Chapter 14. Intermolecular Bonding

14.1. Phases

Substances exist in three different phases (Gr. *phasis* - appearance), solid, liquid or gas. Substances exist in different phases depending on the temperature and external pressure. Some substances have more than one solid phase, but each substance has at most one liquid and one gas phase. *Phase diagrams* show which phase exists for each temperature and pressure. Fig. 14.1 shows the shapes of the boundary curves between phases for typical substances. More complex materials may have additional solid phases, or may be restricted to condensed (solid or liquid) phases due to decomposition at high temperatures.

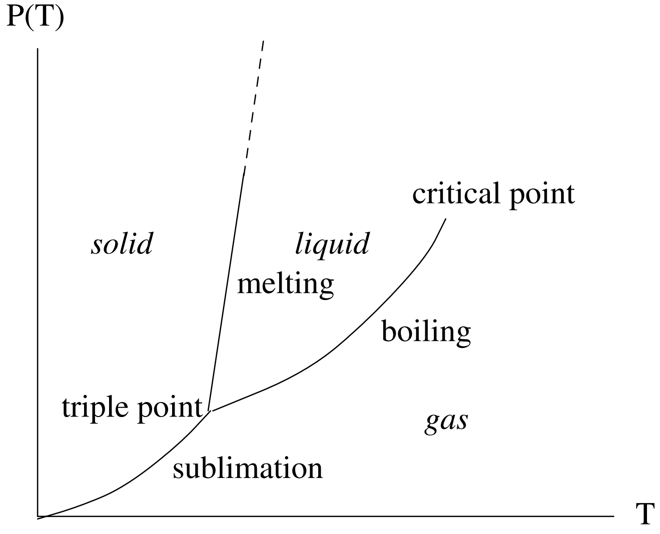

Fig. 14.1 Typical Phase Diagram

The curves separating the phases are named for the processes causing transitions across them. The curve which separates the solid and liquid phases is called the *melting curve*, that which separates the liquid and gas phases is called the *boiling, or vaporization curve*, and that which separates the solid and gas phases is called the *sublimation curve*. There is a point at which three phases coexist called the *triple point*. The point at which melting (and its reverse, freezing) occurs under one atmosphere pressure is called the *normal melting point*. The point at which boiling (and its reverse, condensation) occurs under one atmosphere pressure is called the *normal boiling point*, and the point where the boiling curve ends is called the *critical point*. (There is no evidence that melting curves end like boiling curves do.) These phase parameters characterize the various substances. The relative values of the parameters for various substances reflect the relative strengths of interactions between the molecules of the substances, called **intermolecular interactions** .

14.2. Kinetic verses Potential Energy

Molecules are so incredibly tiny, it would take a million trillion water molecules to begin to make a drop of water large enough to be visible to the naked eye.[1] Therefore nearly all the chemical experiments we perform involve enormous numbers of molecules. These molecules interact to varying degrees according to their intermolecular potential energies and move according to the laws of the kinetic-molecular theory of matter, which says that *all matter is discrete (molecular) in nature*, and that *the thermal energy of molecules is due to molecular motion*. Since liquids and solids expand by large amounts when they vaporize into gases, and since attractive forces between molecules fall off with increasing distance, it may be concluded that *the kinetic energy of the molecules of a gas dominates over any attractive potential energy interactions which may exist between the molecules*. However, as the temperature (thermal energy) decreases, the kinetic energy (thermal motion) decreases proportionally, and interactive forces begin to dominate. Eventually *all gases condense at sufficiently low temperature*.

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[1] Another dramatic example: there are so many molecules in the 5.6 million billion tons of the earth's atmosphere (average molar mass 29), that every breath an individual takes (about 2 L of air) has on average 27 of the molecules of Julius Caesar's *last breath* (or any person who has ever lived). (This can be calculated from the Ideal Gas Law below.) Talk about Spaceship Earth!

The fact that noble gases such as helium condense at all demonstrates there must be some type of mutually attractive forces between the atoms. This is not necessarily the type of bond that makes stable compounds, called *chemical bonds, as helium is chemically inert and bonds to no element. These very weak intermolecular forces are called* **van der Waals forces** in honor of the scientist who first discussed them in the context of non-ideal gas behavior.[2] *All molecules have van der Walls interactions to some degree* because all molecules condense at sufficiently low temperature. Conversely, *all molecules can be vaporized at sufficiently high temperature* (and may even be decomposed by the kinetic energy). This illustrates the fundamental interplay between the two forces at work on molecules, kinetic, tending to drive them apart, and attractive, tending to draw them together. Since molecular behavior is described accurately by wave mechanics, very detailed calculations have quantitatively confirmed the existence of van der Waals forces.

