Chapter 11
Substances with Higher Density

If one changes from dilute (ideal) gases to real gases with higher density, the interaction between the particles and the phenomenon of condensation cannot be neglected any longer. The consideration of such effects results in the *van der Waals equation*, a modification of the general gas law. A closer look at the process of condensation leads us to the critical phenomena, meaning the unusual physical properties displayed by substances near their *critical points*. If we are interested to know how the phase transition liquid $\rightleftarrows$ gaseous can be influenced by factors such as temperature and pressure, we can use the T and p dependence of the chemical potential for calculating the *boiling pressure curve* (vapor pressure curve) of a given pure substance. This curve illustrates how the vapor pressure of the substance varies with temperature and is an example of a so-called *phase boundary*. The other phase transitions can also be represented in a $p(T)$ diagram in the form of phase boundaries, producing a complete *phase diagram*. Such a diagram is a kind of "map" which shows the conditions of temperature and pressure at which a certain phase is most stable and illustrates the ranges of existence of stable phases.

11.1 The van der Waals Equation

The *general gas law* is an approximation that becomes more exact the more diluted a gas is. If a gas becomes denser, deviations from the general gas law become increasingly noticeable. We will use an example to illustrate this: Oxygen can be obtained in steel cylinders at pressures up to 20 MPa (200 bar). Under these circumstances, the particles have almost no space to move in, their packing density is similar to a liquid. The characteristics of such a compressed gas are naturally different from those of a dilute gas.

The Dutchman Johannes Diderik van der Waals came up with an enlightening idea for understanding the behavior of gases at higher densities. He based it upon two very simple assumptions:

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1. Every particle possesses a certain spatial extension and therefore occupies a certain volume. It excludes all other particles from this space.
2. The particles attract each other. The forces of attraction are weak but increase quickly as the particles move closer together.

These forces of attraction between uncharged particles with complete electron shells in gases or liquids are called *van der Waals forces*. Among them are the interactions between permanent electric dipole moments (also called dipole–dipole forces or Keesom interaction, named after the Dutch physicist Willem Hendrik Keesom), as well as the interactions between permanent moments and moments induced by polarization (dipole-induced dipole forces) and the interactions between induced moments only (instantaneous dipole-induced dipole forces or London dispersion forces, named after the German-American physicist Fritz London). Interactions between electric dipoles are comparable to the more familiar ones between magnetic dipoles. The dispersion forces mentioned last originate from the formation of "temporary" dipole moments through fluctuations in the electron distribution where for a short time, even nonpolar particles display an irregular distribution of electron density that results in a positive or negative partial charge. This dipole, which was created by "spontaneous polarization," can, itself, induce a "temporary" dipole moment in a neighboring particle. The fact that even noble gases at low enough temperatures will become liquid suggested the existence of such dispersion forces. A characteristic of all these attractive interaction energies between uncharged particles with permanent or temporary dipole moments is that they decrease with the 6th power of the distance between the molecules: $W_{\text{pot}} \sim -1/r^6$.

Among the van der Waals forces are also the strongly increasing repulsive forces when the particles "touch" each other. The particles move so closely together that their electron shells overlap and, as a result of Pauli's exclusion principle, they begin to repel each other. For practical reasons, we often chose $W_{\text{pot}} \sim 1/r^{12}$ for the repulsive interaction energy. Attracting and repulsing contributions to the interaction energy can be summed up by the Lennard-Jones (12-6) potential (Fig. 11.1):

$$W_{\text{pot}} = \frac{A}{r^{12}} - \frac{B}{r^6}.$$

The short-range repulsive interaction effect was taken into account by van der Waals by the first of the assumptions above. This assumption implies that the gas particles do not have the entire volume of a container available for motion. The volume needed to be reduced by a contribution determined by the volume from which the particles exclude each other. This volume unavailable for molecular motion is called the *co-volume* (van der Waals volume) of a gas. The assumed attraction in point 2 leads to the gas particles moving more closely together, just as if there was additional pressure upon them. This "pressure" or "pull" (or "tensile stress") caused by the forces of attraction is called the *internal pressure* or *cohesion pressure* of a gas. Van der Waals assumed that the general gas law should continue to be valid, except for the following two changes, a lessening of volume by the

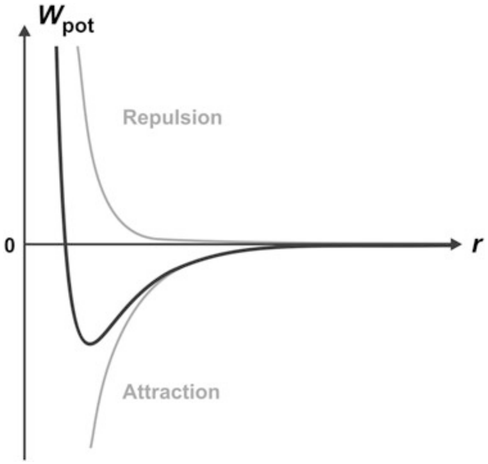


Fig. 11.1 Lennard-Jones potential (*black*) as the sum of the attracting and repelling parts (*gray*).

"unavailable" co-volume V_W and an increase of pressure by the internal pressure p_{int}:

$$(p + p_{int}) \cdot (V - V_W) = nRT. \qquad (11.1)$$

We obtain the formula above by replacing, or rather "correcting," the pressure with $p + p_{int}$, and the volume with $V - V_W$ in the general gas law. The van der Waals volume V_W, from which the particles exclude each other, naturally grows along with the number of particles, meaning with the amount of gas n, so we can conclude that:

$$V_W \sim n. \qquad (11.2)$$

However, internal pressure p_{int} increases with the square of the gas concentration $c = n/V$,

$$p_{int} \sim c^2 \sim \left(\frac{n}{V}\right)^2. \qquad (11.3)$$

To derive this, let us visualize more exactly how "internal pressure" comes to be. We envision a plane section with the surface A at an arbitrary position in a gas (Fig. 11.2). We assume that each particle attracts every other one within the "range" l of the intermolecular forces. In particular, the particles on one side of the section attract the ones on the other side. This assumption has a simple consequence: The greater the number N_1 of particles on one side of the surface in the volume $V_1 = A \cdot l$, and the greater the particle number N_2 on the other side of it in the

