

4

Monolayer materials

4.1 Fatty acids and related compounds

A simple long-chain fatty acid such as n-octadecanoic acid (stearic acid) consists of a linear chain (C_nH_{2n+1}) – an *alkyl chain* – terminating in a carboxylic acid group (COOH). The polar acid head confers water solubility while the hydrocarbon chain prevents it (section 2.2). It is the balance between these two opposing forces that results in the formation of an insoluble monolayer at the air/water interface. Any change in the nature of either the alkyl chain or the polar end group will affect the monolayer properties.

The solubility of fatty acids in water decreases as the length of the alkyl chain is increased. To obtain an insoluble monolayer of a nonionized fatty acid (i.e., the situation at sufficiently low pH values), the molecule must contain at least 12 carbon atoms. For example, n-dodecanoic acid (lauric acid – $C_{11}H_{23}COOH$) forms a slightly soluble gaseous monolayer at low temperatures. The addition of two more carbon atoms, to form n-tetradecanoic acid (myristic acid), causes the gas phase to condense at low surface pressures and an expanded monolayer phase to be formed (Stenhagen, 1955). If this monolayer is held at a surface pressure of 10 mNm^{-1} and a temperature of 20°C , then the loss in monolayer area due to solubility in the water subphase is $0.1\% \text{ min}^{-1}$. This contrasts with n-octadecanoic acid ($C_{17}H_{35}COOH$ – stearic acid) which shows a decrease in monolayer area of less than $0.001\% \text{ min}^{-1}$ under similar conditions (Gaines, 1966; Hann, 1990). These figures simply reflect the different solubilities of the two long-chain compounds in the water subphase at 20°C : $2.0 \text{ kg}/100 \text{ m}^3$ and $0.29 \text{ kg}/100 \text{ m}^3$ for n-tetradecanoic acid and n-octadecanoic acid respectively.

The addition of further carbon atoms also results in the appearance of condensed monolayer phases. Table 4.1 lists some common fatty acids used

Table 4.1 Long-chain fatty acid compounds used for monolayer studies.

Structure	Systematic name	Common name	Melting point [°C]
$C_{13}H_{27}COOH$	n-tetradecanoic	myristic	55
$C_{14}H_{29}COOH$	n-pentadecanoic		53
$C_{15}H_{31}COOH$	n-hexadecanoic	palmitic	63
$C_{17}H_{35}COOH$	n-octadecanoic	stearic	71
$C_{19}H_{39}COOH$	n-eicosanoic	arachidic	77
$C_{21}H_{43}COOH$	n-docosanoic	behenic	80
$C_{22}H_{45}COOH$	n-tricosanoic		79

in monolayer work. These tend to be the compounds containing an even number of carbon atoms that occur in nature. The longer chain materials shown in the table are popular with LB workers; high quality multilayer films may be built up readily from n-eicosanoic acid, n-docosanoic acid and n-tricosanoic acid (section 3.8.4).

4.1.1 The headgroup

Long-chain organic compounds terminating in a group other than a carboxylic acid (COOH) may form condensed insoluble monolayers at the air/water interface. The polarity of the headgroup will determine the stability of the layer (Gaines, 1966). The absence of a polar group (i.e. a simple long-chain hydrocarbon) or a weakly polar head (e.g., CH_2I or CH_2Cl) will simply result in drops or lenses on the water surface. On the other hand, if the dipole moment associated with the headgroup is large (e.g., SO_3^-), then the compound becomes too soluble in the aqueous subphase.

The high surface pressure condensed LS, S and CS monolayer states (chapter 2) are found to occur with long-chain amphiphilic compounds possessing a variety of polar ends. This is evidence that these phases are associated with different arrangements of the hydrocarbon chains (Stenhagen, 1955). Examples are shown in table 4.2. At low temperatures, the area per molecule for monolayers of most of these materials is about 0.2 nm^2 . However, there are some instances where a long straight compound with a polar group at one end does not exhibit the usual high pressure monolayer phases. This may be due to a peculiarly shaped polar head, to interactions between neighbouring polar groups, or simply to the large size of the head group. Particularly interesting examples are the long-chain nitriles (alkyl cyanides, $C_nH_{2n+1}C\equiv N$). Although the CN headgroup is small, the limiting area per molecule for these materials is about 0.28 nm^2 , suggesting that electrical interactions between the polar groups are important in determining the packing in these monolayers (the

Table 4.2 Different polar

(^aAfter Hann, 1990. ^bAfter 1987. ^cAfter Gaines, 1987)

Class of compound	Chemical formula
alcohols	$C_nH_{2n+1}OH$
esters	$C_nH_{2n+1}CO$
amides	$C_nH_{2n+1}CONH_2$
amines	$C_nH_{2n+1}NH_2$
nitriles	$C_nH_{2n+1}CN$

dipole moments of

tively).
Some of the con-
deposition under a
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C_nH_{2n+1}

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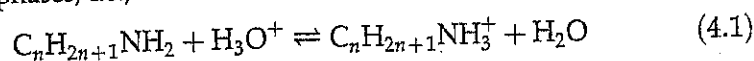
Table 4.2 Different polar head groups used for monolayer and multilayer studies.