In comparing the properties of substances under varying conditions, it is useful to have a feeling for the magnitudes of the parameters involved. Differences in densities of liquids and gases may be used to estimate that the distance between molecules decreases on condensation, by about one order of magnitude.[3] Since it has been found that *attraction potential energies fall off roughly as the sixth power of the distance* ($n = 6$ in Eq. (12.5)), the interaction energy in the gas phase is a *millionfold* less than in the condensed phase.

14.3. Classes of Intermolecular Bonds

Several types of interactions can exist between atoms and molecules. "True" chemical bonds, interatomic, or *intra*molecular (internal) ionic and covalent bonds between atoms, are bound by energies of the order of hundreds of kJ (cf. Tables 12.1 and 12.2). Such substances are stable to hundreds or even thousands of degrees Kelvin before the chemical bonds are disrupted by thermal energy. Typically, ionic substances (e.g. NaCl) are solids at room temperatures, as are *networked* covalent substances (e.g. Si and metals). Small molecules that are

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[2] Johannes Diderick van der Waals (Dutch, 1837-1923) His success at describing phases of matter in terms of intermolecular interactions was rewarded by a Nobel Prize in physics in 1910.

[3] By definition, the density of liquid water is 1 g/cm^3, or 18 mL/mol near 0°C. Assuming steam is a nearly ideal gas, its density can be estimated from the molar volume at STP (0 °C, 1 atm), 22,400 mL/mol, which is about 1000 times less than the liquid density. The distance ratio is proportional to the cube root of the volume ratio.

covalently bonded (e.g. diatomics with filled octets) will be gases (e.g Cl_2), liquids (e.g. Br_2), or solids (e.g. I_2) at ordinary temperatures, depending on the strength of the forces *between* their molecules.

It is important conceptually to understand that intermolecular bonds can be described by wave mechanics in the same was as intramolecular bonds can be described. Potential energy curves have been calculated for the interaction between two molecules and they agree quantitatively with experimental values. *Binding energy curves for intermolecular interactions look very similar to the binding energy curves of molecules, such as Fig. 12.10, except that they are orders of magnitude more shallow* (tens of kJ/mol vs. hundreds of kJU/mol). For example, the chemical bond between two nitrogen atoms is 960 kJ/mol (at 109 nm interatomic separation) (Table 12.1), while that between two dinitrogen *molecules* is 1.35 kJ/mol (at 364 nm intermolecular separation). Fig. 14.2 shows some typical van der Waals potential curves.

