

CHAPTER

1

INTRODUCTION

“Aside from the logical and mathematical sciences, there are three great branches of natural science which stand apart by reason of the variety of far reaching deductions drawn from a small number of primary postulates. They are mechanics, electromagnetics, and thermodynamics.

These sciences are monuments to the power of the human mind; and their intensive study is amply repaid by the aesthetic and intellectual satisfaction derived from a recognition of order and simplicity which have been discovered among the most complex of natural phenomena. . . Yet the greatest development of applied thermodynamics is still to come. It has been predicted that the era into which we are passing will be known as the chemical age; but the fullest employment of chemical science in meeting the various needs of society can be made only through the constant use of the methods of thermodynamics.”

Lewis and Randall (1923)

Lewis and Randall eloquently summarized the broad significance of thermodynamics as long ago as 1923. They went on to describe a number of the miraculous scientific developments of the time and the relevant roles of thermodynamics. Historically, thermodynamics has guided the development of steam engines, refrigerators, nuclear power plants, and rocket nozzles, to name just a few. The principles remain important today in the refinement of alternative refrigerants, heat pumps and improved turbines, and also in technological advances including computer chips, superconductors, advanced materials, and bioengineered drugs. These latter day “miracles” on first thought might appear to have little to do with power generation and refrigeration cycles. However, as Lewis and Randall point out, the implications of the postulates of thermodynamics are far reaching and will continue to be important in the development of even newer technologies. Much of modern thermodynamics focuses on characterization of the properties of mixtures, as their constituents partition into stable phases, inhomogeneous domains, and/or react. The capacity of thermodynamics to bring “quantitative precision in place of the old, vague ideas”¹ is as germane today as it was then.

1. Lewis, G.N., Randall, M. *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, NY, 1923.

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Before overwhelming you with the details that comprise thermodynamics, we outline a few “primary postulates” as clearly as possible and put them into the context of what we will refer to as classical equilibrium thermodynamics. In their simplest human terms, our primary premises can be expressed as:

1. You can’t get something for nothing.
2. Generation of disorder results in lost work.¹

Occasionally, it may seem that we are discussing principles that are much more sophisticated. But the fact is that all of our discussions can be reduced to these fundamental principles. When you find yourself in the midst of a difficult problem, it may be helpful to remember that. We will see that coupling these two observations with some slightly sophisticated reasoning (mathematics included) leads to many clear and reliable insights about a wide range of subjects from energy crises to high-tech materials, from environmental remediation to biosynthesis. The bad news is that the level of sophistication required is not likely to be instantly assimilated by the average student. The good news is that many students have passed this way before, and the proper course is about as well-marked as one might hope.

There is less than universal agreement on what comprises “thermodynamics.” If we simply take the word apart, “thermo” sounds like “thermal” which ought to have something to do with heat, temperature, or energy, and “dynamics” ought to have something to do with movement. And if we could just leave the identification of thermodynamics as the study of “energy movements,” it would be sufficient for the purposes of this text. Unfortunately, such a definition would not clarify what makes thermodynamics distinct from, say, transport phenomena or kinetics, so we should spend some time clarifying the definition of thermodynamics in this way before moving on to the definitions of temperature, heat, energy, etc.

The definition of thermodynamics as the study of energy movements has evolved considerably to include classical thermodynamics, quantum thermodynamics, statistical thermodynamics, and irreversible thermodynamics as well as equilibrium and non-equilibrium thermodynamics. Classical thermodynamics has the general connotation of referring to the implications of constraints related to multivariable calculus as developed by J.W. Gibbs. We spend a significant effort applying these insights in developing generalized equations for the thermodynamic properties of pure substances. Statistical thermodynamics focuses on the idea that knowing the precise states of 10^{23} atoms is not practical and prescribes ways of computing the average properties of interest based on very limited measurements. We touch on this principle in our introduction to entropy and in our ultrasimplified kinetic theory of ideal gases, but we will generally refrain from detailed formulation of all the statistical averages. Irreversible thermodynamics and non-equilibrium thermodynamics emphasize the ways atoms and energy move over periods of time. At this point, it becomes clear that such a broad characterization of thermodynamics would overlap with transport phenomena and kinetics in a way that would begin to be confusing at the introductory level. Nevertheless, these fields of study represent legitimate subtopics within the general domain of thermodynamics.

These considerations should give some idea of the narrowness and the breadth that are possible within the general study of thermodynamics. This text will try to find a happy medium. One general unifying principle about the perspective offered by thermodynamics is that there are certain properties that are invariant with respect to time. For example, the process of diffusion may indicate some changes in the system with time, but the diffusion coefficient can be considered to be a property

1. The term “lost work” refers to the loss of capability to perform work, and is discussed in more detail in Sections 2.4, 3.3, and 3.4.

which only depends on a temperature, density, and composition profile. A thermodynamicist would consider the diffusion process as something straightforward given the diffusion coefficient, and focus on understanding the diffusion coefficient. A transport specialist would just estimate the diffusion coefficient as best as he could and get on with it. A kineticist would want to know how fast the diffusion was relative to other processes involved. In more down to earth terms, if we were touring about the countryside, the thermodynamicists would want to know where we were going, the transport specialists would want to know how long it takes to get there, and the kineticists would want to know how fast the gasoline was running out.

Through the study of thermodynamics we utilize a few basic concepts: energy, entropy, and equilibrium. The ways in which these are related to each other and to temperature, pressure, and density are best understood in terms of the molecular mechanisms which provide the connections. These connections, in turn, can be summarized by the equation of state, our quantitative description of the substance. Showing how energy and entropy evolve into insight about molecular characteristics and their impacts on process applications is the primary goal of this text. These insights should stick with you long after you have forgotten how to estimate any particular thermodynamic property, a heat capacity or activity coefficient, for example. We will see how assuming an equation of state and applying the rules of thermodynamics leads to accurate and extremely general insights relevant to many applications.

1.1 THE MOLECULAR NATURE OF ENERGY

Having described the basic meaning of thermodynamics through its emphases and how it relates to other fields of study, we must proceed systematically to describe some of the terms that will be applied over the long term.

Energy is a word which applies to many aspects of the system. Its formal definition is in terms of the capability to perform work. We will not quantify the potential for work until the next chapter, but you should have some general understanding of work from your course in introductory physics. Energy may take the form of kinetic energy or potential energy, and it may refer to energy of a macroscopic or a molecular scale.

Energy is the sum total of all capacity for doing work that is associated with matter: kinetic, potential, submolecular (i.e., molecular rearrangements by reaction), or subatomic (i.e., ionization, fission, fusion).

Kinetic energy is the energy associated with motion of a system. Motion can be classified as translational, rotational or vibrational.

Potential energy is the energy associated with a system due to its position in a force field.

In the study of “energy movements,” we must continually ask, “How much energy is here now, and how much is there?” In the process, we need to establish a point for beginning our calculations. According to the definition above, we might intuitively represent zero internal energy by a perfect vacuum. But then, knowing the internal energy of a single proton inside the vacuum would require knowing how much energy it takes to make a proton from nothing. Since this is not entirely practical, this intuitive choice is not a good choice. This is essentially the line of reasoning that gives rise to the necessity of defining reference states. It should be clear from this reasoning that there is no absolute value of energy that is always the most convenient; there are only changes in energy from one reference state to another. Thus it is common in the study of thermodynamics to speak of energy changes relative to some reference conditions that are likely to apply throughout any particular process of interest. These reference conditions may change from, say, defining the internal energy of liquid water to be zero at 0.01°C (as in the steam tables) to setting it equal to zero for the

 Energy will be tabulated relative to a convenient reference state.

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elements of hydrogen and oxygen (as in the heat of reaction), depending on the situation. In studies of activity and chemical reactions, we will need to be somewhat careful in specifying the exact nature of the reference state. Since we will focus on changes in kinetic energy, potential energy, and energies of reaction, we will not need to specify reference states any more fundamental than the elements, thus do not consider subatomic particles.

Potential Energy

Kinetic energy is commonly covered in detail during introductory physics courses so we will assume it is already familiar. Students may be somewhat less comfortable with the concept of potential energy, however, especially as it relates to molecular interactions. Therefore, we spend some time with it here.

Macroscopic Potential Energy

Potential energy is associated with the “work” of moving a system some distance through a force field. On the macroscopic scale, we are well aware of the effect of gravity. This is a very common force field. As an example, the earth and the moon are two spherical bodies which are attracted by a force which varies as r^{-2} . The potential energy represents the work of moving the two bodies closer together or farther apart, which is simply the integral of the force over distance. So the potential function varies as r^{-1} . These kinds of operations should be familiar from a course in introductory physics. They are the same at the microscopic level except that the forces vary with position according to different laws.

Intermolecular Potential Energy

In consideration of potential energy on a molecular scale, it is important to realize that uncharged atoms do exert forces on each other. For a rigorous description, the origin of the intermolecular potential must be traced back to the solution of Schrödinger’s quantum mechanics equation for the motions of electrons around nuclei. We cannot afford that level of rigor in this course. In fact, that level of rigor is not currently available for some of the complex molecules to be considered in this course. On the other hand, there are several generalities which arise from this rigorous approach which can be appreciated from a somewhat intuitive perspective. For instance, atoms are comprised of dense nuclei of positive charge with electron densities of negative charge built around the nucleus in shells. The outermost shell is referred to as the valence shell. Technically, we could say that this insight represents a generalization based on solutions of Schrödinger’s equation (which was in turn based on compiled experimental data detailing the differences between subatomic particles and the macroscopic particles which Newton’s laws accurately describe). This much should be familiar from an elementary course in chemistry or physics. Another generalization which may be less familiar is that electron density often tends to concentrate in lobes in the valence shell for elements like C, N, O, F, S, Cl. These lobes may be occupied by protons that are tetrahedrally coordinated as in CH_4 , or they may be occupied by unbonded electron pairs that fill out the tetrahedral coordination as in NH_3 or H_2O . These elements (H, C, N, O, F, S, Cl) and some noble gases like He, Ne, and Ar provide virtually all of the building blocks for the molecules to be considered in this text. The two generalizations discussed here are sufficient to describe what we need to know about intermolecular forces at the introductory level.

By considering the implications of atomic structure and atomic collisions, it is possible to develop subclassifications of intermolecular forces. These are:

1. Electrostatic forces between charged particles (ions) and between permanent dipoles, quadrupoles, and higher multipoles.

 Engineering model potentials permit representation of attractive and repulsive forces in a tractable form.