(^aAfter Hann, 1990. ^bAfter Gaines, 1966. ^cAfter Fukuda and Shiozawa, 1980. ^dAfter Jones, 1987. ^eAfter Gaines, 1982. ^fAfter Stenhagen, 1955.)

Class of compound	Chemical formula	monolayer formation	LB film deposition
alcohols	$C_nH_{2n+1}OH$	similar to fatty acids; no dissociation and isotherm independent of pH (2-10) and of dilute salt solutions.	difficult to form LB films. ^{a,b}
esters	$C_nH_{2n+1}COOR$	ethyl stearate ($C_{17}H_{35}CO_2C_2H_5$) and similar compounds form condensed monolayers with areas per molecule of $\approx 0.2 \text{ nm}^2$.	ethyl stearate may be built into LB multilayers; X-type and Y-type deposition possible. ^c
amides	$C_nH_{2n+1}CONH_2$	condensed isotherms with area per molecule of $\approx 0.2 \text{ nm}^2$. ^b	alternate-layer deposition with a fatty acid. ^d
amines	$C_nH_{2n+1}NH_2$	condensed isotherms for $n > 13$; ionize at low pHs.	docosylamine ($n = 22$) deposits readily. ^{a,b,e}
nitriles	$C_nH_{2n+1}CN$	limiting area per molecule $\approx 2.8 \text{ nm}^2$ for $n \approx 18$. ^f	

dipole moments of CH_3CN and CH_3COOH are 3.9 D and 1.7 D, respectively).

Some of the compounds shown in table 4.2 also exhibit good LB film deposition under appropriate conditions. Long-chain amines mirror the behaviour of fatty acids. Compounds such as n-docosylamine are protonated on acidic subphases, i.e.,



The monolayer can be stabilized by negatively charged counterions in the subphase (e.g., SO_4^{2-}). This is analogous to the addition of divalent cations to fatty acid subphases.

Alternate-layer LB deposition (section 3.1) offers a means of building up multilayers of compounds that do not readily transfer as LB films by themselves. The alternation of a long-chain amide with a fatty acid, noted in table 4.2, is just one example. Occasionally the alternate layers deposit more readily than the monolayers of the separate components. For example, when a long-chain fatty acid (e.g., n-tricosanoic acid) is alternated with a long-chain amine (e.g., n-docosylamine), the deposition is facilitated by the transfer of a proton from the acid to the amine head group to form a salt, as shown in figure 4.1.

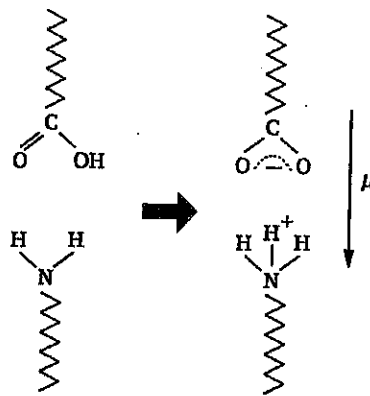


Figure 4.1 Proton transfer in long-chain acid/amine alternate-layer-LB film.

4.1.2 The alkyl chain

A simple modification to the alkyl group in a long-chain fatty acid is to replace some, or all, of the hydrogen atoms with fluorine. Since a fluorocarbon chain $(CF_2)_n$ is more hydrophobic than a hydrocarbon chain, it is expected that shorter chains will be needed to confer monolayer-forming properties on a particular polar headgroup. This is found to be the case. Monolayers of many amphiphiles containing fluorocarbon chains are more stable than those formed from their hydrocarbon counterparts (Elbert et al., 1984). The totally fluorinated molecule $C_{10}F_{21}COOH$ and the partially fluorinated species $C_8F_{17}(CH_2)_nCOOH$, with $n = 2, 4, 6$, form stable monolayers (Hann, 1990). The latter material may also be readily transferred to a solid substrate using the LB process. This is significant, as a disadvantage of the LB deposition method (compared to thermal evaporation or spin-coating) is that the alkyl chain is largely redundant in multilayers designed for electronic or electrooptic applications. The presence of these chains not only 'dilutes' the effect of, say, nonlinear dye groups, but also provides a highly insulating region in an LB film intended as a good electrical conductor.