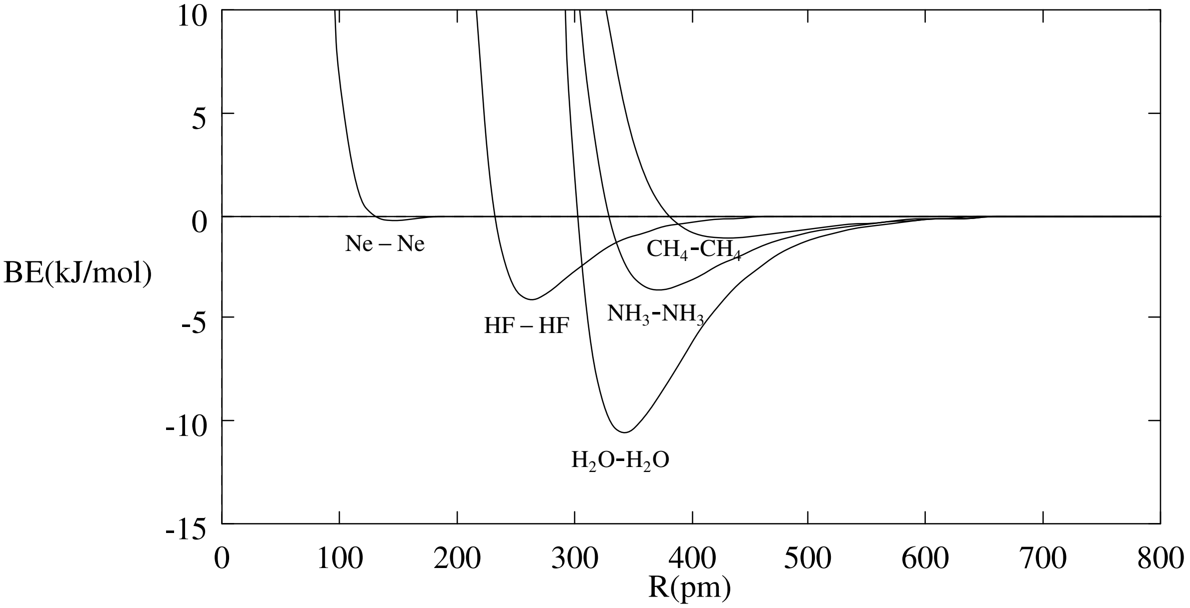

Fig. 14.2 Intermolecular Potential Energy PE(R) Curves

In terms of such curves, the addition of thermal energy to a system at rest can be visualized as vibrational motion back and forth on the curve up to a point corresponding to the amount of kinetic energy possessed by the system. Potential and kinetic energy are interconverted with their sum remaining constant according to the law of conservation of energy. Vaporization occurs when there is sufficient kinetic energy to exceed the energy to dissociate the molecules (send them to infinite intermolecular separation). Such reasoning distinguishes gas, liquid and solid phases of matter. Calculating phase parameters from fundamental theories for a given substance is very difficult for all but the simplest systems.

Like the intramolecular forces between the atoms in chemical bonds, *intermolecular* forces *between* molecules may be also classified into categories. *All molecules experience very weak intermolecular forces due to instantaneous distortions of their electron clouds, called* **dispersion forces**. Dispersion contributions to intermolecular attractions were first calculated from wave mechanics by Fritz London in 1930 and were shown to increase with the number of electrons and to fall off with the sixth power of the separation distance ($n = 6$ in the Mie Eq. (12.5)). For example the noble gas dispersion energies are 0.917 kJ/mol (He), 0.260 kJ/mol (Ne), 1.16 kJ/mol (Ar), 6.53 kJ/mol (Xe). Polar molecules have **dipole-dipole** attractions in addition to the dispersion forces (refer to the Molecular Polarity Heuristic of Chapter 12). Such attractions fall off similarly with the sixth power of distance, but are not as large in magnitude as dispersion attractions. Together, these interactions constitute the total van der Waals forces between molecules. In addition to the van der Waals interactions, molecules containing one of the three highly electronegative elements fluorine, nitrogen or oxygen are particularly attracted to an hydrogen atom attached to a fluorine, nitrogen or oxygen atom on an adjacent molecule. This special competition for hydrogen between two strongly electronegative elements, E - - H – E, is called a **hydrogen bond**, first identified by Linus Pauling.

The trends in intermolecular attraction shown in Fig. 14.2 demonstrate the contributing factors. The examples constitute an isoelectronic series of molecules containing ten total electrons across the second row of the periodic table. The separation at the minima reflect molecular sizes, which increase with decreasing nuclear charge on the central atom (toward the left in the periodic table; see the Periodic Trend Heuristic of Chapter 8), and with increasing number of hydrogen atoms. The depths of the minima reflect strength of attraction. Neon (Ne) and methane (CH_4), which have only dispersion attractions, have the smallest attractions.[4] Hydrogen fluoride (HF), ammonia (NH_3) and water (H_2O) are polar and form

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[4] Methane is non-polar due to molecular symmetry; see the Molecularity Polarity Heuristic in Chapter 12.

hydrogen bonds. The well depths support the experimental observations that ammonia forms a single hydrogen bond (the only possibility with a single one pair of electrons), as does hydrogen fluoride (which could possibly form hydrogen bonds with up to three neighbors through three lone pairs), and water forms its maximum of two hydrogen bonds with its two lone pairs.[5] Quantitatively, it appears that for these small molecules, dispersion bonding contributes about 1 kJ/mol, polarity something comparable to dispersion, and hydrogen bonding about 3 kJ/mol of hydrogen bonds.

14.4. Kinetic Molecular Energy

According to the statistical mechanical energy of Table 13.1, the value of the *average* thermal kinetic energy (denoted by the bar) per mol at room temperature is:

$$\boxed{\overline{\mathrm{KE}} = \frac{s}{2} N_A kT = \frac{s}{2} RT = 1.25s \text{ kJ/mol at 300 K} \qquad (14.1)}$$

where N_A is Avogadro's number, and the parameter s is a small number proportional to the number of degrees of motion freedom the molecules have (refer to the discussions of molecular motion in Section 12.11, and Section 13.11). The product of N_A and k has the value 8.31441 J/mol-k and is given the symbol R (molar gas constant in energy units). For motion in three dimensions s has a value of at least three (three for translation in a gas, six for vibration in a solid) and $\overline{\mathrm{KE}} \geq 3.75$ kJ/mol. Eq. (14.1), called *the equipartition theorem*, shows that molecules posses only a few kJ/mol of average kinetic energy at room temperature.