2. Induction forces between a permanent dipole (or quadrupole) and an induced dipole.
3. Forces of attraction (dispersion forces) and repulsion between nonpolar molecules.
4. Specific (chemical) forces leading to association and complex formation, especially evident in the case of hydrogen bonding.

Further, attractive forces will be quantified by negative numerical values, and repulsive forces will be characterized by positive numerical values.

Electrostatic Forces

The force between two point charges described by Coulomb's Law is very similar to the law of gravitation and should be familiar from elementary courses in chemistry and physics,

$$F \propto \frac{q_i q_j}{r^2}$$

where q_i and q_j are the charges, and r is the separation of centers. Upon integration, $u = \int F dr$, the potential energy is proportional to inverse distance,

$$u \propto \frac{q_i q_j}{r}$$

If all molecules were perfectly spherical and rigid, the only way that these electrostatic interactions could come into play is through the presence of ions. But a molecule like NH_3 is not perfectly spherical. NH_3 has three protons on one side and a lobe of electron density in the unbonded valence shell electron pair. This permanent asymmetric distribution of charge density gives rise to a permanent dipole on the NH_3 molecule. This means that ammonia molecules lined up with the electrons facing each other will repel while molecules lined up with the electrons facing the protons will attract. Since electrostatic energy drops off as r^{-1} , one might expect that the impact of these forces would be long range. Fortunately, with the close proximity of the positive charge to the negative charge in a molecule like NH_3 , the charges tend to cancel each other as the molecule spins and tumbles about through a fluid. This spinning and tumbling makes it reasonable to consider a spherical average of the intermolecular energy as a function of distance that may be constructed by averaging over all orientational angles between the molecules at each distance. In a large collection of molecules randomly distributed to each other, this averaging approach gives rise to many cancellations, and the net impact is that

$$u_{\text{dipole-dipole}} = \frac{-\mathcal{G}_{\text{dipole}}}{r^6 \epsilon_0 k_B T} \quad 1.1$$

This surprisingly simple result is responsible for a large part of the attractive energy between polar molecules. This energy is attractive because the molecules tend to spend somewhat more time lined up attractively than repulsively, and the r^{-6} power arises from the many cancellations that occur in a fluid.

Induction Forces

When a molecule with a permanent dipole approaches a molecule with no dipole, the positive charge of the dipolar molecule will tend to pull electron density away from the nonpolar molecule and "induce" a dipole moment into the nonpolar molecule. The magnitude of this effect depends on

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the strength of the dipole and a fundamental property of the nonpolar molecule called “polarizability.” For example, the pi bonding in benzene makes it fairly polarizable. A similar consideration of the spherical averaging described in relation to electrostatic forces results in

$$U_{\text{in}} = \frac{-2^2 b}{r^6} \quad 1.2$$

Disperse Attraction Forces (Dispersion Forces)

 The r^{-6} dependence of attractive forces has a theoretical basis.

When two nonpolar molecules approach, they may also induce dipoles into each other. Clearly these would be weak, and this is why the forces between the noble gases are so weak. Nevertheless, their dependence on radial distance may be analyzed similarly to the electrostatic forces, and this gives the same form for the attractive forces:

$$U_{\text{disp}} = \frac{-2^2 b}{r^6} \quad 1.3$$

Repulsive Forces

Another aspect of the collisions between molecules that we have not addressed yet is what happens when the electron clouds begin to interpenetrate significantly. Clearly this would give rise to a strong repulsive force which is generally referred to as a repulsive dispersion force. This force increases rapidly as radial distance decreases, and quickly outweighs the attractive force when the atoms get too close together. Two atoms do not like to be in the same place at the same time. A common and useful way to express this is

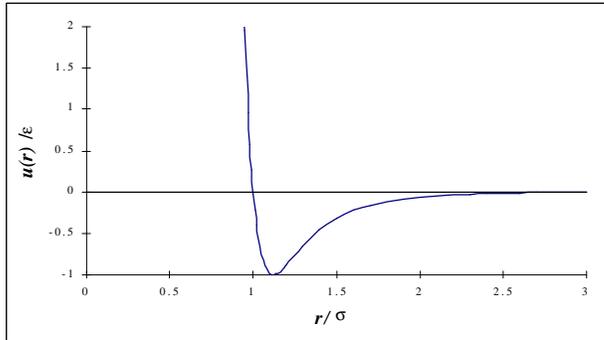
$$U_{\text{disp}}^{\text{rep}} = \frac{c}{r^{12}} \quad 1.4$$

Specific (Chemical) Forces

What happens when the strength of interaction between two molecules is so strong at certain orientations that it does not make sense to spherically average over it? For instance, it would not make sense to spherically average when two atoms were permanently bound in a specific orientation. But if they were permanently bound together we would call that a chemical reaction and handle it in a different way. An interesting problem arises when the strength of interaction is too strong to be treated entirely by spherically averaging and too weak to be treated as a normal chemical reaction which forms permanent stable chemical species. Clearly, this problem is difficult and it would be tempting to try to ignore it. In fact, most of this course will deal with theories that treat only what can be derived by spherically averaging. But it should be kept in mind that these specific forces are responsible for some rather important properties, especially in the form of hydrogen bonding. Since many systems are aqueous or contain amides or alcohols, ignoring hydrogen bonding entirely would substantially undermine the accuracy of our conceptual foundation. Fortunately, the nature of these forces is such that we can often approximate them as strong association forces to obtain a crude engineering model that is workable.

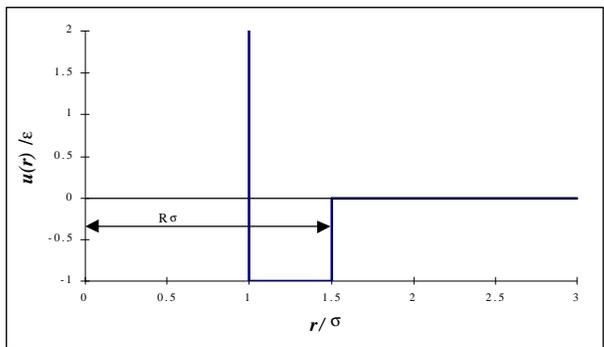
Examples of Model Potentials

Based on the forms of these electrostatic, induction, and dispersion forces, it should be easy to appreciate the form of the Lennard-Jones potential in Fig. 1.1. Other models of the potential function are possible, such as the square-well potential or the Sutherland potential also shown in Fig. 1.1. These latter potential models represent simplified forms of the Lennard-Jones model that are accurate enough for many applications.



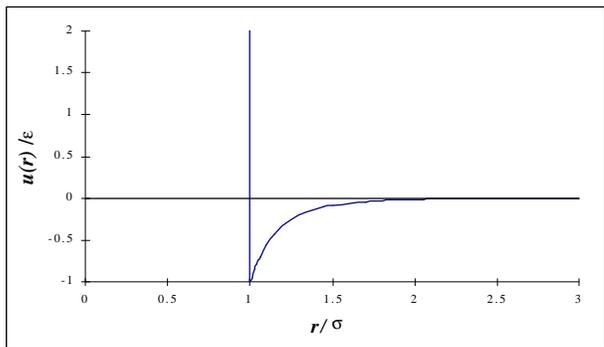
$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

The Lennard-Jones potential



$$u(r) = \begin{cases} \infty & \sigma \geq r \\ -\epsilon & \sigma < r < R\sigma \\ 0 & r \geq R\sigma \end{cases}$$

The square-well potential for $R = 1.5$.



$$u(r) = \begin{cases} \infty & r \leq \sigma \\ -\epsilon(\sigma/r)^6 & r > \sigma \end{cases}$$

The Sutherland potential.

Figure 1.1 Schematics of three engineering models for pair potentials on a dimensionless basis.

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The key features of all of these potential models are the representation of the size of the molecule by the parameter σ and the attractive strength (i.e. “stickiness”) by the parameter ϵ . Note that we would need a more complicated potential model to represent the shape of the molecule. Typically, molecules of different shapes are represented by binding together several potentials like those above with each potential site representing one molecular segment. For example, *n*-butane could be represented by four Lennard-Jones sites that have their relative centers located at distances corresponding to the bond-lengths in *n*-butane. The potential between two butane molecules would then be the sum of the potentials between each of the individual Lennard-Jones sites on the different molecules. In similar fashion, potential models for very complex molecules can be constructed.

We can gain considerable insight about the thermodynamics of fluids by intuitively reasoning about the relatively simple effects of size and stickiness. For example, a large molecule like buckminsterfullerene would have a larger value for σ than would methane. Water and methane are about the same size, but their difference in boiling temperature indicates a large difference in their stickiness. As you read through this chapter, it should become apparent that water has a higher boiling temperature because it sticks to itself more strongly than does methane. With these simple insights, you should be able to understand the molecular basis for a large number of macroscopic phenomena.

Example 1.1 Intermolecular potentials for mixtures

Our discussion of intermolecular potentials has focused on describing single molecules, but it is actually more interesting to compare and contrast the potential models for different molecules that are mixed together. We can use the square-well potential as the basis for this exercise and focus simply on the size (σ_{ij}) and stickiness (ϵ_{ij}) of each potential model, where the subscript ij indicates an interaction of molecule i with molecule j . For example, ϵ_{11} would be the stickiness of molecule 1 to itself, and ϵ_{12} would be its stickiness to a molecule of type 2. The size parameter for interaction between different molecules is reasonably well represented by $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$. The estimation of the stickiness parameter for interaction between different molecules requires some intuitive reasoning. For mixtures of hydrocarbons, it is conventional to estimate the stickiness by a geometric mean. To illustrate, sketch on the same pair of axes the potential models for methane and benzene, assuming that the stickiness parameter is given by $\epsilon_{12} = (\epsilon_{11} \epsilon_{22})^{1/2}$.

Solution:

Methane(1) has fewer atoms in it than benzene(2), so we can assume it is smaller. Let's depict this by saying $\sigma_{22} = 2\sigma_{11}$. This means that $\sigma_{12} = 1.5\sigma_{11}$. Similarly, methane's boiling temperature is lower so its stickiness should be smaller in magnitude. Let's depict this by $\epsilon_{22} = 4\epsilon_{11}$ and this means $\epsilon_{12} = 2\epsilon_{11}$. Thus we obtain Fig. 1.2.

1.2 THE MOLECULAR NATURE OF ENTROPY

To be fair to both of the central concepts of the course, we must mention entropy at this point, in parallel with the mention of energy. Unfortunately, there is no simple analogy that can be drawn like that of the potential energy between the earth and moon. The study of entropy is fairly specific to the study of thermodynamics. The proper development of the subject must await Chapter 3.