The hydrocarbon chain (C_nH_{2n+1}) in the compounds discussed so far has been *saturated*. This term means that the carbon skeleton is 'saturated' with hydrogen, i.e., besides its bonds with other carbons, each carbon bonds to enough hydrogens to satisfy its valency of four. In saturated hydrocarbon chains, there are only single bonds. If an alkyl chain includes one or more carbon-carbon double or triple bonds, it is referred to as *unsaturated*. The double bond is stronger than a single bond, and also the $C=C$ bond (a *vinyl* group) is much more reactive than the $C-C$ bond. A double bond introduces a constraint because the two parts of a molecule linked by such a bond cannot rotate about it and the bond may disrupt the ordering of the chain. A single *trans*-double bond (appendix A) in the alkyl chain does not produce as much disruption as the

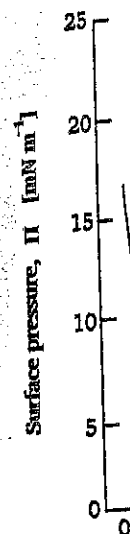


Figure 4.2 Surface pressure of a monolayer of stearic acid in the presence of HCl for *cis* and *trans*-double bonds. Reproduced from Hann, 1966.

presence of a *cis*-bond. The introduction of a *cis*-bond (behenic acid) provides a monolayer at $80^\circ C$ while the melt of *trans*-behenic acid is at $62^\circ C$ and that of *cis*-behenic acid is at $34^\circ C$. Figure 4.2 compares the surface pressures of these two unsaturated monolayers.

A widely studied unsaturated monolayer is that of tricosenoic acid ($C_{22}H_{42}O_2$) which contains a *cis*-bond at the end of the packing. The monolayer is very similar to that of stearic acid and may be deposited on a substrate corresponding to the

4.2 Simple substituents

The amphiphilic LB film of an aliphatic compound

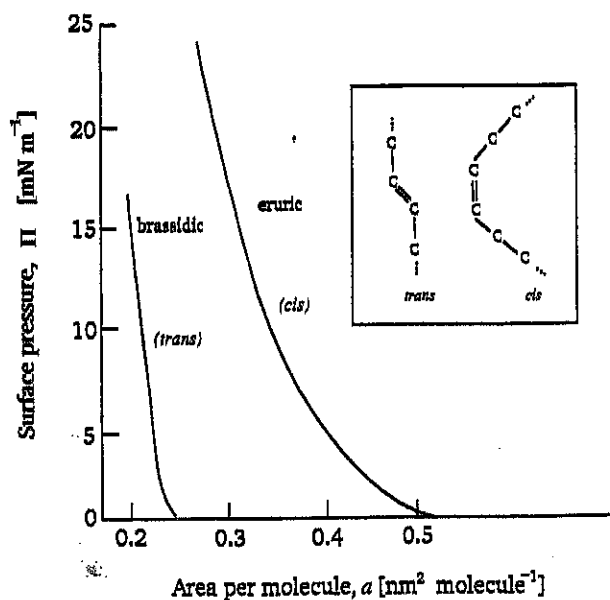


Figure 4.2 Surface pressure versus area isotherms at 21 °C and on 10^{-3} M HCl for erucic and brassidic acids ($C_8H_{17}-CH=CHC_{11}H_{22}COOH$). The *cis*- and *trans*-double bonds of the two compounds are shown (After Gaines, 1966. Reproduced with permission from G. L. Gaines.)

presence of a *cis*-bond. This can be demonstrated readily using molecular models and is reflected in the melting points of the materials (Hann, 1990). The introduction of *trans*- and *cis*-double bonds into *n*-docosanoic acid (behenic acid) provides a good example: the saturated fatty acid melts at 80 °C while the melting point of *trans*-13-docosenoic acid (brassidic acid) is 62 °C and that of *cis*-13-docosenoic acid (erucic acid) is further reduced to 34 °C. Figure 4.2 contrasts the surface pressure versus area isotherms for these two unsaturated fatty acids (Gaines, 1966). Clearly, the compound containing the *cis*-bond has a more expanded isotherm than *trans*-material.

A widely studied compound containing a single double bond is 22-tricosenoic acid ($C_{22}H_{43}COOH$), figure 4.3. This molecule has a single C=C bond at the end of the hydrocarbon chain, minimizing the disruption in the packing. The limiting area per molecule for a monolayer of this material is very similar to that for unsaturated long-chain fatty acids. Monolayers may be deposited over a range of surface pressures and temperatures, corresponding to the different monolayer states (chapter 3, table 3.2).

