Chapter 3
Changes of State

Abstract Thermodynamics is introduced as a quantitative method of characterizing the changes of state of systems. The topic is subdivided in three categories. Problems dealing with *thermal state variables* and equations of state are found in Sect. 3.2, along with a compact summary of essential theory. Problems focusing on the *caloric state variables* are discussed in Sect. 3.3, again preceded by a summary of basic concepts. Finally, a set of problems dealing with heterogeneous systems, phase transitions, and mixtures is presented in Sect. 3.4.

This chapter deals with a field in physical chemistry that offers a direct approach from our every-day viewpoint: changes in state. A walk through a winter landscape may stir deep feelings in us about the beauty of nature in its entirety, but it may also be a good starting point for developing conceptions about processes in nature and their origin. If we look, for example, at a foggy lake in winter with ice cakes floating downstream, we see water in its different forms: water as a liquid, as vapor, or as ice. The melting of a snow-flake on a warm surface, or the vaporization of a rain drop are concrete examples of changes of state. But even a change in pressure, temperature, or volume is a change of state. Thermodynamics is the result of human reflection about such processes, and it provides the necessary concepts for understanding the general principles behind them, such as the phase diagram of a substance, which relates its states of aggregation to pressure and temperature (Fig. 3.1).

3.1 Systems

For the analysis of processes in nature, it is indispensable to subdivide the considered totality of interacting matter into parts. Typically, we are only interested in the evolution of a certain amount of matter, clearly distinguished by the environment, the surroundings. Usually, the properties of the surroundings are not well-known, but neglecting them completely would be too crude an approximation. Therefore, the concept of the system is introduced, which can be subdivided into subsystems, separated by well-defined boundaries. A system that exchanges neither matter nor heat with its surroundings is called an **isolated system**. A system that only

J. Vogt, *Exam Survival Guide: Physical Chemistry*,
DOI 10.1007/978-3-319-49810-2_3

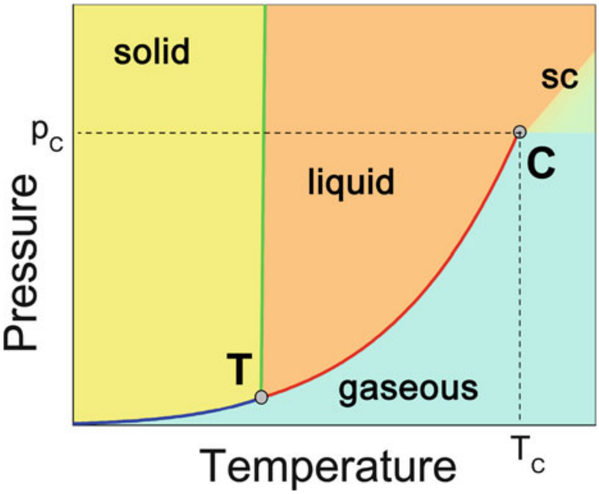

Fig. 3.1 Schematic phase diagram of a pure substance near the triple point (T) with coexistence lines of solid and liquid, gas and liquid, gas and solid. C is the critical point. SC marks the *supercritical phase*

exchanges heat with its surroundings is called a **closed system**. An open system exchanges both heat and matter with its surroundings. A chemical system usually contains a very large number of atoms or molecules, to the order of 10^{23}. On a macroscopic scale, one is primarily interested in only a few **state variables**, which result as the average of the movement of all the interacting atoms and molecules constituting the system. **Intensive** quantities characterizing a system do not depend on the size of the system, whereas **extensive** quantities do. Extensive properties of subsystems are additive. Note that for extensive quantities such as the volume V, capital letters are used in general. Lower case letters are reserved for the related (intensive) molar quantity, e.g., the molar volume v.