What we can say at this point is that entropy has been conceived to account for losses in the prospect of performing useful lost work. The energy can take on many forms and be completely accounted for without contemplating how much energy has been “wasted” by converting work into

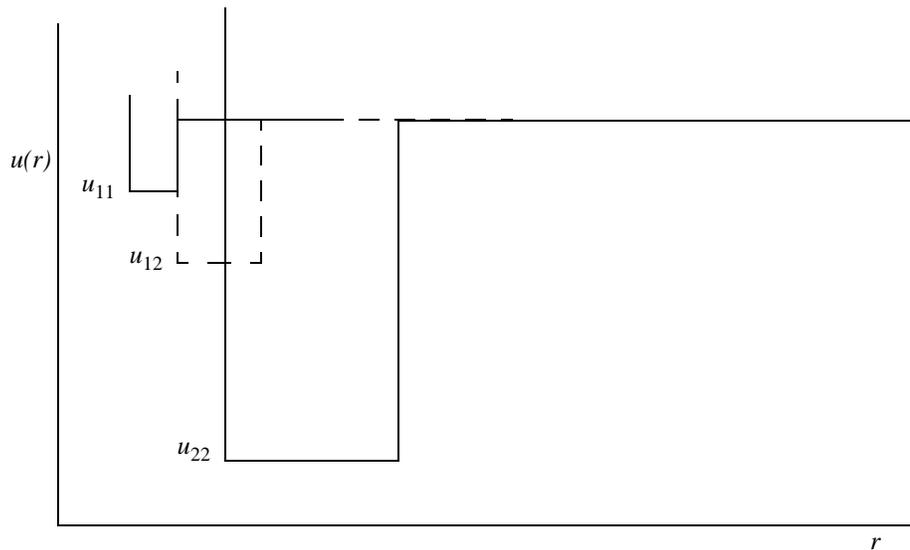


Figure 1.2 Sketch of intermolecular square-well potential models for a mixture of methane and benzene for $R = 1.5$ as explained in Example 1.1.

something like warm water. Entropy accounts for this kind of wastefulness. It turns out that the generation of such wastes can be directly related to the degree of disorder involved in conducting our process. Thus generation of disorder results in lost work. Furthermore, work that is lost by not maintaining order cannot be converted into useful work. To see the difference between energy and entropy, consider the following example. Oxygen and nitrogen are mixed as ideal gases at room temperature and pressure. How much energy is evolved in the mixing process? How much work must be exerted to separate them again? The answer to the first question is that no energy is involved. Ideal gases are point masses with no potential energy to affect the mixing. For the answer to the second question, however, we must acknowledge that a considerable effort would be involved. The minimum amount required is given by the “lost work,” which we will discuss in Chapter 3.

1.3 BRIEF SUMMARY OF SEVERAL THERMODYNAMIC QUANTITIES

Internal Energy

It may be somewhat confusing that kinetic and potential energy exist on the macroscopic level and the microscopic level. It is frequently convenient to lump the microscopic energies together and consider them as the *internal energy* of the system which is given the symbol U . The remaining potential energy and kinetic energy are the macroscopic properties of the complete system and can be accounted for separately. The internal energy is a function of the temperature and density of the system, and it does not usually change if the entire system is placed on, say, an airplane. This is the convention followed throughout the remainder of Unit I. In Units II and III, we reexamine the molecular potentials as to how they affect the bulk fluid properties. Thus, throughout the remainder of Unit I, when we refer to kinetic and potential energy of a body of fluid as a system, we will be referring to the kinetic energy of the center of mass of the system and the gravitational potential energy of the center of mass of the system.

 The sum of microscopic random kinetic energy and intermolecular potential energies are the internal energy.



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Work

Work is a familiar term from physics. We know that work is a force acting through a distance. There are several ways forces may interact with the system which all fit under this category. We will discuss the details of how we calculate work and determine its impact on the system in the next chapter.

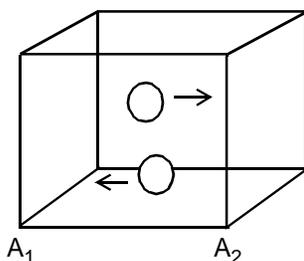
Density

Density is a measure of the mass per unit volume and may be expressed on a molar basis or a mass basis. In some situations, it is expressed as number of particles per unit volume.

Pressure — An Ultrasimplified Kinetic Theory

Pressure is the force exerted per unit area. We will be concerned primarily with the pressure exerted by the molecules of fluids upon the walls of their containers. For our purposes, the kinetic theory of pressure should provide a sufficient description.

Suppose we have two hard spherical molecules in a container that are bouncing back and forth in the x -direction only and not contacting each other.



We wish to quantify the forces acting on each wall. Since the particles are only colliding with the walls at A_1 and A_2 in our idealized model, these are the only walls we need consider. Let us assume that particles bounce off the wall with the same speed which they had before striking the wall, but in the opposite direction (a perfectly elastic collision where the wall is perfectly rigid and absorbs no momentum). Thus, the kinetic energy of the particles will be fixed. If \mathbf{u} is the initial velocity of the particle (recall that \mathbf{u} is a vector quantity and u is a scalar) before it strikes a wall, the change in velocity due to striking the wall is $-2\mathbf{u}$. The change in velocity of the particle indicates the presence of interacting forces between the wall and the particle. If we quantify the force necessary to change the velocity of the particle, we will also quantify the forces of the particle on the wall by Newton's third principle. To quantify the force, we may apply Newton's second principle stated in terms of momentum:

The time rate of change of the momentum of a particle is equal to the resultant force acting on the particle and is in the direction of the resultant force.

$$\frac{d\mathbf{p}}{dt} = \mathbf{F} \tag{1.5}$$

The application of this formula directly is somewhat problematic since the change in direction is instantaneous, and it might seem that the time scale is important. This can be avoided by determining the time-averaged force,¹ \mathbf{F}_{avg} exerted on the wall during time Δt :

1. See an introductory physics text for further discussion of time-averaged force.

Section 1.3 Brief Summary of Several Thermodynamic Quantities **13**

$$\int_{t_i}^{t_f} \mathbf{F} dt = \mathbf{F}_{avg} \Delta t = \int_{t_i}^{t_f} \frac{d\mathbf{p}}{dt} dt = \Delta \mathbf{p} \tag{1.6}$$

where $\Delta \mathbf{p}$ is the total change in momentum during time Δt . The momentum change for each collision is $-2mu$ where m is the mass per particle. Each particle will collide with the wall every t_1 seconds, where $t_1 = 2L/u$, where L is the distance between A_1 and A_2 . The average force is then

$$\mathbf{F}_{avg} = -2m\mathbf{u} \frac{u}{2L} \tag{1.7}$$

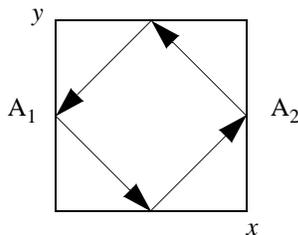
where \mathbf{u} is the velocity before the collision with the wall. Pressure is the force per unit area, and the area of a wall is L^2 , thus

$$P = \frac{m}{L^2} (u_1^2 + u_2^2) \tag{1.8}$$

P is proportional to the number of particles in a volume and to the kinetic energy of the particles.

where the subscripts denote the particles.

If the particle motions are generalized to motion in arbitrary directions, collisions with additional walls in the analysis does not complicate the problem dramatically because each component of the velocity may be evaluated independently. To illustrate, consider a particle bouncing around the centers of four walls in a horizontal plane. From the top view, the trajectory would appear as below:



For the same velocity as the first case, the force of each collision would be reduced because the particle strikes merely a glancing blow. The x -component of the force can be related to the magnitude of the velocity by noting that $u_x = u_y$, such that $u = (u_x^2 + u_y^2)^{1/2} = u_x 2^{1/2}$. The time between collisions with wall A_1 would be $4L/(u2^{1/2})$. The formula for the average force in two dimensions then becomes:

$$F_{avg, A_1} = -2m\mathbf{u}_x \frac{u\sqrt{2}}{4L} = -2m \frac{u}{\sqrt{2}} \frac{u\sqrt{2}}{4L} = -2m\mathbf{u} \frac{u}{2L} \tag{1.9}$$

and the pressure due to two particles that don't collide with each other in two dimensions becomes:

$$P = \frac{m}{2L^2} (u_1^2 + u_2^2) \tag{1.10}$$

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The extension to three dimensions is more difficult to visualize, but comparing Eqn. 1.8 to Eqn. 1.10, you should not be surprised to learn that the pressure in three dimensions is:

$$P = \frac{m}{3L^3} (u_1^2 + u_2^2) \quad 1.11$$

The problem does get more complicated when collisions between particles occur. We can ignore that possibility here because the ideal gases being considered are point masses that do not collide with each other. Computation involving molecular collisions demands a computer and is called molecular dynamics simulation. Despite the need for a computer, the program is fundamentally nothing more than computing the trajectories of two billiard balls colliding, as described briefly in the homework problems.

Temperature

The most reliable definition of temperature is that it is a numerical scale for uniquely ordering the “hotness” of a series of objects.¹ We are guaranteed that a universal scale of temperature can be developed because of the “zeroth law” of thermodynamics: if two objects are in equilibrium with a third, then they are in equilibrium with each other. The zeroth law is a law in the sense that it is a fact of experience that must be regarded as an empirical fact of nature. The significance of the zeroth law is that we can calibrate the temperature of any new object by equilibrating it with objects of known temperature. Temperature is therefore an empirical scale that requires calibration according to specific standards. The Celsius and Fahrenheit scales are in everyday use. The conversions are:

$$(T \text{ in } ^\circ\text{C}) = \frac{5}{9}((T \text{ in } ^\circ\text{F}) - 32)$$

When we perform thermodynamic calculations, we must usually use absolute temperature in Kelvin or Rankine. These scales are related by

$$(T \text{ in K}) = (T \text{ in } ^\circ\text{C}) + 273.15$$

$$(T \text{ in } ^\circ\text{R}) = (T \text{ in } ^\circ\text{F}) + 459.67$$

$$(T \text{ in R}) = 1.8 \cdot (T \text{ in K})$$

 Thermodynamic calculations use absolute temperature in °R or K.

 Temperature primarily reflects the kinetic energy of the molecules.