The types of motion available to the system (degrees of freedom) and the phase of the system determine the value of s, which is a sum of contributions for the various types of motion. As shown in Table 13.1, for translational motion s = 3 (for the three dimensions of space). For rotation of linear molecules, s = 2 and for non-linear rotation, s = 3. Each vibrational degree of freedom contributes s = 2 to the total average kinetic energy. The equipartition theorem is strictly applicable only at sufficiently high temperature that excited states of motion can be significantly populated. The gas phase consists of isolated molecules with the ability to translate and rotate (if polyatomic) from very low temperatures, but polyatomic

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[5] Refer to the Lewis Structure Algorithm for electronic structures in Chapter 12.

gases can vibrate only at relatively high temperatures. (This is a consequence of the magnitudes of the differences in quantized energy levels as discussed in Section 8.11). Liquids and solids consist of networks of molecules with varying degrees of rigidity. The basic motion of solids is vibration, although rotation may may set in at higher temperatures in molecular solids and liquids.

Table 14.1 list the possibilities of the maximum values of s for various types of substances (condensed refers to liquid or solid).

Table 14.1 Contributions to s at High Temperature

Substance	s_{tr}	s_{rot}	s_{vib}	s_{total}
atomic gas	3	0	0	3
linear molecular gas	3	2	6a – 10	6a – 5
nonlinear molecular gas	3	3	6a – 12	6a – 6
atomic condensed	0	0	6	6
linear molecular condensed	0	2	6a – 10	6a – 9
nonlinear molecular condensed	0	3	6a – 12	6a – 9

Example 14.1 Determine the high-temperature limiting average kinetic energy of monatomic gases, diatomic gases, non-linear triatomic gases, and diatomic liquids and solids.

Monatomic gases have s = 3 (only translational motion), diatomic gases are linear and have $s = 6 \times 2 - 5 = 7$, and non-linear triatomic gases have $s = 6 \times 3 - 6 = 12$. Diatomic liquid molecules vibrate and may rotate to some extent, but simple solid molecules usually only can vibrate. For diatomic liquids $s = 6 \times 2 - 8 = 4$; for diatomic solids $s = 6 \times 2 - 10 = 2$.

According to Ea. (13.1) the high temperature average kinetic energies are 3.75 kJ/mol for monatomic gases, 8.75 kJ/mol for diatomic gases, 15 kJ/mol for non-linear triatomic gases, 5 kJ/mol for diatomic liquids, and 2.5 kJ/mol for diatomic solids.

Thus we see for diatomic substances the kinetic energy increases from 2.5 kJ/mol for the solid phase to 5 kJ/mol for the liquid phase to 8.75 kJ/mol for the gas phase.

It is worth reminding ourselves from the discussion of the Boltzmann distribution in Section 13.9 that translation and rotation will occur at room temperatures but vibration and electronic excitation will usually not. Due to the magnitudes of van der Waals energies compared with thermal energies however, condensed substances always have some fraction, however small, of their molecules vaporizing at finite temperatures, and gases always have some fraction (however small) of their molecules "condensed" (bound). We are interested in the phase of the (usually overwhelming) *majority* of the molecules under "ambient" (ordinary) conditions, where we may say that substances which are gases at ordinary temperatures have average thermal energies greater than their attractive potential energies, and liquids and solids have average thermal energies less than their attractive potential energies.

14.5. Intermolecular Bonding versus Temperature

According to Eq. (14.1), there are only a few kJ/mol of kinetic (thermal) energy available at room temperature, so it is not surprising that neon, methane, hydrogen fluoride and ammonia are gases at room temperature, but that water is still a liquid. Hydrogen bonding contributes significantly to the properties of water, (which moderates the Earth's climate through high heat of vaporization and heat capacity), and to biological molecules (such as the double helix structure of DNA).

Melting, boiling and critical points reflect the strengths of intermolecular forces. For example, the critical temperatures of the substances in Fig. 14.2 increase in the order of increasing binding strength, 44 K for neon, 191 K for methane, 405 K for ammonia, 461 for hydrogen fluoride, and 647 K for water. The molar heat of vaporization is the heat energy required to vaporize one mol of a liquid and reflects the attractions between molecules and follows the same trend, 1.8 kJ/mol for neon, 8.2 kJ/mol for methane, 23.4 kJ/mol for ammonia, 28.7 kJ/mol for hydrogen fluoride and 40.7 kJ/mol for water. Note that the heat of vaporization for water is about double that of ammonia and hydrogen fluoride, reflecting the numbers of hydrogen bonds.

The interplay between the cohesive forces of attractive molecular potential energies and the disruptive forces of kinetic energy is summarized in Fig. 14.3.