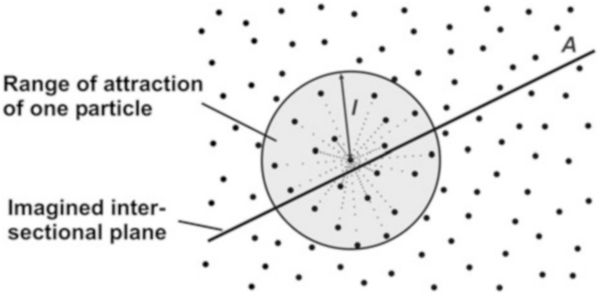


Fig. 11.2 Illustration of "internal pressure." *A*: imagined intersectional plane through the gas. The *gray circle* with the radius *l*, the "range" of the intermolecular forces, characterizes the "range of attraction" for an individual particle.

volume $V_2 \sim l^3$ within the range *l*, the stronger the total force of attraction, i.e., $F \sim N_1 \cdot N_2$. Because N_1 as well as N_2 are proportional to the particle density N/V and, therefore, to concentration $c = n/V$, the internal pressure (meaning the internally directed pull that is produced by the substance itself leading to a moving together of the particles) results in:

$$p_{\text{int}} = F/A \sim N_1 \cdot N_2/A \sim (V_1 \cdot c) \cdot (V_2 \cdot c)/A \sim A \cdot l \cdot l^3 \cdot c^2/A \sim n^2/V^2.$$

The dependencies for internal pressure and for co-volume will now be inserted into Eq. (11.1). In this form, it is known as the *van der Waals equation*:

$$\left(p + \frac{an^2}{V^2}\right) \cdot (V - bn) = nRT \qquad \text{van der Waals equation.} \tag{11.4}$$

It was derived by van der Waals in his dissertation of 1873.

The two substance-specific proportionality constants *a* and *b* are called *van der Waals constants*. In the case of water they are:

$$a(\mathrm{H_2O}) = 0.55\,\mathrm{Pa\,m^6\,mol^{-2}},$$

$$b(\mathrm{H_2O}) = 2.7 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}} \approx\approx V_\mathrm{m}(\mathrm{H_2O|l})(\approx\approx \text{read: approximately equal}).$$

Further values of empirically determined constants for various gases can be found in Table 11.1.

The *a* constants for the various gases are quite different from each other due to strongly varying forces of interaction. In contrast, the *b* constants vary only slightly from each other. This means that the space required by the different particles is relatively similar.

If the van der Waals equation is transformed, the $p(V)$ isotherms can be calculated:

$$p = \frac{nRT}{V - bn} - \frac{an^2}{V^2}. \tag{11.5}$$

Table 11.1 Van der Waals constants for various gases (from: Lide D R (ed) (2008) CRC Handbook of Chemistry and Physics, 89th edn. CRC Press, Boca Raton).

Gas	a (Pa m^6 mol^{-2})	b (m^3 mol^{-1})
H_2	0.0245	2.7×10^{-5}
He	0.0035	2.4×10^{-5}
N_2	0.137	3.9×10^{-5}
O_2	0.138	3.2×10^{-5}
Cl_2	0.634	5.4×10^{-5}
Ar	0.136	3.2×10^{-5}
CO_2	0.366	4.3×10^{-5}
CH_4	0.230	4.3×10^{-5}
C_2H_2	0.452	5.2×10^{-5}
NH_3	0.423	3.7×10^{-5}
H_2O	0.554	3.1×10^{-5}

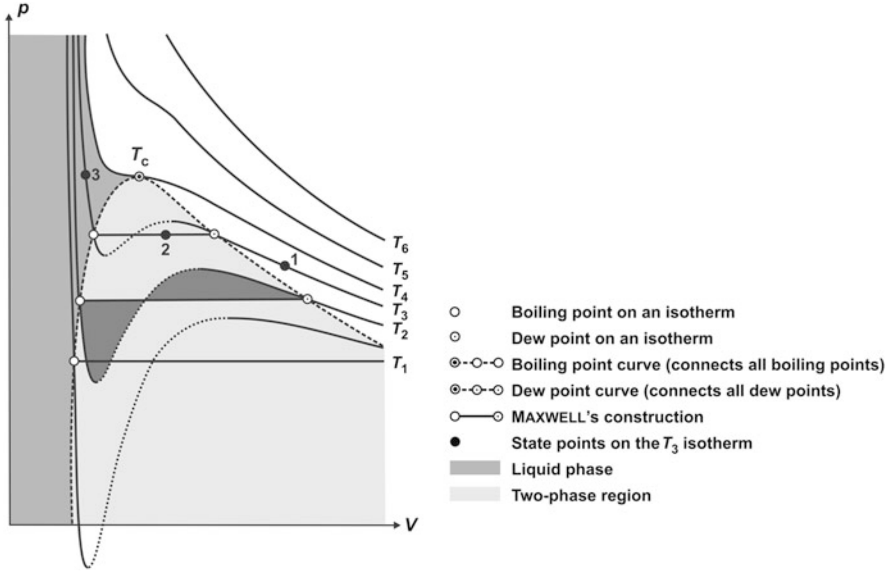


Fig. 11.3 $p(V)$ isotherms of a real gas according to van der Waals equation (with $T_1 < T_2 < \ldots < T_6$).

Figure 11.3 shows some of these isotherms for different temperatures $T_1 < T_2 < \ldots < T_6$. The graphic makes it clear that, at higher temperatures, the isotherms obtained by the van der Waals equation resemble the hyperbolas of the Boyle–Mariotte law. This is understandable because at high temperatures, the product nRT becomes so great that the second term in Eq. (11.5) can be ignored. In addition, at high volumes (and low pressures), $V \gg bn$, so that the van der Waals equation gives way to the general gas law, $p = nRT/V$.