This definition is rigorous, but it does not provide the kind of conceptual picture that permits an easy grasp of its significance and how it relates to other important properties. A better conceptual picture is provided by considering that temperature primarily provides a measure of the kinetic energy of a system of molecules. As the molecules move faster, the temperature goes up. The absolute temperature scale has the advantage that the temperature can never be less than absolute zero. This observation is easily understood from the kinetic perspective. The kinetic energy cannot be less than zero; if the molecules are moving, their kinetic energy must be greater than zero. To better understand the connection between temperature and kinetic energy, we can apply the ideal gas law as described on page 17.

1. Denbigh, K., *The Principles of Chemical Equilibrium*, Cambridge University Press, 3rd ed., p. 9, London, 1971.



Heat – Sinks and Reservoirs

Heat is energy in transit between the source from which the energy is coming and a destination toward which the energy is going. When developing thermodynamic concepts, we frequently will assume that our system transfers heat to/from a *sink* or *reservoir*. A heat reservoir is an infinitely large source or destination of heat transfer. The reservoir is assumed to be so large that the heat transfer does not affect the temperature of the reservoir. A sink is a special name sometimes used for a reservoir which can accept heat without a change in temperature. The assumption of constant temperature makes it easier to concentrate on the thermodynamic behavior of the system while making a reasonable assumption about the part of the universe assigned to be the reservoir.

 A reservoir is an infinitely large source or destination for heat transfer.

The mechanics of heat transfer are also easy to picture conceptually from the molecular kinetics perspective. In heat conduction, faster moving molecules collide with slower ones, exchanging kinetic energy and equilibrating the temperatures. In this manner, we can imagine heat being transferred from the hot surface to the center of a pizza in an oven until the center of the pizza is cooked. In heat convection, packets of hot mass are circulated and mixed, accelerating the equilibration process. Heat convection is important in getting the heat from the oven flame to the surface of the pizza. Heat radiation, the remaining mode of heat transfer, occurs by an entirely different mechanism having to do with waves of electromagnetic energy emitted from a hot body that are absorbed by a cooler body. Radiative heat transfer is typically discussed in detail during courses devoted to heat transfer.

1.4 BASIC CONCEPTS

The System

A **system** is that portion of the universe which we have chosen to study.

A **closed** system is one in which no mass crosses the system boundaries.

An **open** system is one in which mass crosses the system boundaries. The system may gain or lose mass or simply have some mass pass through it.

System boundaries are established at the beginning of a problem, and simplification of balance equations depends on whether the system is open or closed. *Therefore, the system boundaries should be clearly identified. If the system boundaries are changed, the simplification of the mass and energy balance equations should be performed again, because different balance terms are likely to be necessary.* These guidelines will become more apparent in Chapter 2.

 The placement of system boundaries is a key step in problem solving.

The Mass Balance

Presumably, students in this course are familiar with mass balances from an introductory course in material and energy balances. The relevant relation is simply:

$$\left[\begin{array}{c} \text{rate of mass} \\ \text{accumulation within} \\ \text{system boundaries} \end{array} \right] = \left[\begin{array}{c} \text{rate of mass flow} \\ \text{into system} \end{array} \right] - \left[\begin{array}{c} \text{rate of mass flow} \\ \text{out of system} \end{array} \right]$$

$$\dot{m} = \sum_{\text{inlets}} \dot{m}^{\text{in}} - \sum_{\text{outlets}} \dot{m}^{\text{out}}$$

1.12  The mass balance.



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where $\dot{m} = \frac{dm}{dt}$, \dot{m}^{in} and \dot{m}^{out} are the absolute values of mass flow rates entering and leaving, respectively.

We may also write

$$dm = \sum_{inlets} dm^{in} - \sum_{outlets} dm^{out} \tag{1.13}$$

where mass differentials dm^{in} and dm^{out} are *always positive*. When all the flows of mass are analyzed in detail for several subsystems coupled together, this simple equation may not seem to fully portray the complexity of the application. The general study of thermodynamics is similar in that regard. A number of simple relations like this one are coupled together in a way that requires some training to understand. *In the absence of chemical reactions*, we may also write a mole balance by replacing mass with moles in the balance.

Intensive Properties

Intensive properties are those properties which are independent of the size of the system. For example, in a system at equilibrium without internal rigid/insulating walls, the temperature and pressure are uniform throughout the system and are therefore intensive properties. Likewise, mass or mole-specific properties are independent of the size of the system. For example, the molar volume ($[=]$ length³/mole), mass density ($[=]$ mass/length³), the specific internal energy ($[=]$ energy/mass) are intensive properties. Notationally in this text, intensive properties are not underlined.

 The distinction between intensive and extensive properties is key in selecting and using variables for problem solving.

Extensive Properties

Extensive properties depend on the size of the system. For example the volume ($[=]$ length³) and energy ($[=]$ energy). Extensive properties are underlined, e.g. $\underline{U} = n U$, where n is the number of moles and U is molar internal energy.

States and State Properties – The Phase Rule

Two state variables are necessary to specify the state of a *single-phase* pure fluid, i.e., two from the set P, V, T, U . Other state variables to be defined later in the text which also fit in this category are molar enthalpy, molar entropy, molar Helmholtz energy and molar Gibbs energy. *State variables must be intensive properties*. As an example, specifying P and T permits you to find the specific internal energy and specific volume of steam. Note, however, that you need to specify only one variable, the temperature or the pressure, if you want to find the properties of saturated vapor or liquid. This reduction in the needed specifications is referred to as a reduction in the “degrees of freedom.” As another example in a ternary, two-phase system, the temperature and the mole fractions of two of the components of the lower phase are state variables (the third component is implicit in summing the mole fractions to unity), but the total number of moles of a certain component is not a state variable because it is extensive. In this example, the pressure and mole fractions of the upper phase may be calculated once the temperature and lower-phase mole fractions have been specified. The number of state variables needed to completely specify the state of a system is given by the Gibbs phase rule:

$$F = C - P + 2 \tag{1.14}$$

where F is the number of state variables needed to specify the state of the system (F is also known as the number of degrees of freedom), C is the number of components, and P is the number of phases. More details on the Gibbs phase rule are given in Chapter 13.

i The Gibbs phase rule provides the number of state variables (intensive properties) to specify the state of the system.

Equilibrium

A system is in equilibrium when there is no driving force for a change of intensive variables within the system.

Steady-State Open Systems

The term *steady state* is used to refer to open systems in which the inlet and outlet mass flowrates are invariant with time and there is no mass accumulation. In addition, steady state requires that state variables at all locations are invariant with respect to time. Note that state variables may vary with position. Steady state does not require the system to be at equilibrium. For example, in a heat exchanger operating at steady state with a hot and cold stream, each stream will have a temperature gradient along its length, and there will always be a driving force for heat transfer from the hotter stream to the colder stream.

i Steady-state flow is very common in the process industry.

The Ideal Gas Law

Throughout Unit I, we frequently use thermodynamic charts and tables to obtain thermodynamic properties for various compounds. The most prevalent compounds in our study are water and the ideal gas. Properties of water are obtained from the steam tables to be discussed below. Properties of the ideal gas are calculated from the ideal gas model:

$$P\underline{V} = nRT \tag{ig} 1.15$$

P - V - T properties of the ideal gas law are shown in Fig. 1.3. The ideal gas model represents many compounds, such as air, nitrogen, oxygen, and even water vapor at temperatures and pressures near ambient conditions. Use of this model simplifies calculations while the concepts of the energy and entropy balances are developed throughout Unit I. This does not imply that the ideal gas model is applicable in all situations. Analysis using more complex fluid models is delayed until Unit II. We rely on thermodynamic charts and tables to obtain properties for fluids which may not be considered ideal gases until Unit II.

i The ideal gas law is a *model* that is not always valid, but gives an initial guess.

One application of the ideal gas law would be timely to promote better understanding of the connection of temperature with kinetic energy. We can apply the ideal gas law in conjunction with Eqn. 1.11 which was derived for a spherical (monatomic) molecule.

$$nRT = P\underline{V} = \frac{m}{3L^3} \left(\sum_{i=1}^N u_i^2 \right) L^3 \tag{ig} 1.16$$

where m is the mass per particle. Rearranging shows how the temperature is related to the average molecular kinetic energy,

$$T = \frac{m}{3R} \frac{\sum_{i=1}^N u_i^2}{n} = \frac{2}{3R} \frac{\sum_{i=1}^N \frac{mu_i^2}{2}}{N/N_A} = \frac{2N_A}{3R} \left\langle \frac{mu^2}{2} \right\rangle \tag{ig} 1.17$$

where $\langle \rangle$ brackets denote an average, and N_A denotes Avogadro's number.

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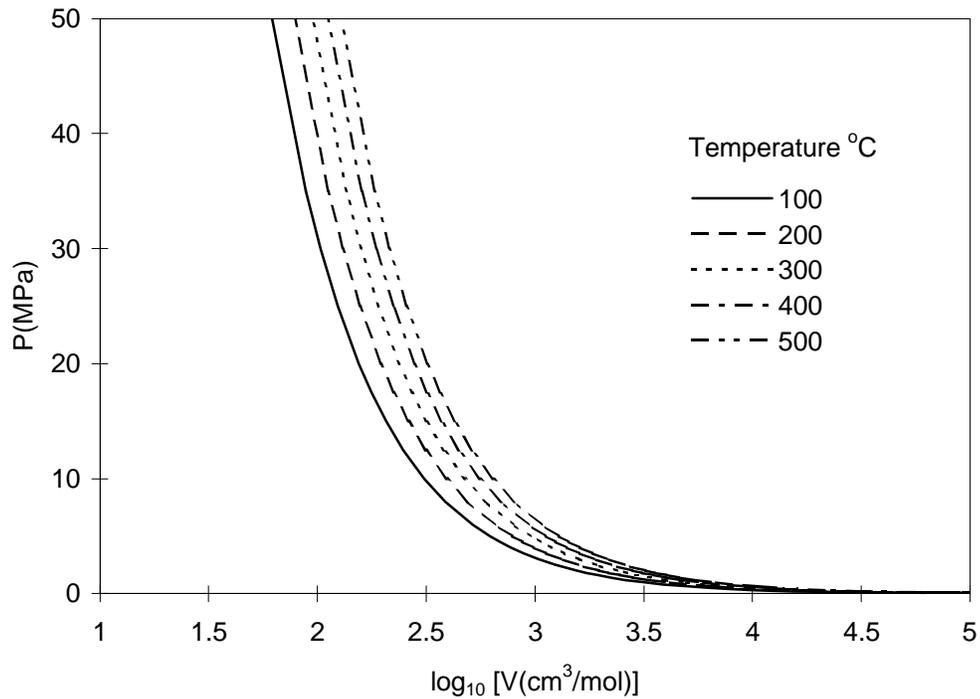


Figure 1.3 Ideal gas behavior at five temperatures.