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[5] The heat of vaporization decreases with increasing temperature to zero at the critical point. Values quoted are for the normal boiling temperature. The molar heat of vaporization for water at 25 °C is 44.01 kJ/mol.

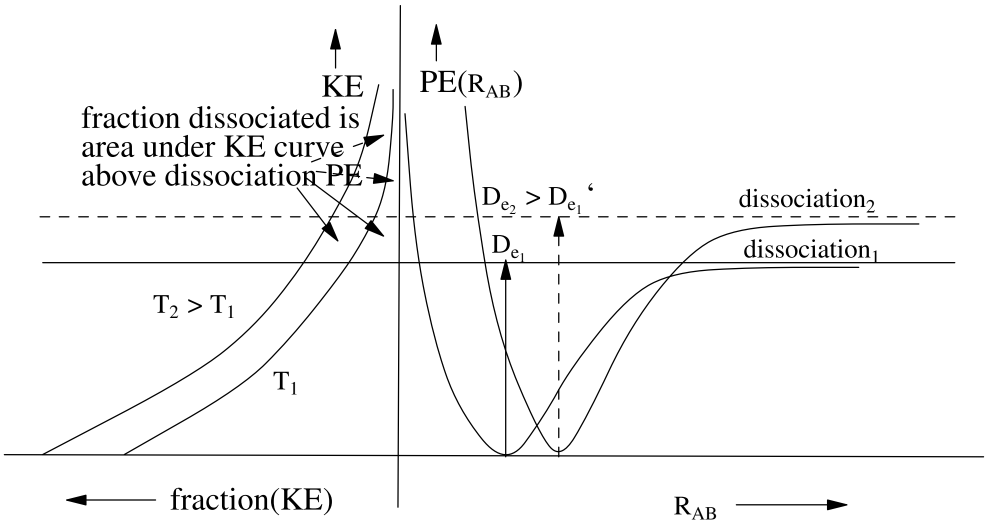

Fig. 14.3 Competition Between Potential and Kinetic Energy

On the right, the interactive potential energy is depicted as a function of intermolecular separation. On the left, the Boltzmann decreasing exponential distribution of kinetic energy is depicted (Eq. (13.17). The curves are joined with a common vertical axis of energy. Molecules with less thermal energy than the energy of dissociation are bound in a condensed phase, while the those with greater thermal energy separate into the gas phase. The total fraction of molecules which escape the condensed phase is proportional to the area under the Boltzmann distribution curve beyond the value of kinetic energy equal to the dissociation energy. As the temperature is increased, the Boltzmann distribution shifts to higher kinetic energies and the number of molecules which escape increases for a given temperature. Similarly, the fraction of molecules of substances with smaller dissociation energies increases over that of more tightly bound molecules.

14.6. Vaporization

Vaporization occurs out of a condensed (liquid or solid) phase when the molecules at the surface have sufficient kinetic energy to overcome the intermolecular attractions in the condensed phase. Assuming gas phase molecules are far apart from each other so that their potential attraction $\mathrm{PE_{gas}}$ is negligible and that the molecules in the condensed phase are sufficiently bound that their kinetic energy $\mathrm{KE_{condensed}}$ is negligible, the energy of vaporization can be estimated to be

$$\Delta E_{\mathrm{vaporization}} = E_{\mathrm{gas}} - E_{\mathrm{condensed}} = (PE_{\mathrm{gas}} + KE_{\mathrm{gas}}) - (PE_{\mathrm{condensed}} + KE_{\mathrm{condensed}}) \approx \frac{c}{2} D_e + \frac{3}{2} RT \quad (14.2)$$

where c is the number of neighbors in the condensed phase, called the *coordination number*, $PE_{\mathrm{condensed}} = -D_e$ and $KE_{\mathrm{gas}} = \frac{3}{2} RT$ for the translation of the gas molecules. The factor of 1/2 on c is due to the fact that dissociation involves a pair of molecules. Table 14.2 lists various contributions to the intermolecular potential energy for a variety of substances and the calculated and experimental values of the vaporization energy.

