamic system could be considered as a reservoir of energy.
 - Work and heat are how energy crosses the boundary of the system.

Microscopic Interpretation of Internal Energy and Heat

- The thermodynamic definition of internal energy is based on adiabatic work processes.
- The adiabatic perturbation of quantum mechanics corresponds to the reversible adiabatic process of thermodynamics,
- In the microscopic equivalent of the adiabatic work process, the change in the system's internal energy is the change in the mechanical energy of the particles in the system.
 - The distribution of particles over the energy levels is not changed.
- Nonadiabatic process and the associated heat transfer will now be considered.

- When a system exchanges both work and heat with the surroundings, the microscopic energy spectrum is changed and the distribution of particles over the energy levels are changed.
- Consider the expansion of a perfect gas at constant temperature.
 - The energy spectrum depends on the size of the box. Therefore when the size of the box is increased, the energy of each level decreases.
 - If the kinetic energy of the particles stays the same, then some particles move to higher energy levels.
- In an adiabatic expansion, the kinetic energy of the particles decreases.
- In an isothermal expansion, some energy is added from the surroundings as heat to promote some particles to higher energy levels.

- In summary:
 - Energy entering or leaving the system as reversible adiabatic work changes the energy levels, but not the population of the energy levels.
 - Energy entering or leaving the system reversibly as heat changes the population of the energy levels but not the energy levels.
 - Energy entering or leaving the system as irreversible work changes both the energies levels and the populations of the energy levels.
- It will be demonstrated later that these conclusions hold for real systems.
 - Needed first will be a macroscopic measure of the distribution of particles and the concept of entropy.

- Consider the internal energy U of a perfect gas from a microscopic perspective.
 - The volume of the box is changed while the temperature is held constant.
 - If it is a perfect monatomic gas, then the only way the molecules can have energy is as kinetic energy.
 - The number of molecules is constant, therefore the total energy of the gas is independent of the volume of the box in a constant temperature process.
- Thus the result is the same for the quantum mechanical perfect gas as for the classical mechanical gas.

$$U = \frac{3}{2}nRT$$

where U can be identified with the thermodynamic internal energy.

- The internal energy of a gas depends only on temperature and is independent of density or pressure.
 - This statement allows the definition of a perfect gas without reference to microscopic assumptions.
- It was previously concluded that the work associated with the reversible expansion of an ideal gas is:

$$w = - \int_{V_1}^{V_2} p_{app} dV = - \int_{V_1}^{V_2} p dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

- But $\Delta U = q + w$, therefore: $q = -w = nRT \ln \frac{V_2}{V_1}$
- Also recall that for a reversible adiabatic process:

$$\frac{dE}{dV} = -\frac{2}{3} \frac{E}{V}$$

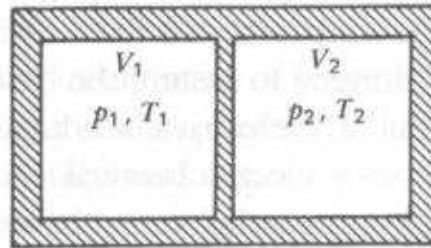
- But U is the same as E . Therefore:

$$dU = -\frac{2}{3} \frac{U}{V} dV = -\frac{2}{3} \left(\frac{3}{2} nRT \right) \frac{dV}{V} = -\frac{nRT}{V} dV = -pdV$$

- $dU = -pdV$ is true for the reversible adiabatic expansion of any fluid.
 - This is consistent with $dU = \delta w$ for reversible adiabatic work.

Constraints, Work, and Equilibrium

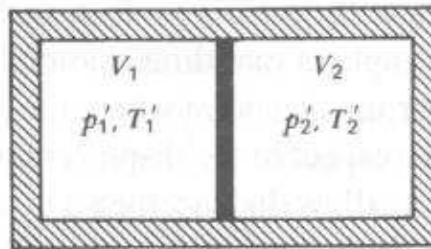
- Constraints are the boundary conditions defining a thermodynamic system.
- A change in boundary conditions can change the equilibrium state of the system.
- Consider Figure 13.7.