Eqn. 1.17 may seem to be confined to ideal monatomic gases since that was the origin of its derivation, but it is actually applicable to any monatomic classical system, including monatomic liquids and solids. This means that for a pure system of a monatomic ideal gas in thermal equilibrium with a liquid, the average velocities of the molecules are independent of the phase in which they reside. The liquid molecular environment is still different from the gas molecular environment because liquid molecules are confined to move primarily within a much more crowded environment where the potential energies are more significant. Unless a molecule’s kinetic energy is sufficient to escape the potential energy, it simply collides with a higher frequency in its local environment. What happens if the temperature is raised such that the liquid molecules can escape the potential energies of its neighbors? We call that “boiling,” and the pressure must increase to keep the system in vapor-liquid phase equilibrium. The energy required to promote “boiling” is related to the heat of vaporization. Now you can begin to understand what temperature is and how it relates to other important thermodynamic properties.

For completeness, we may also mention that kinetic energy is the only form of energy for an ideal gas, so the internal energy of a monatomic ideal gas is given by:

$$\underline{U} = \frac{Nm \langle u^2 \rangle}{2} = \frac{nN_A m \langle u^2 \rangle}{2} = \frac{3}{2} nRT \tag{ig} 1.18$$

The proportionality constant between temperature and internal energy is known as the ideal gas heat capacity at constant volume, denoted C_V . Eqn 1.18 shows that $C_V = 1.5R$ for a monatomic ideal gas. If you refer to the tables of constant pressure heat capacities (C_p) on the end flap of the

text and note that $C_p = C_v + R$, you may be surprised by how accurate this ultrasimplified theory actually is for species like helium, neon, and argon at 298 K.

Note that Eqn. 1.18 shows that $U^{ig} = U^{ig}(T)$. In other words, the internal energy depends only on the temperature for an ideal gas. The observation that $U^{ig} = U^{ig}(T)$ is true for any ideal gas, not only for ultrasimplified, monatomic ideal gases. We make the most of this fact in Chapter 5, where we show how to compute changes in energy for any fluid at any temperature and density by systematically correcting the relatively simple ideal gas result.

Real Fluids

The thermodynamic behavior of real fluids differs from the behavior of ideal gases in most cases. Real fluids condense, evaporate, freeze and melt. Characterization of the volume changes and energy changes of these processes is an important skill for the chemical engineer. Many real fluids do behave *as if they are* ideal gases at typical process conditions. Application of the ideal gas law simplifies many process calculations for common gases, *e.g.*, air at room temperature and moderate pressures. However you must always remember that the ideal gas law is an approximation (sometimes an excellent approximation) that must be applied carefully to any fluid. P - V behavior of a real fluid (water) and an ideal gas can be compared in Figs. 1.3 and 1.4. The behaviors are presented along *isotherms* (lines of constant temperature) and the deviations from the ideal gas law for water are obvious. Water is one of the most common substances that we work with, and water vapor behaves nearly as an ideal gas at 100°C ($P^{sat} = 0.1014$ MPa), where experimentally the vapor volume is 1.6718 m³/kg (30,092 cm³/mol) and by the ideal gas law we may calculate $V = RT/P = 8.314 \cdot 373.15 / 0.1014 = 30,595$ cm³/mol. However, the state is the normal boiling point, and we are well aware that a liquid phase can co-exist at this state. This is because there is another density of water at these conditions that is also stable.¹

We will frequently find it convenient to work mathematically in terms of molar density or mass density, which is inversely related to molar volume or mass volume, $\rho = 1/V$. Plotting the isotherms in terms of density yields a P - ρ diagram that qualitatively looks like the mirror image of the P - V diagram. Density is convenient to use because it always stays finite as $P \rightarrow 0$, whereas V diverges. Examples of P - ρ diagrams are shown in Fig. 6.1 on page 195.

The conditions where two phases coexist are called *saturation conditions*. The terms *saturation pressure* and *saturation temperature* are used to refer to the state. The volume (or density) is called the saturated volume (or saturated density). Saturation conditions are shown in Fig. 1.4 as the “hump” on the diagram. The hump is called the *phase envelope*. Two phases coexist when the system conditions result in a state *inside* or *on* the envelope. The horizontal lines *inside* the curves are called *tie* lines that show the two volumes (saturated liquid and saturated vapor) that can coexist. The curve labeled “sat’d liquid” is also called the *bubble* line, since it represents conditions where boiling (bubbles) can occur in the liquid. The curve labeled “sat’d vapor” is also called a *dew* line, since it is the condition where droplets (dew) can occur in the vapor. Therefore, *saturation* is a term that can refer to either *bubble* or *dew* conditions. When the total volume of a system results in a system state *on* the saturated vapor line, only an infinitesimal quantity of liquid exists, and the state is indicated by the term *saturated vapor*. Likewise, when a system state is *on* the saturated liquid line, only an infinitesimal quantity of vapor exists, and the state is indicated by term *saturated liquid*. When the total volume of the system results in a system *in between* the saturation vapor and saturation liquid volumes, the system will have vapor and liquid phases coexisting, each phase occupying a finite fraction of the overall system. Note that each isotherm has a unique saturation pressure.

 Real fluids have saturation conditions, bubble points, and dew points.

1. This stability is determined by the Gibbs energy and we will defer proof until Chapter 8.

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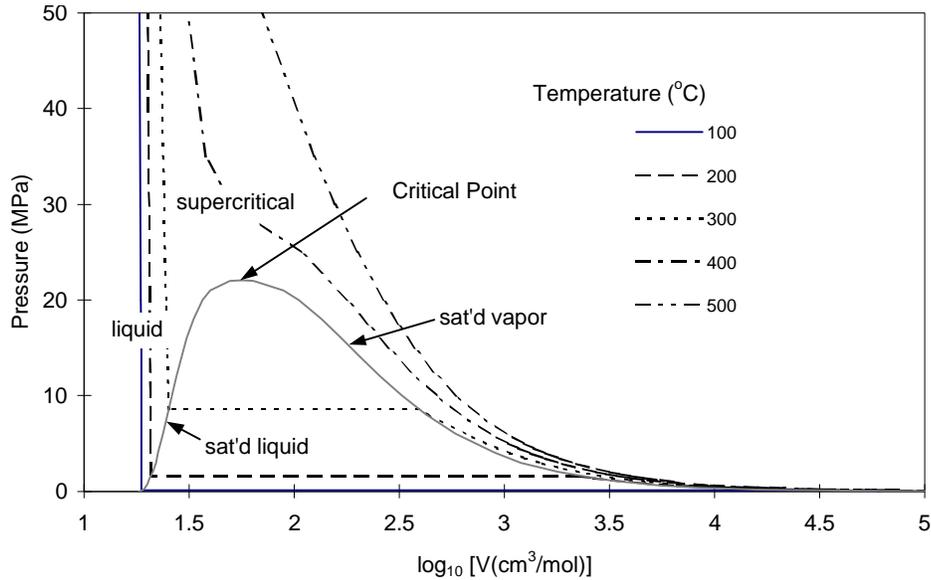


Figure 1.4 *P-V-T behavior of water at the same temperatures used in Fig. 1.3. The plot is prepared from the steam tables in Appendix E.*

This pressure is known as the *saturation* or *vapor pressure*. Although the vapor pressure is often used to characterize a pure liquid's bubble point, recognize that it also represents the dew point for the pure vapor.

Following an isotherm from the right side of the diagram along a path of decreasing volume, the isotherm starts in the vapor region, and the pressure rises as the vapor is isothermally compressed. As the volume reaches the saturation curve at the vapor pressure, a liquid phase begins to form. Notice that further volume decreases do not result in a pressure change until the system reaches the saturated liquid volume, after which further decreases in volume require extremely large pressure changes. Therefore, liquids are often treated as *incompressible* even though the isotherms really do have a finite rather than infinite slope. The accuracy of the incompressible assumption varies with the particular application.

L Liquids are quite incompressible.

As we work process problems, we will need to use properties such as the internal energy of a fluid.¹ Properties such as these are available for most common fluids in terms of a table or chart. For steam, both tables and charts are commonly used, and in this section we will introduce the steam tables available in Appendix E.

Steam Tables

When dealing with water, some conventions have developed for referring to the states which can be confusing if the terms are not clearly understood. *Steam* refers to a vapor state, and *saturated steam* is vapor at the dew point. For water, in the two-phase region, the term *wet steam* is used to indicate a vapor + liquid system.

1. Calculation of these properties requires mastery of several fundamental concepts as well as application of calculus and will be deferred. We calculate energies for ideal gas in Chapter 2 and for real fluids in Chapter 7.

Steam tables are divided into four tables. The first table presents *saturation* conditions indexed by temperature. This table is most convenient to use when the temperature is known. Each row lists the corresponding saturation values for pressure (vapor pressure), internal energy, volume and two other properties we will use later in the text: enthalpy and entropy. Special columns represent the energy, enthalpy, and entropy of vaporization. These properties are tabulated for convenience although they can be easily calculated by the difference between the saturated vapor value and the saturated liquid value. Notice that the vaporization values decrease as the saturation temperature and pressure increase. The vapor and liquid phases are becoming more similar as the saturation curve is followed to higher temperatures and pressures. At the *critical point*, the phases become identical. Notice in Fig. 1.4 that the two phases become identical at the highest temperature and pressure on the saturation curve, so this is the critical point. For a pure fluid, the critical temperature is the temperature at which vapor and liquid phases are identical on the saturation curve, and is given the notation T_c . The pressure at which this occurs is called the critical pressure, and is given the symbol P_c .

 The critical temperature and critical pressure are key characteristic properties of a fluid.

The second steam table organizes saturation properties indexed by pressure, so it is easiest to use when the pressure is known. Like the temperature table, vaporization values are presented. The table duplicates the saturated temperature table, i.e. plotting the saturated volumes from the two tables would result in the same curves. The third steam table is the largest portion of the steam tables, consisting of superheated steam values. *Superheated* steam is vapor above its saturation temperature at the given pressure. The adjective *superheated* specifies that the vapor is above the saturation temperature at the system pressure. The adjective is usually used only where necessary for clarity. The difference between the system temperature and the saturation temperature, $(T - T^{sat})$, is termed the *degrees of superheat*. The superheated steam tables are indexed by pressure and temperature. The saturation temperature is provided at the top of each pressure table so that the superheat may be quickly determined without referring to the saturation tables.