3.2 Equation of State, Thermal State Variables

The **thermal state variables** are the temperature T, the pressure p, and the volume V of the system consisting of a certain amount of substance n. There is always an **equation of state**

$$f(p, V, T, n) = 0 \tag{3.1}$$

that links these three thermal state variables. If the system under consideration is a **perfect gas**, the equation of state is

$$\boxed{pV = nRT} \tag{3.2}$$

with the molar gas constant $R = 8.3144621(75)\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The concept of the perfect gas assumes the particles to be point masses without extension, and the model neglects all intermolecular interactions.

Another well-known equation of state is the one proposed by **van der Waals**:

$$\boxed{\left(p + \frac{a\,n^2}{V^2}\right)(V - nb) = nRT} \tag{3.3}$$

It contains two model parameters, a and b, which can be fitted for each substance to experimental p–V–T data. To some extent, the van der Waals model involves the existence of the *critical point* and a possible coexistence of condensed phase and gas phase, but it is of limited accuracy (see also Problem 3.4).

The **virial equation** for 1 mole of substance relates pressure p, temperature T, and the molar volume v in the following way:

$$\boxed{\frac{p\,v}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \cdots} \tag{3.4}$$

It has the advantage of directly linking the p–V–T behavior of a substance to intermolecular interaction. The second virial coefficient B is a temperature-dependent quantity, which is related to pair interaction between molecules, the third virial coefficient C is related to interaction among three molecules, etc.

In the course of a change of state of the system, the thermal state variables are subject to changes. A change in volume, for example, results as a consequence of changes in pressure and temperature:

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \tag{3.5}$$

Given a specific equation of state, the differential quotients themselves can be determined. Moreover, especially in the case of *condensed phases*, they can be expressed by important material properties such as the **isobaric thermal expansion**

coefficient,

$$\boxed{\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p} \tag{3.6}$$

or the **isothermal compressibility**

$$\boxed{\kappa = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T} \tag{3.7}$$

Thermodynamics is able to derive relations between material properties such as α and κ without assuming any microscopic theory of matter (see Problem 3.1). Note that a material property in general depends on the temperature or pressure.

3.2.1 Problems

Problem 3.1 (Thermal State Variables)

a. For an arbitrary isochoric change of state, show that the following equation holds:

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa} \tag{3.8}$$

b. For an arbitrary change of state, show that the following relation holds

$$d(\ln V) = \alpha\, dT - \kappa\, dp \tag{3.9}$$

Solution 3.1 In this problem, we use the concept of the total differential to show some useful relations. It is worth mentioning that thermodynamics does not necessarily assume a microscopic theory of matter that would allow the prediction of material properties such as the compressibility of a substance or its expansion coefficient. Nevertheless, thermodynamics allows the formulation of relations between such material properties. One example is Eq. (3.8).

To show Eq. (3.8) in **subproblem (a)**, we consider the total differential of the volume, which is zero for an isochoric change of state:

$$\text{isochoric} \;\Leftrightarrow\; dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \overset{!}{=} 0 \tag{3.10}$$

$$\Leftrightarrow \left(\frac{\partial V}{\partial T}\right)_p dT = -\left(\frac{\partial V}{\partial p}\right)_T dp; \quad dV = 0 \tag{3.11}$$

$$\Leftrightarrow \left(\frac{dp}{dT}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \tag{3.12}$$

As (see Sect. A.3.5.3 in the appendix)

$$\left(\frac{dp(T,V)}{dT}\right)_V = \left(\frac{\partial p(T,V)}{\partial T}\right)_V, \tag{3.13}$$

we have thus shown Eq. (3.8). For the proof of Eq. (3.9) in **subproblem (b)**, we start again with the total differential of the volume (Eq. (3.5)), and divide by V:

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \tag{3.14}$$

$$\Leftrightarrow \frac{dV}{V} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p dT + \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T dp \tag{3.15}$$

With the definition of α (Eq. (3.6)) and κ (Eq. (3.7)), we have

$$\Leftrightarrow \frac{dV}{V} = \alpha\, dT - \kappa\, dp \tag{3.16}$$

$$\Leftrightarrow d(\ln V) = \alpha\, dT - \kappa\, dp \tag{3.17}$$

which is what was to be shown.