Below a certain temperature (T_4), minima and maxima appear. These delineate a physically unrealistic part of the curve (which is therefore shown by a dashed line).

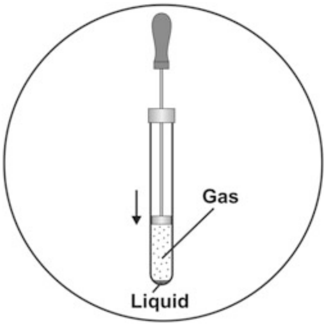
Volume would increase along with increase of pressure in this range, which contradicts experience. In order to understand the behavior of real gases at low temperatures, we must study *condensation*.

11.2 Condensation

When a gas is expanded, its internal pressure decreases quickly as a consequence of the quadratic concentration dependency. The internal pressure eventually becomes imperceptible and can be ignored when dealing with dilute gases. Conversely, internal pressure increases sharply when the density of a gas is increased. This happens so strongly that, at very high concentrations, a gas will become unstable and collapse. This is called *condensation*. Experiment 11.1 illustrates this phenomenon.

In the condensed state, particles adhere to each other. The short distances between them lead to their attraction being very strong and they hold together tightly. This is what causes the stability of a condensed state. The particles' speed is the same as it would be in a gas of the same temperature. At room temperature, this is a few hundred $\mathrm{m\ s^{-1}}$, which is just about the speed of sound! This "frantic swarm of particles" can only hold together under the enormous internal pressure of several thousand bar. Although these particles adhere to each other, they will also quickly slide by each other, when the temperature is not too low. Because of the high speed at which they move, they change positions very fast. This makes it possible for such a dense swarm of particles to adapt to any container form, to *flow* out through tiny openings and to *flow* through pipes. During all these changes, the volume of the substance (of the ensemble of particles) remains just about constant. As we discussed in Sect. 1.6, substances with these kinds of characteristics are called *liquids*.

Let us take a closer look at the process of condensation, the transition from a gas to a liquid (Fig. 11.4). We imagine a cylinder with a moveable piston in it enclosing a certain amount of gas. The temperature should have a constant value during the entire process. It should therefore be possible for the excess entropy that would cause warming (or when missing, would cause supercooling) to escape through the



Experiment 11.1 *Using pressure to liquefy a gas*: If butane (the fuel in a gas lighter) is filled into a glass pressure cylinder with a piston and the piston is pressed down, it produces a visible amount of liquid.

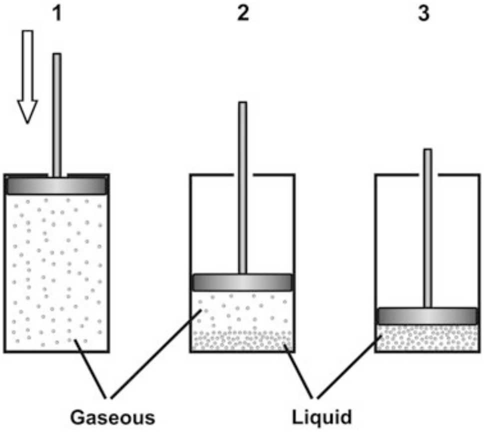


Fig. 11.4 Compressing a gas using a moveable piston (1), beginning condensation (2) and final compression of the liquid produced by condensation (3).

walls into the surroundings (or to be absorbed from there). Numbers 1, 2, and 3 refer to states indicated on the van der Waals isotherm at temperature T_3 (Fig. 11.3).

1. A gradual decrease of volume leads to a slow rise in "thermal" pressure, caused by molecular collisions, which drives the particles apart. Internal pressure simultaneously increases tending to concentrate the particles in a small space.
2. Because internal pressure increases more quickly than thermal pressure there exists a point at which the increase of thermal pressure cannot compensate for the increase of the internal pressure anymore. At this so-called *dew point*, the gas begins to "collapse," i.e., to condense.

   The gas does not condense all at once, but only a fraction of it does at first. In the process, a small number of particles disappear from the space occupied by the gas making the concentration and internal pressure decrease and causing the gas phase to restabilize.

   If the volume is further decreased, the processes repeat. More liquid forms while the rest of the gas stabilizes. If this is carried out further and further, the entire gas is eventually "squeezed" into a liquid state. Pressure will remain constant as long as temperature is unchanged during the condensation process. The gas above the liquid is usually called the liquid's *vapor*. The pressure in the gas compartment is called the *vapor pressure* of the liquid. Vapor pressure is independent of the amount of liquid it is associated with, whether it is one drop or a whole containerful.
3. Further compression leads to a strong increase of pressure because a liquid is much harder to compress than a gas.

We return once more to the van der Waals isotherms (Fig. 11.3): The van der Waals curves describe fairly exactly compression of gases up to the dew point. If the volume is decreased beyond this point, pressure does not increase, but condensation sets in. This occurs at constant pressure, meaning that the corresponding piece of the curve must be horizontal until the gas phase completely disappears at the *boiling point*. These lines have been constructed so that the areas enclosed by the van der Waals curves above and below the straight line are equal (Maxwell construction or equal area rule) (compare Fig. 11.3 where the two areas in the case of the T_2 isotherm are dark gray). Both gas and liquid exist simultaneously along these lines. The subsequent steep rise in pressure with further decrease of volume is characteristic of the low compressibility of liquids.

11.3 Critical Temperature

As temperature rises, it becomes harder to bring about a condensation process. The gas involved must be much more strongly compressed before it begins to condense and the two-phase region becomes more and more constricted. As we know, higher temperatures are related to faster particle motion. At higher velocities, higher internal pressure, i.e., higher compression is necessary to force the particles to collapse. If the temperature is continuously raised, making condensation more difficult, we eventually reach a critical value above which condensation is no longer possible. This limit is called the *critical temperature* T_c. Together with T_c, the corresponding values of critical pressure p_c and critical volume V_c make up the *critical point* of the substance in question. At this critical point, the corresponding van der Waals isotherm displays a saddle point, meaning a point of inflection with a horizontal tangent that simultaneously determines the maximum of the two-phase region (Fig. 11.3). Above this critical temperature, gases cannot be liquefied by compression. The critical temperatures for gases with weak attractive forces, such as helium, hydrogen, nitrogen, and oxygen, are far below room temperature so they remain gaseous even under high pressures. Gases like carbon dioxide, ammonia and water vapor, however, have higher critical temperatures and can be liquefied at room temperature if enough pressure is applied (Table 11.2).