 Superheat.

The fourth steam table has liquid-phase property values at temperatures below the critical temperature and above each corresponding vapor pressure. Liquid at these states is sometimes called *subcooled* liquid to indicate that the temperature is below the saturation temperature for the specified pressure. Another common way to describe these states is to identify the system as *compressed* liquid, which indicates that the pressure is above the saturation pressure at the specified temperature. The adjectives *subcooled* and *compressed* are usually only used where necessary for clarity. Notice by scanning the table that pressure has a small effect on the volume and internal energy of liquid water. By looking at the saturation conditions together with the general behavior of Fig. 1.4 in our minds, we can determine the state of aggregation (vapor, liquid or mixture) for a particular state.

 Subcooled, compressed.

Example 1.2 Introduction to steam tables

For the following states, specify if water exists as vapor, liquid or a mixture: (a) 110°C and 0.12 MPa; (b) 200°C and 2 MPa; (c) 0.8926 MPa and 175°C.

Solution:

- (a) Looking in the saturation temperature table, the saturation pressure at 110°C is 0.143 MPa. Below this pressure, water is vapor (steam).
- (b) From the saturation temperature table, the saturation pressure is 1.5549 MPa, therefore water is liquid.
- (c) This is a saturation state listed in the saturation temperature table. The water exists as saturated liquid, saturated vapor, or a mixture.

Linear Interpolation

Since the information in the steam tables is tabular, we must interpolate to find values at states that are not listed. To interpolate, we assume the property we desire (e.g., volume, internal energy) varies linearly with the independent variables specified (e.g., pressure, temperature). The assumption of linearity is almost always an approximation, but is a close estimate if the interval of the calculation is small. Suppose we seek the value of volume, V , at pressure, P , and temperature, T , but the steam tables have only values of volume at P_1 and P_2 which straddle the desired pressure value as shown in Fig. 1.5. The two points represent values available in the tables and the solid line represents the true behavior. The dotted line represents a linear fit to the tabulated points.

Linear interpolation is a necessary skill for problem solving using thermodynamic tables.

If we fit a linear segment to the tabulated points, the equation form is $y = mx + b$, where y is the dependent variable (volume in this case), x is the independent variable (pressure in this case), m is the slope $m = \frac{\Delta y}{\Delta x} = \frac{V_2 - V_1}{P_2 - P_1}$, and b is the intercept. We can interpolate to find V without directly determining the intercept. Since the point we desire to calculate is also on the line with slope m , it also satisfies the equation $m = \frac{\Delta y}{\Delta x} = \frac{V - V_1}{P - P_1}$. We can equate the two expressions for m to find the interpolated value of V at P .

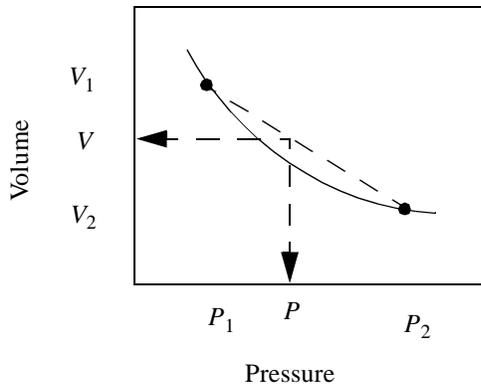


Figure 1.5 Illustration of linear interpolation.

There are two quick ways to think about the interpolation. First, since the interpolation is linear, the fractional change in V relative to the volume interval is equal to the fractional change in P relative to the pressure interval. In terms of variables:

$$\frac{V - V_1}{V_2 - V_1} = \frac{P - P_1}{P_2 - P_1}$$

For example, $(V - V_1)$ is 10% of the volume interval $(V_2 - V_1)$, when $(P - P_1)$ is 10% of $(P_2 - P_1)$. We can rearrange this expression to find:

$$V = V_1 + \frac{P - P_1}{P_2 - P_1}(V_2 - V_1) \quad 1.19$$

If we consider state “1” as the base state, we can think of this expression in words as

$$V = \text{base } V + (\text{fractional change in } P) \cdot (\text{volume interval size})$$

Another way to think of Eqn. 1.19 is by arranging it as:

$$V = V_1 + \frac{V_2 - V_1}{P_2 - P_1}(P - P_1) \quad 1.20$$

which in words is

$$V = \text{base } V + \text{slope} \cdot (\text{change in } P \text{ from base state})$$

Note that subscripts for 1 and 2 can be interchanged in any of the formulas if desired, provided that *all* subscripts are interchanged.

Example 1.3 Interpolation

Find the volume and internal energy for water at: (a) 5 MPa and 325°C, (b) 5 MPa and 269°C.

Solution:

(a) Looking at the superheated steam table at 5 MPa, we find the saturation temperature in the column heading as 263.9°C; therefore, the state is superheated. Values are available at 300°C and 350°C. Since we are halfway in the temperature interval, by interpolation the desired U and V will also be halfway in their respective intervals (which may be found by the average values):

$$U = (2699.0 + 2809.5)/2 = 2754.3 \text{ kJ/kg}$$

$$V = (0.0453 + 0.0520)/2 = 0.0487 \text{ m}^3/\text{kg}$$

(b) For this state, we are between the saturation temperature (263.9°C) and 300°C, and we apply the interpolation formula

$$U = 2597.0 + \frac{269 - 263.9}{300 - 263.9}(2699.0 - 2597.0) = 2611.4 \text{ kJ/kg}$$

$$V = 0.0394 + \frac{269 - 263.9}{300 - 263.9}(0.0453 - 0.0394) = 0.0402 \text{ m}^3/\text{kg}$$

Double Interpolation

Occasionally, we must perform double or multiple interpolation to find values. The following example illustrates these techniques

Example 1.4 Double interpolation

For water at 160°C and 0.12 MPa, find the internal energy.

Solution: By looking at the saturation tables at 160°C, water is below the saturation pressure, and will exist as superheated vapor, but superheated values at 0.12 MPa are not tabulated in the superheated table. If we tabulate the available values we find

	0.1 MPa	0.12 MPa	0.2 MPa
150°C	2582.9		2577.1
160°C			
200°C	2658.2		2654.6

We may either interpolate the first and third columns to find the values at 160°C, followed by an interpolation in the second row at 160°C, or we may interpolate the first and third rows, followed by the second column. The values found by the two techniques will not be identical because of the non-linearities of the properties we are interpolating. Generally, the more accurate interpolation should be done first, which is over the smaller change in U , which is the pressure interpolation. The pressure increment is 20% of the pressure interval $[(0.12 - 0.1)/(0.2 - 0.1)]$; therefore, interpolating in the first row

$$U = 2582.9 + 0.2 \cdot (2577.1 - 2582.9) = 2581.7 \text{ kJ/kg}$$

and in the third row

$$U = 2658.2 + 0.2 \cdot (2654.6 - 2658.2) = 2657.5 \text{ kJ/kg}$$

and then interpolating between these values, using the value at 150°C as the base value, then

$$U = 2581.7 + \frac{1}{5} \cdot (2657.5 - 2581.7) = 2596.9 \text{ kJ/kg}$$

The final results are tabulated in the shaded cells in the table:

	0.1 MPa	0.12 MPa	0.2 MPa
150°C	2582.9	2581.7	2577.1
160°C		2596.9	
200°C	2658.2	2657.5	2654.6

We also may need to interpolate between values in different tables as shown in the following example.

Example 1.5 Double interpolation using different tables

Find the internal energy for water at 0.12 MPa and 110°C.

Solution: We found in Example 1.2 on page 22 that this is a superheated state. From the superheated table we can interpolate to find the internal energy at 110°C and 0.1 MPa

$$U = 2506.2 + \frac{1}{5} \cdot (2582.9 - 2506.2) = 2521.5 \text{ kJ/kg}$$

At 0.2 MPa, 110°C is not found in the superheated table because the saturation temperature is 120.3°C so the values at this pressure cannot be used. Therefore, we can find the desired internal energy by interpolation using the value above and the saturation value at 110°C and 0.143 MPa from the saturation temperature table.

$$U = 2521.5 + \frac{0.12 - 0.1}{0.143 - 0.1} (2517.7 - 2521.5) = 2519.7 \text{ kJ/kg}$$

Interpolation Program

Please note that an interpolation program is included for HP calculators as described in Appendix P. Occasionally, interpolation must be performed when the T and P are both unknown. Computers or spreadsheets can be helpful as shown in the next example.

Example 1.6 Double interpolation using Excel

Steam undergoes a series of state changes and is at a final state where $U = 2650$ kJ/kg and $V = 0.185$ m³/kg. Find the T and P .

Solution: Scanning the steam tables, the final state is in the range 1.0 MPa $< P < 1.2$ MPa, $200^\circ\text{C} < T < 250^\circ\text{C}$. The final state requires a double interpolation using U and V . One easy method is to set up the table in Excel. In each of the tables below, the pressure interpolation is performed first in the top and bottom rows, dependent on the pressure variable in the top of the center column, which can be set at any intermediate pressure to start. The temperature interpolation is then entered in the center cell of each table using the temperature variable. The formulas in both tables reference a common temperature variable cell and a common pressure variable cell. Solver is started and T and P are adjusted to make $U = 2650$ kJ/kg subject to the constraint $V = 0.185$ m³/kg. (See Appendix B for Solver instructions.) The converged result is shown at $T = 219.6^\circ\text{C}$ and $P = 1.17$ MPa.

 Example use of Excel for double interpolation.

		P ^f		
U(kJ/kg) table		P = 1 MPa	1.164752	P = 1.2 MPa
T ^f	T = 200°C	2622.2	2614.539	2612.9
	219.4486791		2650	
	T = 250°C	2710.4	2705.705	2704.7

V(m ³ /kg) table		P = 1 MPa		P = 1.2 MPa
	T = 200°C	0.2060	0.175768	0.1693
			0.185	
	T = 250°C	0.2327	0.199502	0.1924

Extrapolation

Occasionally the values we seek are not conveniently between points in the table and we can apply the “interpolation” formulas to extrapolate as shown in Fig. 1.6. In this case, T lies outside the interval. Extrapolation is much less certain than interpolation since we frequently do not know “what curve lies beyond” that we may miss by linear approximation. The formulas used for extrapolation are identical to those used for interpolation. With the steam tables, extrapolation is generally not necessary at normal process conditions and should be avoided if possible.