Table 14.2 Energy of Vaporization (All Energies in kJ/mol)

Substance	PE_{rep}	PE_{disp}	PE_{dipole}	$PE_{\mathrm{H-bond}}$	PE_{total}	c	T_{vap}	$\Delta E_{\mathrm{vap_{calc}}}$	$\Delta E_{\mathrm{vap_{obs}}}$
Ar	+1.0	−2.0	0	0	−1.0	12	87.2 K	7.1	7.1
H_2O	+9.8	−3.6	−3.0	−19.5	−16.3	4	373.15 K	37.3	37.6
NaCl	+60	−10	−493	0	−443	3.50	298 K	786	786

The coordination number is estimated for a simple substance like atoms to be the maximum number of nearest neighbors, 12 for spheres. Ice has an open hexagonal structure determined by strong hydrogen bonding, leading to effectively four nearest neighbors. An ionic solid has near attractions followed by next nearest repulsions, etc. The sum of all these contributions can be calculated from geometry and is $2(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \ldots) = 3.49512\cdots$. The vaporization temperatures are normal boiling points except for NaCl, which is calculated for room temperature to compare with the experimental lattice energy. In the case of sodium chloride, the binding energy listed under PE_{dipole} is estimated from Coulomb's Law (Eq. (5.6)) for two unit charges separated by the equilibrium distance in Table 12.1. In the case of NaCl the interaction energy is really a chemical bond, but the estimate still works because it is based on fundamental principles.

The pressure above a condensed substance (liquid or solid) due to vaporization is called the *vapor pressure*, and is proportional to the fraction of molecules in the gas phase. According to Boltzmann's distribution function, Eq. (13.17), the vapor pressure depends on the heat energy of dissociation (molar enthalpy of vaporization at constant pressure, ΔH_v, and the temperature.

$$\boxed{p(T) = Ae^{-\left(\frac{\Delta\tilde{H}_v}{RT}\right)} \qquad (14.3)}$$

where $R = N_A k = 8.3144 \mathrm{J/mol}$ is the Boltzmann constant converted to molar units. The boiling and sublimation curves of phase diagrams, such as Fig. 14.1, therefore follow exponential curves. The value of p_0 is the point at which P = 1; if measured in atmospheres, 1 atm corresponds to the normal boiling point, where $T = T_b$. p_0 is thus seen to have the value $A = e^{(\Delta H_v/kT_b)}$. Note that by taking the logarithm of both sides of the Eq. (14.3) the plot of ln(p) *vs* $\frac{1}{T}$ is a straight line.[6]

> **Example 14.1** Determine the molar heat of vaporization of butane, C_4H_{10} from vapor pressure data, and discuss the result.
>
> The vapor pressure data are given below (with inverse temperature and logarithm of pressure included for convenience). The plot of the data is nearly linear, with some deviation.

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[6] The form of the vapor pressure equation was discovered empirically by B. P. E. Clapeyron in 1834.

Table 14.3 Butane Vapor Pressure as a Function of Temperature

T(K)	1/T	p(atm)	ln(p)
195	0.00513	0.0132	–4.331
214	0.00467	0.0526	–2.944
229	0.00437	0.1316	–2.028
257	0.00389	0.5263	–0.6419
273	0.00366	1.0000	0.0000