4.2 Simple substituted aromatic compounds

The amphiphilic LB materials discussed to this point may be classified as *aliphatic* compounds. Another major class of organic compounds is called

ayer LB film.

ty acid is to replace fluorocarbon chain it is expected that ing properties on a use. Monolayers of more stable than rt et al., 1984). The partially fluorinated stable monolayers transferred to a solid disadvantage of the n or spin-coating) is esigned for electronic only 'dilutes' the s a highly insulating actor.

discussed so far has been saturated' with hydro- rbon bonds to enough d hydrocarbon chains, one or more carbon- saturated. The double bond (a vinyl group) is l introduces a constraint d cannot rotate about it ngle *trans*-double bond much disruption as the

$$\begin{aligned}
 (b) \quad Z &= 1 + \frac{BP}{RT} \\
 &= 1 + \frac{(0.0169 \text{ L mol}^{-1})(600 \text{ bar})}{(8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1})(500 \text{ K})} \\
 &= 1.244 \\
 \bar{V} &= \frac{ZRT}{P} = (1.244)(6.93 \times 10^{-2} \text{ L mol}^{-1}) \\
 &= 8.62 \times 10^{-2} \text{ L mol}^{-1}
 \end{aligned}$$

We can give this result a molecular interpretation by saying that \bar{V} is greater for the real gas because of the finite volume of the molecules.

1.6 $P-\bar{V}-T$ SURFACE FOR A ONE-COMPONENT SYSTEM

To discuss more general equations of state, we will now look at the possible values of P , \bar{V} , and T for a pure substance. The state of a pure substance is represented by a point in a Cartesian coordinate system with P , \bar{V} , and T plotted along the three axes. Each point on the surface of the three-dimensional model in Fig. 1.11 describes the state of a one-component system that contracts on freezing. We will not be concerned here with the solid state, but will consider that part of the surface later (Section 6.3). Projections of this surface on the $P-\bar{V}$ and $P-T$ planes are shown. There are three two-phase regions on the surface: $S+G$, $L+G$, and $S+L$. These are ruled surfaces, that is, they may be thought of as being generated by a moving straight line, in this case one perpendicular to the $P-T$ plane. These three surfaces intersect at the **triple point** t where vapor, liquid, and solid are in equilibrium.

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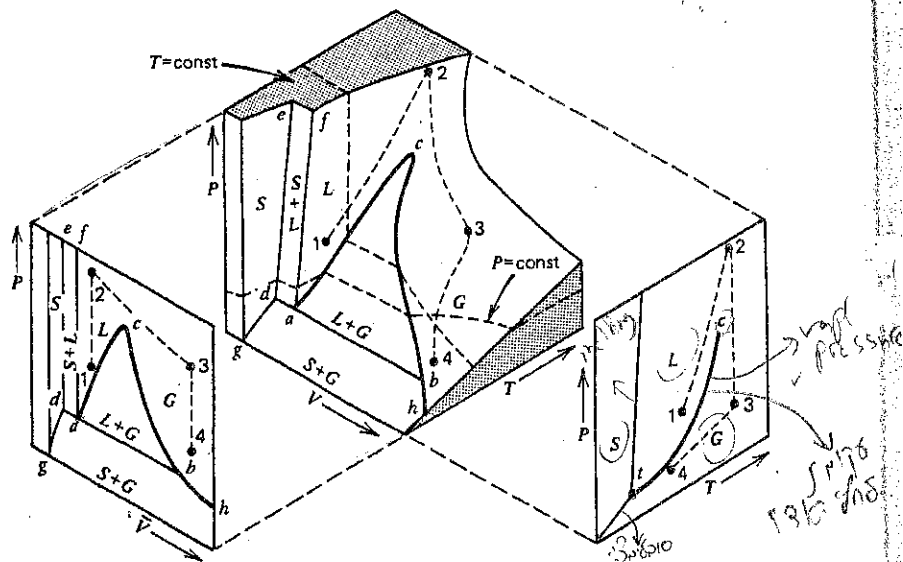


Figure 1.11 $P-\bar{V}-T$ surface for a one-component system that contracts on freezing. (From K. E. Bett, J. S. Rowlinson, and G. Saville, *Thermodynamics for Chemical Engineers*. Cambridge, MA: MIT Press, 1975. Reproduced by permission of The Athlone Press.)

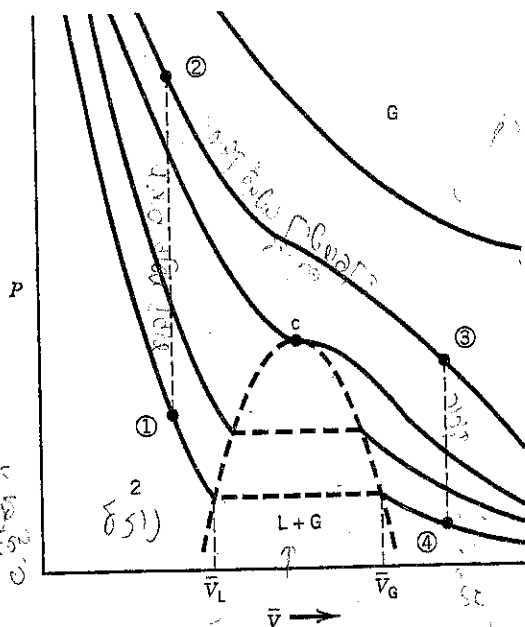


Figure 1.12 Pressure–molar volume relations (e.g., isotherms) in the region of the critical point. The dashed horizontal lines in the two-phase region are called tie lines. The path 1–2–3–4 shows how a liquid can be converted to a gas without the appearance of a meniscus. If liquid at point 4 is compressed isothermally, the volume decreases until the two-phase region is reached. At this point there is a large decrease in volume at constant pressure (the **vapor pressure** of the liquid) until all of the gas has condensed to liquid. As the liquid is compressed, the pressure rises rapidly.