Phase Equilibrium and Quality

Along the saturation curve in Fig. 1.4 on page 20, there is just one degree of freedom ($F = C - P + 2 = 1 - 2 + 2 = 1$). If we seek saturation, we may choose either a T^{sat} or a P^{sat} , and the other is determined. The vapor pressure increases rapidly with temperature as shown in Fig. 1.7 on page 28. A plot of $\ln P^{sat}$ vs. $\frac{1}{T^{sat}}$ is nearly linear and over large intervals, so for accurate interpolations, vapor

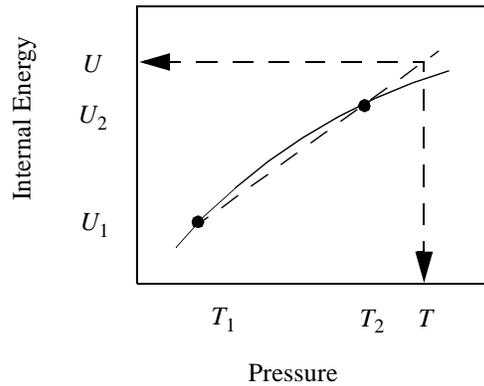


Figure 1.6 Illustration of linear extrapolation.

pressure data should be converted to this form before interpolation. However, the steam tables used with this text have small enough intervals that direct interpolation can be applied to P^{sat} and T^{sat} without appreciable error.

The saturation volume values of the steam tables were used to generate the phase diagram of Fig. 1.4 on page 20. Note that as the critical point is approached, the saturation vapor and liquid values approach each other. The same occurs for internal energy and two properties that will be used in upcoming chapters, enthalpy, H , and entropy, S . When a mixture of two phases exists, we must characterize the fraction that is vapor, since the vapor and liquid property values differ significantly.

The mass percentage that is vapor is called the *quality* and given the symbol q . The properties V , U , H , or S , may be represented with a generic variable M . The *overall* value of the state variable M is

Quality is the vapor mass percentage of a vapor/liquid mixture.

$$M = (1 - q) M^L + qM^V \tag{1.21}$$

which may be rearranged

$$M = M^L + q(M^V - M^L)$$

but $(M^V - M^L)$ is just ΔM^{vap} and for internal energy, enthalpy, and entropy, it is tabulated in columns of the saturation tables. The value of overall M is

$$M = M^L + q\Delta M^{vap} \tag{1.22}$$

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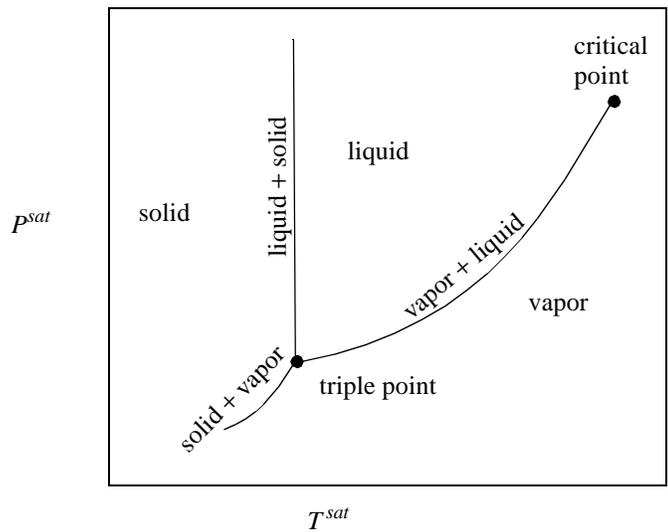


Figure 1.7 *P-T representation of real fluid behavior. Note that only vapor and liquid behavior is shown in Fig. 1.4 on page 20.*

Example 1.7 Quality calculations

Two kg of water coexists as vapor and liquid at 280°C in a 0.05 m³ rigid container. What is the pressure, quality, and overall internal energy of the mixture?

Solution:

The overall mass volume is $V = 0.05 \text{ m}^3 / 2 \text{ kg} = 0.025 \text{ m}^3/\text{kg}$. From the saturation temperature table, the pressure is 6.417 MPa. Using the saturation volumes at this condition to find q ,

$$0.025 = 0.001333 + q (0.0302 - 0.0013) \text{ m}^3/\text{kg}$$

which leads to $q = 0.82$. The overall internal energy is

$$U = 1228.33 + 0.82 \cdot 1358.1 = 2342 \text{ kJ/kg}$$

Example 1.8 Constant volume cooling

Steam is initially contained in a rigid cylinder at $P = 30 \text{ MPa}$ and $V = 10^{2.498} \text{ cm}^3/\text{mole}$ (as shown on Fig. 1.8). The cylinder is allowed to cool to 300°C . What is the pressure, quality, and overall internal energy of the final mixture?

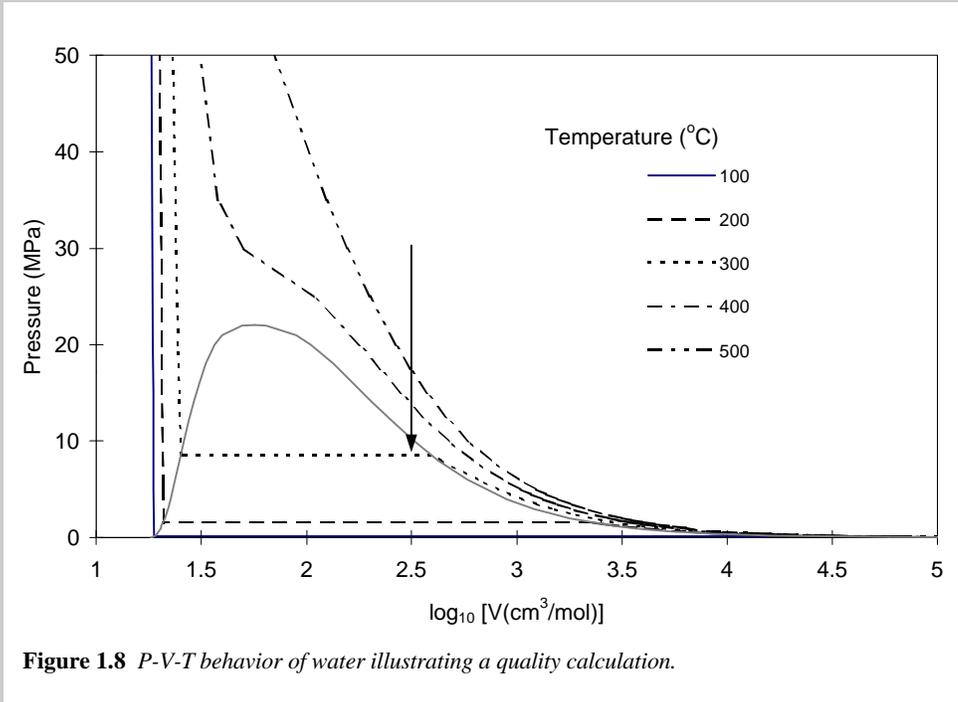


Figure 1.8 P-V-T behavior of water illustrating a quality calculation.

Solution:

The overall mass volume is $V = 10^{2.498} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot 10^{-6} (\text{m}^3/\text{cm}^3) / (18.02 \text{E-}3 \text{ kg/mole}) = 0.01747 \text{ m}^3/\text{kg}$. From the superheated steam table at 30 MPa , the initial temperature is 900°C . When the cylinder is cooled to 300°C , you should notice that there is no pressure in the superheated steam tables that provides a volume of $V = 0.01747 \text{ m}^3/\text{kg}$. Look hard, they are all too large. (Imagine yourself looking for this on a test when you are in a hurry.) Now look in the saturated steam tables at 300°C . Notice that the saturated vapor volume is $0.0217 \text{ m}^3/\text{kg}$. Since that is higher than the desired volume, but it is the lowest vapor volume at this temperature, we must conclude that our condition is somewhere between the saturated liquid and the saturated vapor at a pressure of 8.588 MPa . (When you are in a hurry, it is advisable to check the saturated tables first.)

Using the saturation volumes at 300°C condition to find q ,

$$0.01747 = 0.001404 + q (0.0217 - 0.001404) \text{ m}^3/\text{kg}$$

which leads to $q = (0.01747 - 0.001404) / (0.0217 - 0.001404) = 0.792$. The overall internal energy is

$$U = 1332.95 + 0.792 \cdot 1230.67 = 2308 \text{ kJ/kg}$$

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1.5 SUMMARY

Years from now you may have some difficulty recalling the details presented in this text. That is nothing to be embarrassed about. On the other hand, the two basic premises outlined in this introductory section are so fundamental to technically educated people that you really should commit them to long-term memory as soon as possible. Formally, we may state our two basic premises as the first and second “laws” of thermodynamics.¹

First Law: Overall energy is conserved (you can’t get something for nothing).

Second Law: Overall entropy changes are greater than or equal to zero (generation of disorder results in lost work).

The first law is further developed in Chapter 2. The concepts of entropy and the second law are developed in Chapters 3 and 4. The exact overall relationship of our two basic premises to these two laws may not become apparent until some time later in this text, but you can refer back to appropriate sections of the text at any time. What you should concentrate on is remembering the basic premises and where to look for the details when the need arises. There are times when the endeavor to apply these simple tasks seems daunting, but the answer appears simple in retrospect, once obtained. By practicing adaptation of the basic principles to many specific problems, you will slowly grasp the appropriate connection between the basic premises and finding the details. Try not to be distracted by the vocabulary or the tedious notation that goes into keeping all the coupled systems classified in textbook fashion. Keep in mind that other students have passed through this and found the detailed analysis to be worth the effort.

A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made upon me.

Albert Einstein

Test Yourself

1. Draw a sketch of the force model implied by the square-well potential, indicating the position(s) where the force between two atoms is zero and the positions where it is nonzero.
2. Explain in words how the pressure of a fluid against the walls of its container is related to the velocity of the molecules.
3. What is it about molecules that requires us to add heat to convert liquids to gases?
4. If the kinetic energy of pure liquid and vapor molecules at phase equilibrium must be the same, and the internal energy of a system is the sum of the kinetic and potential energies, what does this say about the intensive internal energy of a liquid phase compared with the intensive internal energy of the gas phase?
5. Explain the terms “energy,” “potential energy,” “kinetic energy,” “internal energy.”

1. There is also a “third law” of thermodynamics, as discussed by Denbigh, K., *The Principles of Chemical Equilibrium*, 4th ed., p. 416, Cambridge University Press, London, 1981. We will not be using the third law in this introductory text, however.