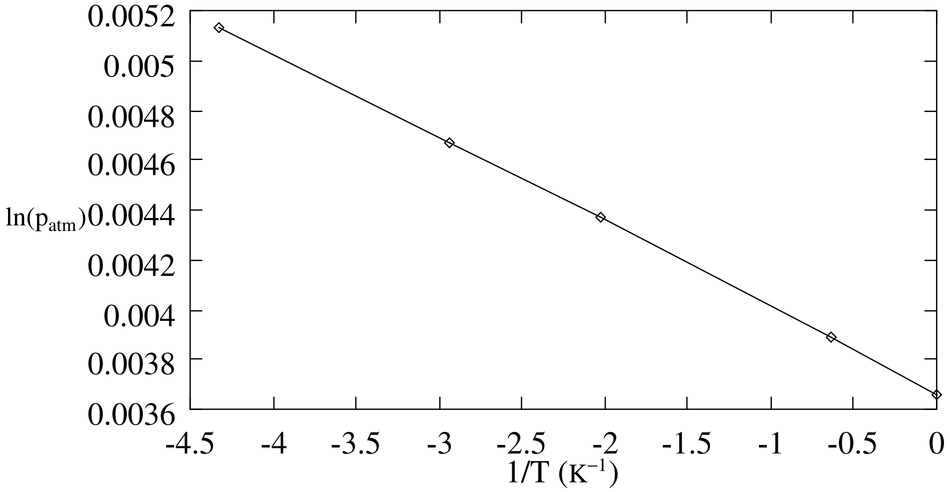

Fig. 14.4 Butane Vapor Pressure as a Function of Temperature

Application of the Algorithm for Determining the Slope of a Curve in Section 3.3 to adjacent points, multiplication by –R, and conversion from Joules to kJ yields the following values for the molar heat of vaporization of butane: 25.1, 25.4, 24.0, 23.2 kJ/mol. The values of ΔH_v are not strictly constant as suggested by the simple Boltzmann model Eq. (13.29) and an obvious shift is seen, consistent with the fact that the energy to vaporize a liquid eventually must fall to zero as the critical point is approached (where liquid is no longer distinguished from vapor).[7] The average[8] molar heat of vaporization is 24.4 kJ/mol, which may be compared with the values of the substances in Fig. 14.2. Butane is a hydrocarbon like methane, but with more atoms. It is not polar because whatever its geometry, the electronegativity of carbon happens to be quite close to that of hydrogen, so no net polarity results even for an asymmetric structure (refer to the Molecular Polarity Heuristic of Chapter 12). Also, even though there are hydrogen atoms in the molecule, there is no hydrogen bonding because there are no highly electronegative elements in the molecule. Thus, any intermolecular attractions must be due to dispersion interactions. Since butane has 4x6+10 = 34 electrons compared with methane with 6+4 = 10 electrons, greater dispersion attraction is expected. The molar heat of vaporization of methane was quoted as 8.2 kJ/mol, and that of butane is about three times as great, consistent with the ratio of numbers of electrons.

14.7. Phase Heuristic

The discussion may be summarized into an algorithm for discussing or predicting phases of matter. Quantitative statements can be deduced from thermodynamics (cf. Chapter 13), but orders of magnitude suffice for the qualitative ideas developed here.

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[7] More detailed considerations show A has a linear dependence on T.

[8] Alternatively, one could use the linear regression program given in Section 3.12 to determine the least-squares slope.

Phase of Matter Heuristic

Purpose: To determine the phase of a given substance at a given temperature.

Procedure:

1. Determine the type of bonding which may exist between the atoms and molecules of the given substance from the Basic Bonding Heuristic. *Intra*molecular chemical ionic and covalent bond forces are of comparable magnitude (hundreds of kJ/mol), both being an order of magnitude larger than *inter*molecular dispersion, dipolar and hydrogen-bond forces (tens of kJ/mol), which are themselves of comparable orders of magnitude.
    a) If ionic bonds exist, the substance will persist as an ionic lattice to high temperatures.
    b) If covalent bonds exist, the molecule will be stable to high temperatures. If a network of covalent bonds holds the atoms together, the molecule will exist as a solid to high temperatures.
2. If the system consists of noble gas atoms or small neutral covalent molecules, the physical phase is determined by the interplay between the attractive dispersion, dipolar and hydrogen-bond intermolecular forces, and the thermal kinetic energy.
    a) All molecules have dispersion forces, which increase with number of electrons.
    b) Only molecules with permanent dipoles have dipolar forces, which increase with difference in bond electronegativity. (See the Molecular Polarity Algorithm.)
    c) Only molecules with hydrogen bound to fluorine, nitrogen or oxygen have hydrogen bond interactions, which increase according to the number of possible hydrogen bonds that may exist and the electronegativities of fluorine, oxygen and nitrogen.

Example 14.2 Compare the melting points of Ne, CH_4, HCl, H_2O, NaCl and C (diamond).

1. The chemical bonding of each substance must be considered (cf. The Basic Bonding Heuristic).
    a) NaCl has ionic bonds and should exist as a solid until high temperature. (Observed melting point is 801 °C.)
    b) Diamond is a three-dimensional tetrahedral network of covalently-bonded carbon atoms. It should have a high melting point. (Observed melting point is 3550 °C.) Ne is a noble gas and CH_4, HCl and H_2O are small covalent molecules which should remain undissociated to high temperatures.
2. Covalent bonds exist in the non-metal molecules CH_4, HCl and H_2O. Their melting points can be ordered on the basis of their intermolecular attractions.
    a) Each molecule has dispersion forces, with Ne, H_2O, CH_4, (10 electrons each) < HCl (18 electrons).
    b) Of the four, only HCl and H_2O are polar.
    c) Of the four, only H_2O has hydrogen bonding.

Assuming that each type of intermolecular force contributes equally to the total intermolecular interaction between molecules, Ne and CH_4 have one type (dispersion), HCl has two (dispersion and polarity), and H_2O has three types (dispersion, polar and hydrogen bonding). Since Ne and CH_4 have the same number of electrons, they should melt at comparable temperatures. The predicted order of melting is (Ne, CH_4) < HCl < H_2O. The observed values are: Ne = –249 °C, CH_4 = –182 °C, HCl = –115 °C, H_2O = +100 °C.

Example 14.3 Discuss the phase of water at room temperature.

According to Eq. 14.1, the average thermal energy at room temperature is about 4 kJ/mol. From Fig. 14.2 we see that the intermolecular bonding energy of water is about 11 kJ/mol, so there is sufficient intermolecular attraction to maintain water in the liquid phase to temperatures somewhat higher than room temperatures. Since the covalent bond energy in water is about 460 kJ/mol, it would take considerably more thermal energy to overcome the covalent bonding forces that maintain its molecular integrity.