If a gas is compressed at a temperature above the critical temperature, the result is a dense fluid whose characteristics are neither clearly liquid nor gaseous. Although this fluid's density is comparable to a liquid, making it possible to be used as a solvent, there is no surface visible between liquid and gas. Such a medium is called a *supercritical fluid*. It combines the positive characteristic of low viscosity of gases with the good solvent power of liquids, making it an attractive solvent for separating processes such as high-pressure extraction, polymer fractionation, and cleaning of monomers.

A further advantage is that it can be entirely removed from a product by expansion leaving no undesired, possibly poisonous, residue. Supercritical carbon

Table 11.2 Critical temperatures and pressures for some substances (from: Lide D R (ed) (2008) CRC Handbook of Chemistry and Physics, 89th edn. CRC Press, Boca Raton).

Substance	Critical temp. T_c (K)	Critical pressure p_c (MPa)
H_2	33.0	1.29
He	5.2	0.23
N_2	126.2	3.39
O_2	154.6	5.04
Cl_2	416.9	7.99
Ar	150.9	4.90
CO_2	304.1	7.38
CH_4	190.6	4.60
C_2H_2	308.3	6.14
NH_3	405.6	11.36
H_2O	647.1	22.06

dioxide is used to extract caffeine from tea or coffee. Supercritical water is used to dissolve quartz (and many other minerals) leading to hydrothermal solutions. The process of crystallizing on seed crystals produces high purity quartz monocrystals that can be cut into disks to be piezoelectric crystals in watches, for example. Hydrothermal solutions make also essential contributions to the formation of most vein deposits and ore stocks.

11.4 Boiling Pressure Curve (Vapor Pressure Curve)

We will consider the process of condensation from another point of view by using a $p(T)$ diagram (Fig. 11.5).

1. We begin with a state in which the gas is strongly expanded so its pressure is very low. We will keep the temperature at a constant value by conducting the entropy squeezed out by compression to the surroundings. A certain pressure will eventually be reached, the so-called dew point mentioned above, at which the gas begins to condense, or to “dew.” Pressure remains constant during the condensation process. Only when the gas is completely condensed and the piston lies upon the surface of the liquid, does the pressure further increase. We conclude that the cylinder contains only gas up to the dew point and above the dew point, only liquid.
2. If this experiment is carried out again at a higher temperature, the process runs the same, but the dew point is shifted to a higher pressure (Fig. 11.6).
3. When all the dew points measured in this way are connected, a steep curve to the right is the result, the so-called *boiling pressure curve* or *vapor pressure curve* (Fig. 11.7). It gives the values of pressure and temperature at which gas and

Fig. 11.5 Representation of the dew point in a $p(T)$ diagram.

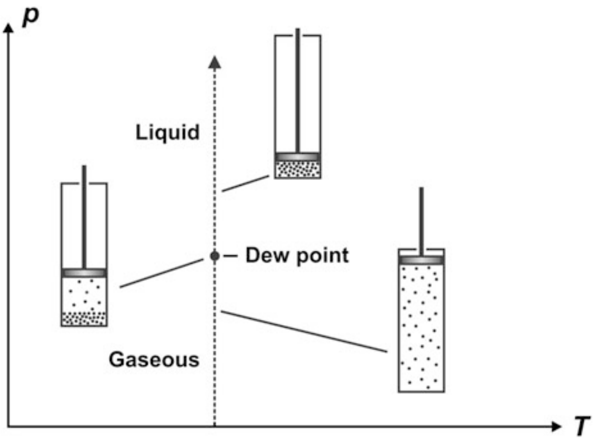


Fig. 11.6 Temperature dependency of dew points.

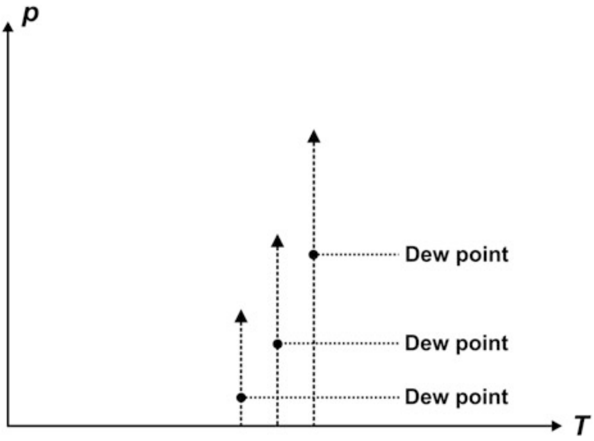
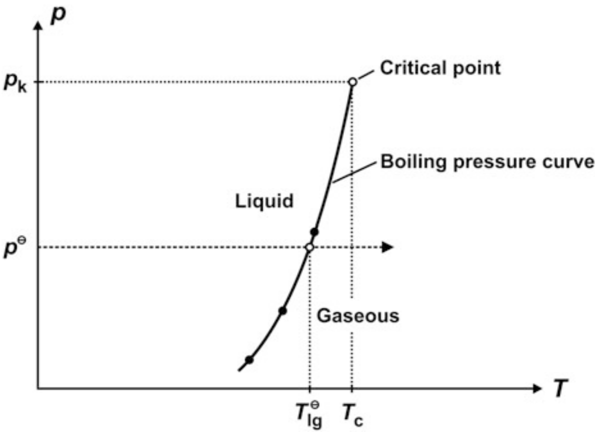


Fig. 11.7 Temperature dependency of a liquid's vapor pressure (boiling pressure curve or vapor pressure curve).



liquid are in equilibrium with each other. Only gas exists at the points below this curve and only liquid exists above it.