6. How is the internal energy of a substance related to the intermolecular pair potentials of the molecules?
7. Are T and P intensive properties? Name two intensive properties and two extensive properties.
8. How many degrees of freedom exist when a pure substance coexists as a liquid and gas?
9. Can an ideal gas condense? Can real fluids that follow the ideal gas law condense?
10. Give examples of bubble, dew, saturation, and superheated conditions. Explain what is meant when wet steam has a quality of 25%.
11. Create and solve a problem that requires double interpolation.

1.6 HOMEWORK PROBLEMS

Note: Some of the steam table homework problems involve enthalpy, H , which is defined for convenience using properties discussed in this chapter, $H \approx U + PV$. The enthalpy calculations can be performed by reading the tabulated enthalpy values from the tables in an analogous manner used for internal energy.

- 1.1 In each of the following, sketch your estimates of the intermolecular potentials between the given molecules and their mixture on the same pair of axes.
 - (a) Chloroform is about 20% larger than acetone and about 10% stickier, but chloroform and acetone stick to each other much more strongly than they stick to themselves.
 - (b) You have probably heard that “oil and water don’t mix.” What does that mean in molecular terms? Let’s assume that oil can be characterized as benzene and that benzene is four times larger than water, but water is 10% stickier than benzene. If the ϵ_{12} parameter is practically zero, that would represent that the benzene and water stick to themselves more strongly than to each other. Sketch this.
- 1.2 For each of the states below, calculate the number of moles of ideal gas held in a three liter container.
 - (a) $T = 673 \text{ K}$, $P = 2 \text{ MPa}$
 - (b) $T = 500 \text{ K}$, $P = 0.7 \text{ MPa}$
 - (c) $T = 450 \text{ K}$, $P = 1.5 \text{ MPa}$
- 1.3 A 5 m^3 tank farm gas storage tank contains methane. The initial temperature and pressure are $P = 1 \text{ bar}$, $T = 18^\circ\text{C}$. Calculate the T and P following each of the successive steps.
 - (a) 1 m^3 (at standard conditions) is withdrawn isothermally.
 - (b) The sun warms the tank to 40°C .
 - (c) 1.2 m^3 (at standard conditions) is added to the tank and the final temperature is 35°C .
 - (d) The tank cools overnight to 18°C .
- 1.4 A 5 m^3 outdoor gas storage tank warms from 10°C to 40°C on a sunny day. If the initial pressure was 0.12 MPa at 10°C , what is the pressure at 40°C , and how many moles of gas are in the tank? Use the ideal gas law.
- 1.5 An automobile tire has a pressure of 255 kPa (gauge) in the summer when the tire temperature after driving is 50°C . What is the wintertime pressure of the same tire at 0°C if the volume of the tire is considered the same and there are no leaks in the tire?

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- 1.6 Calculate the mass density of the following gases at 298 K and 1 bar.
- nitrogen
 - oxygen
 - air (use average molecular weight)
 - CO₂
 - argon
- 1.7 Calculate the mass of air (in kg) that is contained in a classroom that is 12m x 7m x 3m at 293 K and 0.1 MPa.
- 1.8 Five grams of the specified pure solvent is placed in a variable volume piston. What is the molar volume of the pure system when 50% and 75% have been evaporated at: (i) 30°C, (ii) 50°C? Use the Antoine Equation (Appendix E) to relate the saturation temperature and saturation pressure. Use the ideal gas law to model the vapor phase. Show that the volume of the system occupied by liquid is negligible compared to the volume occupied by vapor.
- hexane ($\rho^L = 0.66 \text{ g/cm}^3$)
 - benzene ($\rho^L = 0.88 \text{ g/cm}^3$)
 - ethanol ($\rho^L = 0.79 \text{ g/cm}^3$)
 - water without using the steam tables ($\rho^L = 1 \text{ g/cm}^3$)
 - water using the steam tables
- 1.9 A gasoline spill is approximately 4 liters of liquid. What volume of vapor is created at 1 bar and 293°C when the liquid evaporates? The density of regular gasoline can be estimated by treating it as pure isooctane (2,2,4-trimethylpentane $\rho^L = 0.692 \text{ g/cm}^3$) at 298 K and 1 bar.
- 1.10 LPG is a useful fuel in rural locations without natural gas pipelines. A leak during the filling of a tank can be extremely dangerous because the vapor is more dense than air and drifts to low elevations before dispersing, creating an explosion hazard. What volume of vapor is created by a leak of 40L of LPG? Model the liquid before leaking as propane with $\rho^L = 0.24 \text{ g/cm}^3$. What is the mass density of pure vapor propane after depressurization to 293 K and 1 bar? Compare with the mass density of air at the same conditions.
- 1.11 The gross lifting force of a balloon is given by $(\rho_{\text{air}} - \rho_{\text{gas}})V_{\text{balloon}}$. What is the gross lifting force (in kg) of a hot air balloon of volume 1.5E6 L, if the balloon contains gas at 100°C and 1 atm? The hot gas is assumed to have an average molecular weight of 32 due to carbon dioxide from combustion. The surrounding air has an average molecular weight of 29 and is at 25°C and 1 atm.
- 1.12 The gas phase reaction $A \rightarrow 2R$ is conducted in a 0.1-m³ spherical tank. The initial temperature and pressure in the tank are 0.05 MPa and 400 K. After species A is 50% reacted, the temperature has fallen to 350 K. What is the pressure in the vessel?
- 1.13 A gas stream entering an absorber is 20 mol% CO₂ and 80 mol% air. The flowrate is 1 m³/min at 1 bar and 360 K. When the gas stream exits the absorber, 98% of the incoming CO₂ has been absorbed into a flowing liquid amine stream.
- What are the gas stream mass flowrates on the inlet and outlets in g/min?
 - What is the volumetric flowrate on the gas outlet of the absorber if the stream is at 320 K and 1 bar?

1.14 A permeation membrane separates an inlet air stream, F , (79 mol% N_2 , 21 mol% O_2) into a permeate stream, M , and a reject stream, J . The inlet stream conditions are 293 K, 0.5 MPa, and 2 mol/min; the conditions for both outlet streams are 293 K and 0.1 MPa. If the permeate stream is 50 mol% O_2 , and the reject stream is 13 mol% O_2 , what are the volumetric flowrates (L/min) of the two outlet streams?

1.15 For water at each of the following states, determine the internal energy and enthalpy using the steam tables.

$T(^{\circ}C)$	$P(\text{MPa})$
(a) 100	0.01
(b) 550	6.25
(c) 475	7.5
(d) 80	0.7

1.16 (a) What size vessel holds 2 kg water at $80^{\circ}C$ such that 70% is vapor? What are the pressure and internal energy?

(b) A 1.6-m^3 vessel holds 2 kg water at 0.2 MPa. What are the quality, temperature, and internal energy?

1.17 Determine the temperature, volume, and quality for water under the following conditions:

(a) $U = 3000 \text{ kJ/kg}$, $P = 0.3 \text{ MPa}$

(b) $U = 2900 \text{ kJ/kg}$, $P = 1.7 \text{ MPa}$

(c) $U = 2500 \text{ kJ/kg}$, $P = 0.3 \text{ MPa}$

(d) $U = 350 \text{ kJ/kg}$, $P = 0.03 \text{ MPa}$

1.18 Three kg of saturated liquid water are to be evaporated at $60^{\circ}C$.

(a) At what pressure will this occur at equilibrium?

(b) What is the initial volume?

(c) What is the system volume when 2 kg have been evaporated? At this point, what is ΔU relative to the initial state?

(d) What are ΔH and ΔU relative to the initial state for the process when all three kg have been evaporated?

(e) Make a qualitative sketch of parts (b) through (d) on a P - V diagram, showing the phase envelope.

1.19 Two kg of water exist initially as a vapor and liquid at $90^{\circ}C$ in a rigid container of volume 2.42 m^3 .

(a) At what pressure is the system?

(b) What is the quality of the system?

(c) The temperature of the container is raised to $100^{\circ}C$. What is the quality of the system, and what is the pressure? What are ΔH and ΔU at this point relative to the initial state?

(d) As the temperature is increased, at what temperature and pressure does the container contain only saturated vapor? What is ΔH and ΔU at this point relative to the initial state?

(e) Make a qualitative sketch of parts (a) through (d) on a P - V diagram, showing the phase envelope.

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1.20 A molecular simulation sounds like an exceedingly advanced subject, but it is really quite simple for purely repulsive bodies.¹ To illustrate, write a simple program that computes the time to collision for four purely repulsive disks bouncing in two dimensions around a square box. Let the diameters of your disks, σ , be 0.3 nm, masses be 14 g/mole, and the length of the square box, L , be 0.8 nm. Start the four disks at $(0.25L, 0.25L)$, $(0.75L, 0.25L)$, $(0.25L, 0.75L)$, $(0.75L, 0.75L)$ and with initial velocities of $(u, 0)$, $(0, u)$, $(u/2^{1/2}, -u/2^{1/2})$, $(-u/2^{1/2}, -u/2^{1/2})$.

- (a) Compute u initially from Eqn. 1.17 assuming a temperature of 298 K.
- (b) Write a vector formula for computing the center to center distance between two disks given their velocities, \mathbf{u} , and their positions, \mathbf{r}_0 , at a given time, t_0 . Write a similar formula for computing the distance of each disk from each wall.
- (c) Noting that energy and momentum must be conserved during a collision, write a vector formula for the changes in velocity of two disks after collision. Write a similar formula for the change in velocity of a disk colliding with a wall.
- (d) Each step of your program should compute the time to collision for each disk with each wall, and for disk 1 with disks 2 and 3 and for disk 2 with disk 3. Then find the collision which occurs first and increment the positions of all the disks according to their velocities and the time to collision (Note: $\mathbf{r} - \mathbf{r}_0 = \mathbf{u}(t - t_0)$). Collisions occur when the distance between two disks is equal to one disk diameter.
- (e) Compute the directions of the disk(s) after collision then repeat the process for one million collisions.
- (f) Compute the "pressure" by accumulating over time the momentum changes per unit length for one of the walls and dividing by the total time. This formula for "pressure" assumes that there is only a single plane where molecules exist, therefore, it is really a tension ($\tau = \text{force per unit length}$). What value do you obtain for the quantity $Z = \tau L^2/RT$?

1. Alder, B.J. and Wainwright, T.E., *J. Chem. Phys.*, 31:459 (1959).