14.8. Liquids

Liquids form an intermediate phase between gases, which are dispersed and chaotic, and solids, which are compact and ordered. Intermolecular forces give cohesion to liquids and the molecules tend to clump together and resist movement to some degree. The properties of viscous liquids reflect the structure and bonding. Syrups, for example, contain long chain sugar *polymer* (many body) molecules that associate through many van der Waals interactions and become entangled.

14.9. Heat Capacity

Heat capacity is, as the name implies, the capacity to absorb heat. Molar heat capacity (or heat capacity per mol) is given the symbol C and measured as the ratio of the increase in molar energy to an increase in temperature, $\Delta E/n\Delta t$. In SI units, C is expressed in Joules per mol per Kelvin, or J/mol-K.

Equation (14.1) is called the equipartition theorem, because it describes how energy is divided, or "partitioned" in molecules. It states that the molar heat capacity ratio can be calculated as $C = KE/T = sR/2$, where s is related to the places energy can be stored in molecules.

Example 14.4 Estimate the heat capacities of mercury in the solid, liquid and gas phases.

Mercury is a simple atomic substance. Solid mercury near its melting point (of −38.9 °C) should vibrate with s = 2x3 = 6 degrees of freedom, so C = 3R = 24.9 J/mol-K (R = 8.3144 J/mol-K). This compares favorably with the experimental value of 28.3 J/mol-K. Liquid mercury is still monatomic, so there is little place to store additional energy as heat is added, and the heat capacity should be comparable to that of the solid. This is just what is observed experimentally (28.3 J/mol-K). Gaseous mercury is free to translate and is expected to have s = 3, and C = 3R/2 = 12.5 J/mol-K, exactly the observed value.

Example 14.5 Explain the observed heat capacity values of solid, liquid and gas water, 37.8 J/mol-K, 75.3 J/mol-K and 25.3 J/mol, respectively.

Water is a bent triatomic molecule which hydrogen bonds. The basic vibrational motion in the solid leads to C = 3R = 24.9 J/mol-K, but the observed value is 37.8 J/mol-K. However, solid water is unusual in that ice collapses slightly on melting.[9] This

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[9] Fortunate for us, for if ice were more dense than water, it would sink to the bottom of the oceans where sunlight would not be able to remelt it.

is explained by strong hydrogen bonds which hold the molecules in a relatively open structure. Adding two hydrogen bond vibrations to the molecular vibrations results in s = 3 + 2x3 = 9 and C = 9R/2 = 37.4 J/mol-K, very close to the observed value.

Unlike simple substances such as mercury, the heat capacity of liquid water is considerably higher than that of ice. This suggests that additional degrees of motion are activated in the liquid. If the hydrogen bonds weaken the chemical bonds in liquid water to the extent that vibrational excitation energies are lowered and vibrational states can be populated, the maximum value of s becomes 2x3a = 2x3x3 = 18, and C = 18R/2 = 74.8 J/mol-K, again close to the observed value.

Gaseous water should behave as normal isolated molecules having translation and rotation in three dimensions, but very little vibrational excitation until the temperature becomes very high. We expect s = 3 + 3 = 6 and C = 6R/2 = 24.9 kJ/mol-K, in good agreement with experiment.

Summary

At low temperatures intermolecular forces dominate over thermal energy and substances are found in the solid phase. Higher temperatures produce thermal motion which tends to break up collections of molecules, producing the fluidity of the liquid and gas phases of matter.

The kinetic molecular theory of matter provides quantitative estimates for the properties of substances in different phases.

INTERMOLECULAR BONDING EXERCISES

1. Could molecules survive an encounter with the sun?
2. What is the phase of pure DNA at room temperature?
3. Describe the diamond lattice.
4. Devise a relation between molar heat energy of vaporization and boiling temperature.
5. What is the phase of F_2 at room temperature?
6. Estimate the heat capacity of solid and gas I_2.

INTERMOLECULAR BONDING EXERCISE HINTS

1. Recall the fundamental relation of the kinetic molecular theory, and note that the surface temperature of the sun is about 6,000 K.
2. DNA is a covalently bound one-dimensional molecule about 1 meter long.
3. Each carbon atom has an octet of sigma bonds.
4. Consider the equipartition theorem and the relation between kinetic energy and potential energy.
5. Recall the Periodic Law Algorithm and the discussion of the halogens in this chapter.
6. Iodine vibrates relatively easily (compare ν_e for I_2 with other diatomics in Table 12.1).