is represented by a point in the L + G region of this plot, the system contains two phases, one liquid and one gas, in equilibrium with each other. The molar volumes of the liquid and gas can be obtained by drawing a horizontal line parallel to the \bar{V} axis through the point representing the state of the system and noting the intersections with the boundary line for the L + G region. Such a line, which connects the state of one phase with the state of another phase with which it is in equilibrium, is called a **tie line**. Two tie lines are shown in Fig. 1.12. The pressure in this case is the equilibrium vapor pressure of the liquid. As the temperature is raised, the tie line becomes shorter, and the molar volumes of the liquid and gas approach each other. At the critical point c the tie line vanishes and the distinction between liquid and gas is lost. At temperatures above the critical temperature, there is a single fluid phase.

Figures 1.11 and 1.12 also show how a liquid at point 1 can be converted to a gas at point 4 without the appearance of an interface between two phases. To do this, liquid at point 1 is heated at constant volume to point 2, then expanded at constant temperature to point 3, and finally cooled at constant volume to point 4 where it is a gas. Thus, liquid and vapor phases are really the same in terms of molecular organization, and so when the densities of these two phases for a substance become equal, they cannot be distinguished and there is a critical point. On the other hand, a solid and a liquid have different molecular organizations, and the two phases do not become identical even if their densities are equal. Therefore, solid–liquid, solid–gas, and solid–solid equilibrium lines do not have critical points as do gas–liquid lines.

The projection of the three-dimensional surface on the P - T plane is shown to the right of the main diagram in Fig. 1.11. The vapor pressure curve goes from the triple point t to the **critical point** c . The sublimation pressure curve goes from the triple point t to absolute zero. The melting curve rises from the triple point. Most substances contract on freezing, and for them the slope dP/dT for the melting line is positive.

At high temperatures the substance is in the gas state, and as the temperature is raised and the pressure is lowered the surface is more and more closely represented by the ideal gas equation of state $P\bar{V} = RT$. However, much more complicated equations are required to describe the rest of the surface that represents gas and liquid. Before discussing equations that can represent this part of the surface, we will consider the unusual phenomena that occur near the critical point. Any realistic equation of state must be able to reproduce this behavior at least qualitatively. - 2/1/51c

1.7 CRITICAL PHENOMENA

For a pure substance there is a critical point (P_c, T_c) at the end of the liquid-gas coexistence curve where the properties of the gas and liquid phases become so nearly alike that they can no longer be distinguished as separate phases. Thus, T_c is the highest temperature at which condensation of a gas is possible, and P_c is the highest pressure at which a liquid will boil when heated.

The critical pressures P_c , volumes \bar{V}_c , and temperatures T_c of a number of substances are given in Table 1.2, along with the compressibility factor at the critical point $Z_c = P_c\bar{V}_c/RT_c$, and the Boyle temperature T_B .

Critical phenomena are most easily discussed using the projection of the three-dimensional surface in Fig. 1.11 on the P - \bar{V} plane. Figure 1.12 shows only the parts of the P - \bar{V} plot labeled L, G, and L + G. When the state of the system

Table 1.2 Critical Constants and Boyle Temperatures

Gas	T_c/K	P_c/bar	$\bar{V}_c/\text{L mol}^{-1}$	Z_c	T_B/K
Helium-4	5.2	2.27	0.0573	0.301	22.64
Hydrogen	33.2	13.0	0.0650	0.306	110.04
Nitrogen	126.2	34.0	0.0895	0.290	327.22
Oxygen	154.6	50.5	0.0734	0.288	405.88
Chlorine	417	77.0	0.124	0.275	
Bromine	584	103.0	0.127	0.269	
Carbon dioxide	304.2	73.8	0.094	0.274	714.81
Water	647.1	220.5	0.056	0.230	
Ammonia	405.6	113.0	0.0725	0.252	995
Methane	190.6	46.0	0.099	0.287	509.66
Ethane	305.4	48.9	0.148	0.285	
Propane	369.8	42.5	0.203	0.281	
<i>n</i> -Butane	425.2	38.0	0.255	0.274	
Isobutane	408.1	36.5	0.263	0.283	
Ethylene	282.4	50.4	0.129	0.277	624
Propylene	365.0	46.3	0.181	0.276	
Benzene	562.1	49.0	0.259	0.272	
Cyclohexane	553.4	40.7	0.308	0.272	