4. When a liquid condensate is heated at constant pressure (e.g., ambient air pressure $p^{\ominus}$ of 100 kPa), it will transform into a gaseous state and *boil* as it goes past the boiling pressure curve. The temperature at which this occurs is the *boiling temperature* (boiling point) associated with the pressure in question (e.g., $T_{\mathrm{lg}}^{\ominus}$). The boiling point of a substance is not a constant but depends upon pressure. Tabulated values are based upon standard pressure of 100 kPa. In order to distinguish this special boiling point from other boiling points, we call it the *standard boiling point* and characterize it by $T_{\mathrm{lg}}^{\ominus}$.
5. No dew point exists above the critical temperature T_{c}. This is the highest temperature at which a liquid can exist. For this reason, the boiling pressure curve ends at the critical temperature—in the critical point mentioned above.

How can we now quantitatively approximate the boiling pressure curve? To do this we will need to refer back to the chemical potential. As we have seen, every phase of a substance has its own chemical potential, which is dependent upon temperature and pressure. We can easily calculate these potentials for different temperatures and pressures. At an arbitrary condition, the most stable phase is the one with the lowest chemical potential. The stability range of the liquid phase is characterized by the chemical potential $\mu_{\mathrm{l}}(p, T)$ being lowest there. Where the gaseous phase is stable, $\mu_{\mathrm{g}}(p, T)$ is minimal.

In order to calculate the curve that separates the two stability ranges (the curve that reflects the equilibrium between two phases), we can refer back to the formula derived earlier for calculating the reaction pressure of gases (compare Sect. 5.5) because the boiling process can be considered a reaction:

$$\mathrm{B|l} \rightarrow \mathrm{B|g}.$$

If we proceed as we did in deriving Eq. (5.19), we obtain for the (saturation) vapor pressure p_{lg} in equilibrium in a closed, initially evacuated container:

$$p_{\mathrm{lg}} = p_0 \exp\frac{\mathcal{A}_{\mathrm{lg},0}}{RT}. \tag{11.6}$$

The index $_{\mathrm{lg}}$ (or in more detail, $_{\mathrm{l}\rightarrow\mathrm{g}}$) indicates the type of process. In this case, it is vaporization (the transition from liquid to gaseous state). p_0 is the arbitrarily chosen initial pressure and $\mathcal{A}_{\mathrm{lg},0} = \mu_{\mathrm{l},0} - \mu_{\mathrm{g},0}$ is the drive at the chosen initial state (T_0, p_0). The pressure dependency of the chemical potential of the liquid phase is ignored here. We are allowed to do this because it is generally smaller by several orders of magnitude than that of gases as long as the pressure p does not exceed standard pressure $p^{\ominus}$ by much. For this reason, our approach becomes invalid near the critical point where pressures are usually far above $p^{\ominus}$. In order to calculate the equilibrium pressures corresponding to various temperatures T, we need to use the chemical potentials and the corresponding drive at the chosen temperatures. We

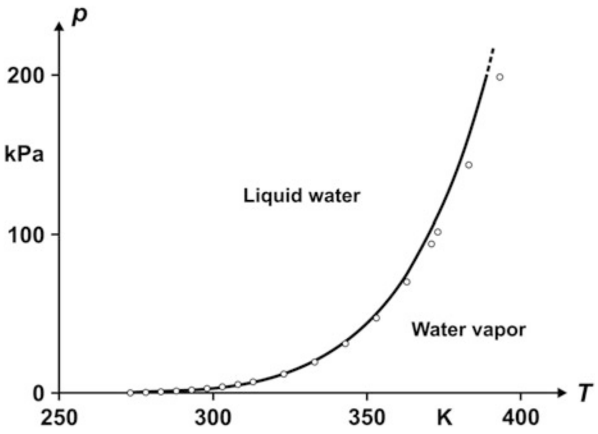


Fig. 11.8 Temperature dependency of saturation vapor pressure of water (comparison of the calculated curve with measured values).

will again make use of our linear approach by replacing $\mathcal{A}_{\mathrm{lg},0}$ by $\mathcal{A}_{\mathrm{lg},0} + \alpha_{\mathrm{lg}}(T - T_0)$ in Eq. (11.6). We obtain:

$$p_{\mathrm{lg}} = p_0 \exp \frac{\mathcal{A}_{\mathrm{lg},0} + \alpha_{\mathrm{lg}}(T - T_0)}{RT} \tag{11.7}$$

or, after transforming the equation and leaving out index $_{\mathrm{lg}}$ for simplicity:

$$\ln \frac{p}{p_0} = \frac{\mathcal{A}_0 + \alpha(T - T_0)}{RT} = \frac{(\mathcal{A}_0 - \alpha T_0)/R}{\vartheta + 273\,\mathrm{K}} + \frac{\alpha}{R}. \tag{11.8}$$

Equation (11.8) formally corresponds to the August vapor pressure formula. In 1862, Ernst Ferdinand August developed a formula based upon water vapor pressure, having the form $\lg\{p\} = -A/(\vartheta + C) + B$; the quantities A, B, C were parameters to be determined empirically, ϑ indicated the Celsius temperature, and $\{p\}$ the numerical value of the pressure.

In Fig. 11.8, the temperature dependency of vapor pressure is shown using water as the example, where the data for standard conditions (298 K, 100 kPa) were used, i.e.:

	$H_2O\|l$	$\rightarrow$ $H_2O\|g$	
$\mu^{\ominus}(\mathrm{kG})$:	−237.1	−228.6	$\Rightarrow$ $\mathcal{A}^{\ominus} = -8.5\ \mathrm{kG}$
$\alpha(\mathrm{G\,K^{-1}})$:	−70	−189	$\Rightarrow$ $\alpha\ = +119\ \mathrm{G\,K^{-1}}$

and therefore,

$$p_{\mathrm{lg}} = 100\,\mathrm{kPa} \times \exp\left(\frac{-8.5 \times 10^3 + 119 \times (T/\mathrm{K} - 298)}{8.314 \times T/\mathrm{K}}\right).$$

If the critical point is far enough away and if we limit ourselves to a relatively small temperature span, Eq. (11.7) will (despite the approximations used) yield a quite useful result. This can be seen in the comparison with experimental values.