$$p_1 \neq p_2$$

$$T_1 \neq T_2$$

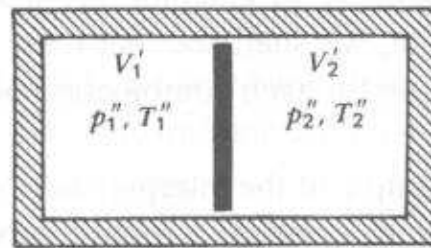
(a)



$$p_1' \neq p_2'$$

$$T_1' = T_2'$$

(b)



$$p_1'' = p_2''$$

$$T_1'' = T_2''$$

(c)

Figure 13.7 Interactions of two gaseous subsystems in a rigid adiabatic container. (a) Fixed adiabatic barrier. (b) Fixed diathermal barrier. (c) Movable diathermal piston.

- Consider a gas enclosed in a rigid cylinder with adiabatic walls.
- A sliding piston divides the gas into two volumes, V_1 and V_2 .
 - If the piston is adiabatic and fixed in place, then the two subsystems are isolated and pressures, p_1 and p_2 , and temperatures, T_1 and T_2 can completely different.
 - There are four independent variables.
- Now replace the fixed adiabatic piston with a fixed diathermal piston.
 - The system is no longer at equilibrium.
 - The piston cannot move, so energy may be transferred only as heat.

- When a new equilibrium is attained, the temperatures will be the same but the pressures can be different.
- There are three independent variables.
- Now allow the piston to move.
 - When the equilibrium is attained, both the pressures and the temperatures will be the same.
 - The system has two independent variables.
- Now allow the piston to be moved by coupling it to an external machine.
 - If work is done on the surroundings adiabatically, then the internal energy of the system will decrease and the temperature will decrease.
- Each constraint imposed on the system means that an additional independent variable is needed to describe the system.

- The type of equilibrium attained by the system is defined by the constraints.
- The nature of the work performed by the system is determined by the constraints under which the work is performed.
 - When a given constraint is removed, the system becomes able to perform a particular kind of work.
 - To restore the system to the original state, reimposing the constraint, work must be performed on it.
- In figure 13.7, pV work can be done when the constraint of a fixed barrier is removed.
- Work must be performed to restore the barrier to its original position.

- Spontaneous attainment of equilibrium reduces internal energy.
 - In Chapter 19, minimization of internal and potential energy will be explored further.
 - The first law of thermodynamics is not enough to indicate whether the process is possible or not.

Thermochemistry and Its Applications

- Some consequences of the first law will now be explored.
 - Thermochemistry deals with how changes in temperature and energy are related.
 - Conditions under which the process occurs must be defined carefully.
 - Heat released by a chemical processes will vary according to the constraints of the process.
 - This is because heat is a path function.

- Specific types of energy changes will be defined.
- Standard states will be defined.
- Also considered will be the molecular interpretation of thermochemical data.

Heat Capacity and Enthalpy

- Consider a vessel with rigid and adiabatic walls, filled with fluid.
 - The system is isolated except for a heater.
 - At equilibrium the temperature of the fluid is T_1 .
 - Current is passed through the heater for a specified time and the electrical energy is dissipated as quantity of heat q .
 - A new equilibrium is established at T_2 .
 - Vessel is rigid, therefore constant V process.

- The heat capacity at constant V may be defined as:

$$C_V = \lim_{\Delta T \rightarrow 0} \left(\frac{q}{\Delta T} \right)_V$$

- By the first law of thermodynamics:

$$\Delta U = q_V$$

since pV work is zero at constant V .

- Therefore

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

- Now consider the same process, but now allow one wall of the container to be a freely moving, but adiabatic, piston.

- The volume of the system can change as heat is added.
- The process will occur at constant p if external pressure is fixed at p_{app} and heat is added so slowly (i.e. reversibly) that at all points $p = p_{app}$.
- The heat capacity at constant p may be defined as:

$$C_p = \lim_{\Delta T \rightarrow 0} \left(\frac{q}{\Delta T} \right)_p$$

- Heat capacity may also be defined with respect to other constraints, but C_p and C_V are the most widely used.
 - Heat capacities are extensive (J K^{-1}).
 - Often defined with respect to particular amounts of a substance:
 - Molar heat capacity is the heat capacity per mole ($\text{J K}^{-1} \text{ mol}^{-1}$).