At the critical point the **isothermal compressibility** [$\kappa = -\bar{V}^{-1}(\partial\bar{V}/\partial P)_T$, equation 1.37] becomes infinite because $(\partial P/\partial\bar{V})_T = 0$. If the isothermal compressibility is very large, as it is in the neighborhood of the critical point, very little work is required to compress the fluid. Therefore, gravity sets up large differences in density between the top and bottom of the container, as large as 10% in a column of fluid only a few centimeters high. This makes it difficult to determine $P\bar{V}$ isotherms near the critical point. The high isothermal compressibility also permits **spontaneous fluctuations** in the density that extend over macroscopic distances. The distance may be as large as the wavelength of visible light or larger. Since fluctuations in density are accompanied by fluctuations in refractive index, light is strongly scattered, and this is called **critical opalescence**.

1.8 THE VAN DER WAALS EQUATION

Although the virial equation is very useful, it is important to have approximate equations of state with only a few parameters. We turn now to the equation that was introduced by van der Waals in 1877, which is based on plausible reasons that real gases do not follow the ideal gas law which can be derived for point particles that do not interact except in elastic collisions (see Chapter 17, Kinetic Theory of Gases). The first reason that van der Waals modified the ideal gas law is that molecules are not point particles. Therefore \bar{V} is replaced by $\bar{V} - b$, where b is the volume per mole that is occupied by the molecules. This leads to

$$P(\bar{V} - b) = RT \tag{1.22}$$

which corresponds to equation 1.14 with $B' = b/RT$ and C' and higher constants equal to zero. This equation can represent compressibility factors greater than unity, but it cannot yield compressibility factors less than unity.

The second reason for modifying the ideal gas law is that gas molecules attract each other and that real gases are therefore more compressible than ideal gases. The forces that lead to condensation are still referred to as van der Waals forces, and their origin is discussed in Section 11.10. Van der Waals provided for intermolecular attraction by adding to the observed pressure P in the equation of state a term a/\bar{V}^2 , where a is a constant whose value depends on the gas.

Van der Waals' equation is

$$(P + a/\bar{V}^2)(\bar{V} - b) = RT \tag{1.23}$$

When the molar volume \bar{V} is large, b becomes negligible in comparison with \bar{V} , a/\bar{V}^2 becomes negligible with respect to P , and van der Waals' equation reduces to the ideal gas law, $P\bar{V} = RT$.

The van der Waals constants for a few gases are listed in Table 1.3. They can be calculated from experimental measurements of P , \bar{V} , and T or from the critical constants, as shown later in equations 1.33 and 1.34.

Figure 1.13 shows three isotherms calculated using the van der Waals equation. At the critical temperature the isotherm has an inflection point at the critical point. At temperatures below the critical temperature each isotherm passes through a minimum and a maximum. The locus of these points shown by the dotted line has been obtained from $(\partial P/\partial\bar{V})_T = 0$. The states within the

*The van der Waals equation can also be written in the form

$$(P + an^2/V^2)(V - nb) = nRT$$

Handwritten notes in Hebrew, including mathematical derivations and conceptual explanations related to the van der Waals equation and critical phenomena.

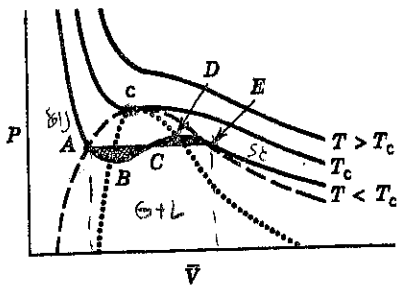


Figure 1.13 Isotherms calculated from the van der Waals equation. The dashed line is the boundary of the L + G region.

Table 1.3 Van der Waals Constants

Gas	$a/L^2 \text{ bar mol}^{-2}$	$b/L \text{ mol}^{-1}$	Gas	$a/L^2 \text{ bar mol}^{-2}$	$b/L \text{ mol}^{-1}$
H ₂	0.247 6	0.026 61	CH ₄	2.283	0.042 78
He	0.034 57	0.023 70	C ₂ H ₆	5.562	0.063 80
N ₂	1.408	0.039 13	C ₃ H ₈	8.779	0.084 45
O ₂	1.378	0.031 83	C ₄ H ₁₀ (n)	14.66	0.122 6
Cl ₂	6.579	0.056 22	C ₄ H ₁₀ (iso)	13.04	0.114 2
NO	1.358	0.027 89	C ₅ H ₁₂ (n)	19.26	0.146 0
NO ₂	5.354	0.044 24	CO	1.505	0.039 85
H ₂ O	5.536	0.030 49	CO ₂	3.640	0.042 67

dotted line have $(\partial P / \partial \bar{V})_T > 0$, that is, the volume increases when the pressure increases. These states are therefore mechanically unstable and do not exist. Maxwell showed that states corresponding to the points between A and B and those between D and E are metastable, that is, not true equilibrium states. The dashed line is the boundary of the two-phase region; the part of the isotherm to the left of A represents the liquid and that to the right of E, gas. The analysis shows that liquid at A is in equilibrium with gas at E. Any state along the line ACE will separate into liquid at A and gas at E. We see that the van der Waals equation with the Maxwell construction can represent the behavior of real substances.