As we have shown in Chap. 9, the temperature coefficient α of the drive corresponds to a molar reaction entropy. In this case, this is the change of entropy $\Delta_{\mathrm{lg}}S = S_{\mathrm{m,g}} - S_{\mathrm{m,l}}$ due to the vaporization process at the initial point, meaning at temperature T_0 and pressure p_0. If we abbreviate to $\Delta_{\mathrm{lg}}S_0$, we obtain:

$$p_{\mathrm{lg}} = p_0 \exp \frac{\mathcal{A}_{\mathrm{lg},0} + \Delta_{\mathrm{lg}}S_0 \cdot (T - T_0)}{RT}. \tag{11.9}$$

If instead of choosing an arbitrary initial state when calculating the boiling pressure curve (characterized by temperature T_0 and pressure p_0), we use the special case of an equilibrium state, meaning a known boiling point, e.g., the standard boiling point $T^{\ominus}_{\mathrm{lg}}$, the relation (11.9) can be simplified: In equilibrium, the drive of the vaporization process equals zero, and we find

$$p_{\mathrm{lg}} = p^{\ominus} \exp \frac{\Delta_{\mathrm{vap}}S^{\ominus} \cdot \left(T - T^{\ominus}_{\mathrm{lg}}\right)}{RT}. \tag{11.10}$$

If we set $y = \ln\left(p_{\mathrm{lg}}/p^{\ominus}\right)$ and $x = T^{-1}$, the result is an equation of a straight line:

$$\underbrace{\ln \frac{p_{\mathrm{lg}}}{p^{\ominus}}}_{y} = \underbrace{-\frac{\Delta_{\mathrm{vap}}S^{\ominus} \cdot T^{\ominus}_{\mathrm{lg}}}{R}}_{m} \cdot \underbrace{\frac{1}{T}}_{x} + \underbrace{\frac{\Delta_{\mathrm{vap}}S^{\ominus}}{R}}_{b}. \tag{11.11}$$

Here, $\Delta_{\mathrm{vap}}S^{\ominus}$ is the *molar entropy of vaporization* at the standard boiling point. Now when $\ln\left(p_{\mathrm{lg}}/p^{\ominus}\right)$ is plotted as a function of $1/T$ for various substances, we notice that the intersection points b with the ordinate of the (extrapolated) straight lines lie rather close together for many nonpolar compounds. This means that the molar vaporization entropies are also similar, with an average of about 88 Ct K^{-1} mol^{-1}. This was already recognized by Frederick Thomas Trouton in 1884 through his work comparing measured values in Tables (*Pictet–Trouton's rule*). The reason for the approximate concordance of molar vaporization entropies is the comparably great increase of "disorder" for a transition from a relatively highly condensed phase to a gas with particles far away from each other. Great deviations from this rule can be explained by strong interactions between the molecules and a higher degree of order in the corresponding phase. For example, hydrogen bridge bonds form in liquid water (and other polar substances) resulting in higher entropy of vaporization $\left(\Delta_{\mathrm{vap}}S^{\ominus}(\mathrm{H_2O}) = 109.1\ \mathrm{Ct\ K^{-1}\ mol^{-1}}\right)$.

11.5 Complete Phase Diagram

The other phase transitions of a pure substance can also be represented in a $p(T)$ diagram in the form of *phase boundaries*, producing a complete *phase diagram*. This diagram shows the conditions of temperature and pressure under which a certain phase is most stable and illustrates the ranges of existence of stable phases.

1. Below a certain temperature, a condensate forms as a solid and not a liquid. The direct transition from a gaseous to a solid state, or vice versa, is called *sublimation* and the vapor pressure curve of a solid substance, the *sublimation* (*pressure*) *curve* (Fig. 11.9). Gas and solid are in equilibrium with each other along this phase boundary. As long as pressure remains below this curve at constant temperature during the compression of the gas, only gas will be present in the cylinder. However, if the pressure lies above this, only a solid condensate will appear.
2. The almost vertical curve in the illustration (Fig. 11.10), called the *melting* (*pressure*) *curve*, separates the regions at which solid or liquid condensate is stable. The slope of this curve has been greatly exaggerated for the sake of clarity.
3. When a solid condensate is heated at constant pressure (e.g., at ambient air pressure of 100 kPa) starting at the absolute zero point, it will go into a liquid state as it exceeds the melting pressure curve: it *melts*. The temperature at which this occurs, where both solid and liquid phase are in equilibrium, is the *melting temperature* (melting point) corresponding to the pressure (e.g., $T_{\mathrm{sl}}^{\ominus}$). When the substance is further heated, it finally reaches the boiling pressure curve and will begin to boil (compare Sect. 11.4).

   Like the boiling point of a substance, its melting point is not a constant but, to a much lesser extent, also depends upon pressure. The *standard melting point* $T_{\mathrm{sl}}^{\ominus}$ is based upon a pressure of 100 kPa.

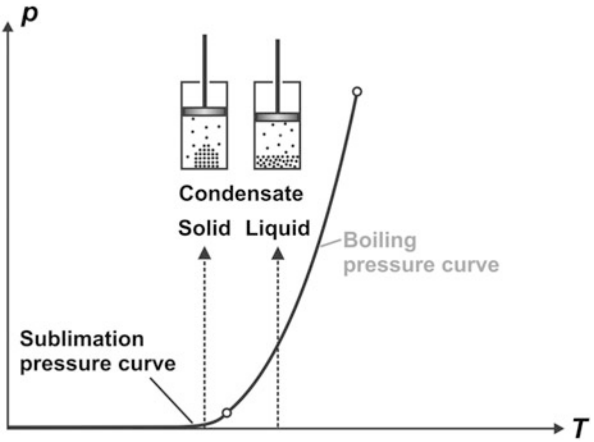
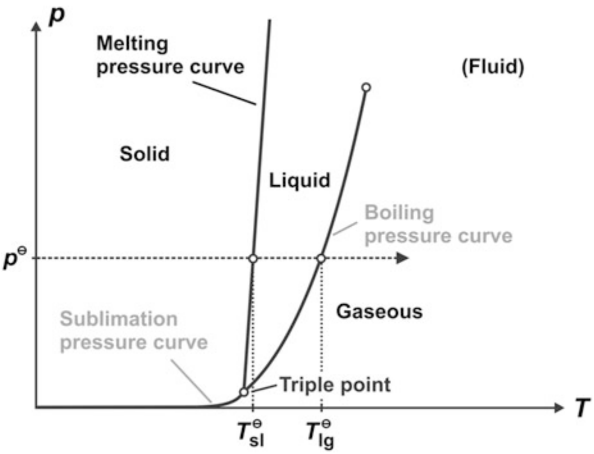


Fig. 11.9 Sublimation and boiling pressure curve of a substance.

Fig. 11.10 Typical phase diagram of a pure substance.



4. The point at which the sublimation, boiling, and melting pressure curves all converge is called the *triple point* because at the conditions of temperature and pressure there, the substance is simultaneously in a solid, liquid, and gaseous state. At the triple point both pressure and temperature are characteristic properties of a pure substance. The triple point of water, for example, is at 273.16 K and 611 Pa. Only at this exact temperature and this exact pressure are ice, liquid water, and water vapor in equilibrium with each other. This triple point is used to define the unit called *Kelvin* (compare Sect. 3.8). If the pressure at the triple point lies noticeably above 100 kPa, the liquid state cannot exist no matter what the temperature, and only sublimation can be observed. An example of this is carbon dioxide (217 K, 518 kPa), which, when exposed to air, changes directly from solid to gas (so it is called "dry ice").

The other phase boundaries can also be calculated using the chemical potential. For example, the sublimation pressure curve can be described analogously to the boiling pressure curve. We only need the drive $\mathcal{A}_{\mathrm{sg},0} = \mu_{\mathrm{s},0} - \mu_{\mathrm{g},0}$ responsible for sublimation and the corresponding change of entropy, the molar sublimation entropy $\Delta_{\mathrm{sg}} S_0$ (both at temperature T_0 and pressure p_0):

$$p_{\mathrm{sg}} = p_0 \exp \frac{\mathcal{A}_{\mathrm{sg},0} + \Delta_{\mathrm{sg}} S_0 \cdot (T - T_0)}{RT}. \tag{11.12}$$

When temperature increases, the sublimation pressure increases just as boiling pressure does, both reciprocally and exponentially ($\sim \mathrm{e}^{-a/T}$).

A linear approach for both the temperature and pressure dependency of the chemical potential is sufficient for calculating the melting pressure curve (compare Sect. 5.4). For the process

$$\mathrm{B|s} \rightarrow \mathrm{B|l}$$

we obtain the following condition in the case of equilibrium ($\mu_\mathrm{s} = \mu_\mathrm{l}$):

$$\mu_{\mathrm{s},0} + \alpha_\mathrm{s} \cdot \Delta T + \beta_\mathrm{s} \cdot \Delta p = \mu_{\mathrm{l},0} + \alpha_\mathrm{l} \cdot \Delta T + \beta_\mathrm{l} \cdot \Delta p.$$

Because of $\mathcal{A}_{\mathrm{sl},0} = \mu_{\mathrm{s},0} - \mu_{\mathrm{l},0}$ as well as $\alpha_\mathrm{sl} = \alpha_\mathrm{s} - \alpha_\mathrm{l}$ and $\beta_\mathrm{sl} = \beta_\mathrm{s} - \beta_\mathrm{l}$, converting results in:

$$\mathcal{A}_{\mathrm{sl},0} + \alpha_\mathrm{sl} \cdot \Delta T = -\beta_\mathrm{sl} \cdot \Delta p$$

and therefore with $\Delta p = p_\mathrm{sl} - p_0$ and $\Delta T = T - T_0$, if one solves for p_sl:

$$p_\mathrm{sl} = p_0 - \frac{\mathcal{A}_{\mathrm{sl},0} + \alpha_\mathrm{sl} \cdot (T - T_0)}{\beta_\mathrm{sl}}. \qquad (11.13)$$

$\mathcal{A}_{\mathrm{sl},0}$ represents the drive of the melting process at the chosen initial state (in this case, a temperature of T_0 and pressure of p_0). The temperature coefficient α_sl of the drive corresponds to the molar reaction entropy $\Delta_\mathrm{sl}S_0$ of the melting process and the pressure coefficient β_sl corresponds to the negative molar reaction volume $-\Delta_\mathrm{sl}V_0$ (compare Chap. 9), both at the initial state (T_0, p_0). This yields:

$$p_\mathrm{sl} = p_0 + \frac{\mathcal{A}_{\mathrm{sl},0} + \Delta_\mathrm{sl}S_0 \cdot (T - T_0)}{\Delta_\mathrm{sl}V_0}. \qquad (11.14)$$

The linear slope of the melting curve (gradient $\Delta_\mathrm{sl}S_0/\Delta_\mathrm{sl}V_0$) is positive for most substances (just as the reciprocally exponential gradient of the vapor pressure curves is) because $\Delta_\mathrm{sl}S_0$ is always positive and $\Delta_\mathrm{sl}V_0$ almost always is. There are very few substances—water is the best-known example (Fig. 11.11)—that contract during melting so that $\Delta_\mathrm{sl}V_0$ becomes negative.