The van der Waals equation is readily used when the volume and temperature are specified, but it is more difficult to use when the pressure and temperature are specified. Multiplying out the terms in van der Waals' equation 1.23 and rearranging in descending powers of \bar{V} , we have

$$\bar{V}^3 - \bar{V}^2 \left(b + \frac{RT}{P} \right) + \bar{V} \frac{a}{P} - \frac{ab}{P} = 0 \quad (1.24)$$

At temperatures below the critical temperature this cubic equation has three real solutions, each value of P giving three values of \bar{V} , as we have seen in Fig. 1.13.

The compressibility factor for a van der Waals gas is given by

$$Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V} - b} - \frac{a}{RT\bar{V}} = \frac{1}{1 - b/\bar{V}} - \frac{a}{RT\bar{V}} \quad (1.25)$$

At low pressures, $b/\bar{V} \ll 1$ so that we can expand the first term using $(1-x)^{-1} = 1 + x + x^2 + \dots$. This yields the virial equation in terms of volume:

$$Z = 1 + \left(b - \frac{a}{RT} \right) \frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}} \right)^2 + \dots \quad (1.26)$$

From this equation we can see that the value of a is relatively more important at low temperatures, and the value of b is relatively more important at high temperatures. To obtain the virial equation in terms of pressure, we can replace \bar{V} in the second term by the ideal gas value to obtain, to first order in P,

$$Z = 1 + \frac{1}{RT} \left(b - \frac{a}{RT} \right) P + \dots \quad (1.27)$$

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$$PV = nRT$$

$$\frac{1}{V} = \frac{P}{RT} \quad V = \frac{RT}{P}$$

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1.23
 $\frac{1}{V} = \frac{P}{RT}$
 $V = \frac{RT}{P}$

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$$\frac{P}{RT} = \frac{1}{V}$$

but this approximation is not good enough to give the correct coefficient for the P^2 term. At the Boyle temperature the second virial coefficient is zero, and so for a van der Waals gas

$$T_B = \frac{a}{bR} \quad (1.28)$$

The values of the van der Waals constants may be calculated from the critical constants for a gas. As may be seen in Fig. 1.12, there is a horizontal inflection-point in the P versus \bar{V} curve at the critical point so that $(\partial P / \partial \bar{V})_{T_c} = 0$ and $(\partial^2 P / \partial \bar{V}^2)_{T_c} = 0$.

Example 1.7

Derive the expressions for the van der Waals constants in terms of the critical constants for a gas.

The van der Waals equation may be written

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \quad (1.29)$$

Differentiating with respect to molar volume and evaluating these equations at the critical point yields

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_{T_c} = \frac{-RT_c}{(\bar{V}_c - b)^2} + \frac{2a}{\bar{V}_c^3} = 0 \quad (1.30)$$

$$\left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_{T_c} = \frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^4} = 0 \quad (1.31)$$

A third simultaneous equation is obtained by writing equation 1.29 for the critical point:

$$P_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2} \quad (1.32)$$

These three simultaneous equations may be combined to obtain expressions for a and b in terms of T_c and P_c or T_c and \bar{V}_c :

$$a = \frac{27R^2 T_c^2}{64P_c} = \frac{9}{8} RT_c \bar{V}_c \quad (1.33)$$

$$b = \frac{RT_c}{8P_c} = \frac{\bar{V}_c}{3} \quad (1.34)$$

Example 1.8

What is the molar volume of ethane at 350 K and 70 bar according to (a) the ideal gas law and (b) the van der Waals equation?

(a) $\bar{V} = RT/P = (0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(350 \text{ K})/(70 \text{ bar})$
 $= 0.416 \text{ L mol}^{-1}$

$P\bar{V} = \beta T$ ideal

(b) The van der Waals constants are given in Table 1.3.

from variable $\Rightarrow P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$
 $70 = \frac{(0.08314)(350)}{\bar{V} - 0.0638} - \frac{5.562}{\bar{V}^2}$

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

This is a cubic equation, but we know it has a single solution because the temperature is above the critical temperature. The most practical way to solve it is to use successive approximations. This yields $\bar{V} = 0.23 \text{ L mol}^{-1}$.

We will see later that equations of state are very important in the calculation of various thermodynamic properties of gases. Therefore, a variety of them have been developed. To represent the P - V - T properties of a one-component system over a wide range of conditions it is necessary to use an equation with many more parameters. As more parameters are used they lose any simple physical interpretation. The van der Waals equation does not fit the properties of any gas exactly, but it is very useful because it does have a simple interpretation and the qualitatively correct behavior.

1.9 THE CHAIN RULE AND THE CYCLIC RULE

This chapter has been full of functions of two variables, and that is a common situation in thermodynamics. We used several partial derivatives, and so now is a good time to think about how many there are, how they are related, and how many are independent. There are six partial derivatives involving V , P , and T :

6 → $\left(\frac{\partial V}{\partial T}\right)_P, \left(\frac{\partial V}{\partial P}\right)_T, \left(\frac{\partial P}{\partial V}\right)_T, \left(\frac{\partial T}{\partial V}\right)_P, \left(\frac{\partial P}{\partial T}\right)_V, \left(\frac{\partial T}{\partial P}\right)_V$ (1.35)

Two of these derivatives are used regularly and have names:

$\alpha = \text{cubic expansion coefficient} = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ (1.36)

$\kappa = \text{isothermal compressibility} = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ (1.37)

The isothermal compressibility κ is always positive because an increase in pressure at fixed T corresponds with a decrease in volume. Two of the remaining derivatives, $(\partial T/\partial V)_P$ and $(\partial P/\partial V)_T$, are simply the reciprocals of the derivatives involved in α and κ . The last two derivatives, $(\partial P/\partial T)_V$ and $(\partial T/\partial P)_V$, are simply reciprocals of each other and may be calculated using the cyclic rule.

If $z = f(x_1, x_2)$ and $x_1 = x_1(y_1, y_2)$, $x_2 = x_2(y_1, y_2)$, then $z = f[x_1(y_1, y_2), x_2(y_1, y_2)]$ is a function of y_1 and y_2 . Thus, we can consider z to be a function of either coordinates x_1, x_2 or coordinates y_1, y_2 . The following equation can be used to calculate the partial derivative of f with respect to x_1 :

$\left(\frac{\partial f}{\partial x_1}\right)_{x_2} = \left(\frac{\partial f}{\partial y_1}\right)_{y_2} \left(\frac{\partial y_1}{\partial x_1}\right)_{x_2} + \left(\frac{\partial f}{\partial y_2}\right)_{y_1} \left(\frac{\partial y_2}{\partial x_1}\right)_{x_2}$ (1.38)

This is known as the chain rule for partial differentiation. Taking $x_1 = T, x_2 = P$ and $y_1 = T, y_2 = V$ gives

$\left(\frac{\partial f}{\partial T}\right)_P = \left(\frac{\partial f}{\partial T}\right)_V + \left(\frac{\partial f}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$ (1.39)

Later we will find the chain rule useful for other coordinate transformations. If we take $f = P$, $(\partial f/\partial T)_P = 0$ because P is constant and f is P , and so

$\left(\frac{dP}{dT}\right)_P = 0$

$$0 = \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (1.40)$$

so that

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1 \quad (1.41)$$

This equation, which is referred to as the **cyclic rule**, can be rearranged to

$$\left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = - \frac{(\partial V / \partial T)_P}{(\partial V / \partial P)_T} \quad (1.42)$$

Using equations 1.36 and 1.37 yields

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa} \quad (1.43)$$

For an ideal gas, $\alpha = 1/T$ and $\kappa = 1/P$.

Comment:

Calculus is used so much in physical chemistry that we have put a section on calculus in Appendix D for quick reference. Since the properties of a system depend on a number of variables, it is important to be clear about which properties are held constant for a measurement or a process and to use subscripts on partial derivatives.

1.10 PARTIAL MOLAR PROPERTIES

This chapter has mostly been about pure gases, but we need to be prepared to consider mixtures of gases and mixtures of liquids. Mixtures have extensive thermodynamic properties (like internal energy U or volume V) that depend on T , P , and the amounts of substances in the mixtures. At fixed T and P , where most measurements in the laboratory are carried out, the extensive thermodynamic properties are functions of the amounts of the N substances in the mixture; this is indicated by $V(n_1, n_2, \dots, n_N)$, for example. All extensive thermodynamic properties are referred to as being homogeneous of degree 1 because

$$V(kn_1, kn_2, \dots, kn_N) = kV(n_1, n_2, \dots, n_N) \quad (1.44)^*$$

Since V is a function of amounts, the differential of V at fixed T and P is given by

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2,\dots,n_N} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1,\dots,n_N} dn_2 + \dots + \left(\frac{\partial V}{\partial n_N}\right)_{T,P,n_1,\dots,n_{N-1}} dn_N \quad (1.45)$$

*A function $f(x_1, x_2, \dots, x_N)$ is said to be homogeneous of degree n if

$$f(kx_1, kx_2, \dots, kx_N) = k^n f(x_1, x_2, \dots, x_N)$$

For such a function Euler's theorem states that

$$nf(x_1, x_2, \dots, x_N) = \sum_{i=1}^N x_i \frac{\partial f}{\partial x_i}$$