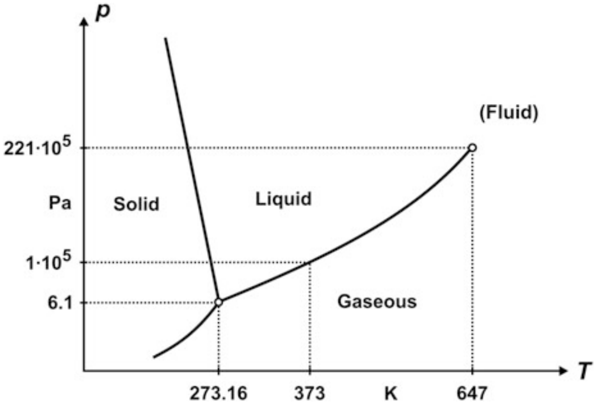


Fig. 11.11 Phase diagram of water (schematic).

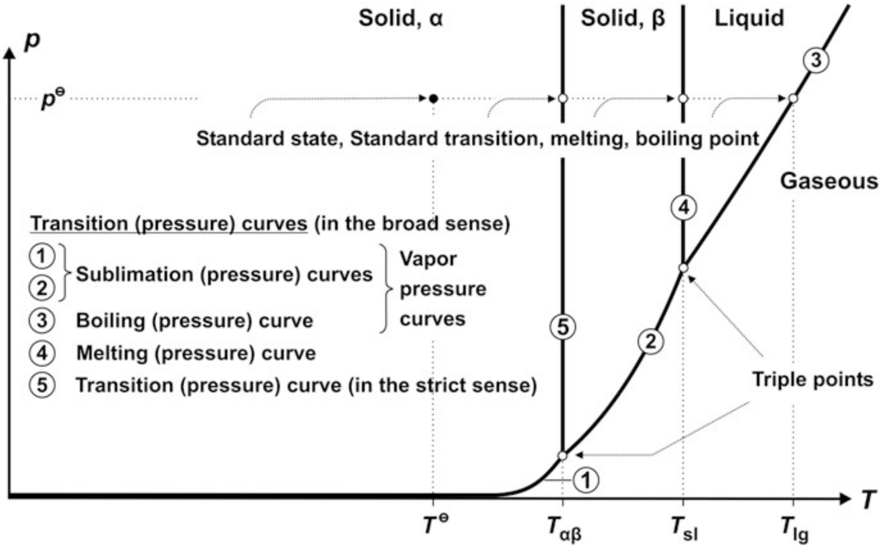


Fig. 11.12 Phase diagram of a substance with two modifications α and β at low pressures.

If we use the special case of an equilibrium point as the initial state, meaning a known melting point, perhaps the standard melting point $T_{\mathrm{sl}}^{\ominus}$, then because the drive of the melting process equals zero, the relation (11.14) simplifies to

$$p_{\mathrm{sl}} = p^{\ominus} + \frac{\Delta_{\mathrm{fus}} S^{\ominus}}{\Delta_{\mathrm{fus}} V^{\ominus}} \cdot \left(T - T_{\mathrm{sl}}^{\ominus}\right). \tag{11.15}$$

Here, $\Delta_{\mathrm{fus}} S^{\ominus}$ is the molar entropy of fusion at the standard melting point and $\Delta_{\mathrm{fus}} V^{\ominus}$ is the change in molar volume that occurs on melting.

While all substances in gaseous state and most substances in liquid state [except for certain compounds consisting of long-chain molecules which may flow like a liquid, but whose molecules may be oriented in a crystal-like way (so-called liquid crystals)] only form a single phase, almost all solid substances exist in various phases or *modifications* (compare Sect. 1.6). Because of these phenomena, which are known as *allotropy* for elements and as *polymorphism* for compounds, the phase diagram includes additional *transition pressure curves* (in the strict sense; Fig. 11.12). They separate the regions of existence of two different modifications (e.g.. α and β) and lead to new triple points. The actual single substance phase diagram for pressure values in the low-pressure range is an example of this.

At other pressures, especially in the high-pressure range, further solid phases γ, δ, ε … can appear (Fig. 11.13), whose regions of existence can be approximated using the same paradigm.

Fig. 11.13 Single substance phase diagram with further modifications at higher pressure.

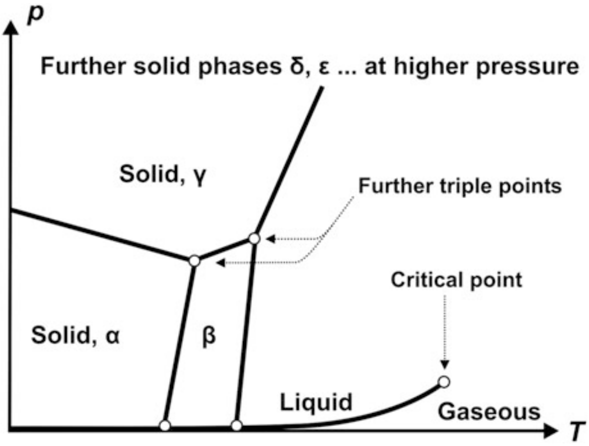
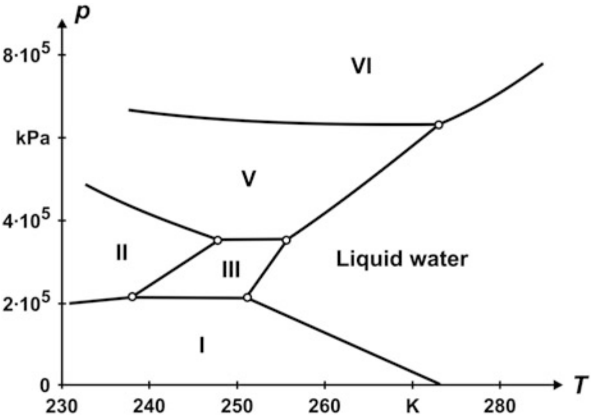


Fig. 11.14 Section of the phase diagram of water at higher pressure.



An example of this is water that, when under high enough pressure, forms not only the usual ice (I) but other solid phases as well (Fig. 11.14). These phases have different arrangements of H_2O molecules. In the figure, we see that phase IV is missing. This is simply because people originally believed that a new phase had been discovered which was later found to actually not exist at all. The numbering was kept, though for the sake of simplicity.