Problem 3.2 (Thermal Expansion of Condensed Phases and Gases) The thermal expansion coefficient of liquid water is $\alpha = 20.0 \times 10^{-5}\,\mathrm{K}^{-1}$, and its compressibility is $\kappa = 0.5 \times 10^{-9}\,\mathrm{Pa}^{-1}$.

Use Eqs. (3.8) and (3.9) to calculate

a. The change in volume of 1 dm^3 water being heated from 25 °C up to 50 °C at atmospheric pressure.
b. The pressure exerted on the walls of a closed container of a volume of 1 dm^3, which is heated to 50 °C after it was completely filled with water at 100,000 Pa and 25 °C.
c. The thermal expansion coefficient α of a perfect gas at 25 °C, and the compressibility κ of a perfect gas at 100,000 Pa.

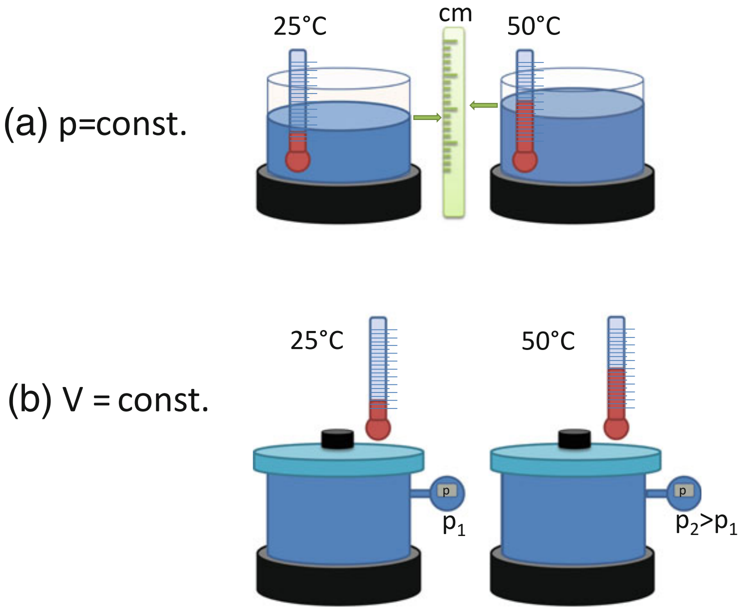

Fig. 3.2 (**a**) Thermal expansion of water at a constant pressure. (**b**) Heating of water at a constant volume causes an increase in pressure

Solution 3.2 Taking liquid water as an example of a condensed phase, we examine the effects of thermal expansion and compressibility in comparison with perfect gas behavior.

In **subproblem (a)** we calculate the change in volume of water, heated at an atmospheric pressure from $T_1 = 298.15$ to $T_2 = 323.15\,\text{K}$. This is the situation in which we heat water in an open cooking pot, as shown in Fig. 3.2a. In our experience, the effect of thermal expansion is small. We adopt Eq. (3.9) for the case of constant pressure ($dp = 0$) and obtain

$$d(\ln V) = \alpha\, dT$$

What comes next is the necessary integration step

$$\int_{\ln V_1}^{\ln V_2} d\ln V = \alpha \int_{T_1}^{T_2} dT$$

Here, we assume that the material property α is independent of temperature within the range T_1 to T_2. The rules for logarithms (see appendix Sect. A.3.3) allow us to evaluate the integrals in the following way:

$$\ln V_2 - \ln V_1 = \ln \frac{V_2}{V_1} = \alpha\,(T_2 - T_1) \Leftrightarrow V_2 = V_1\,\exp\left(\alpha(T_2 - T_1)\right)$$

$$V_2 = V_1\,\exp\left(\alpha(T_2 - T_1)\right) = 1\,\mathrm{dm}^3 \exp\left(20.0 \times 10^{-5}\,\mathrm{K}^{-1} \times 25\,\mathrm{K}\right) = 1.005\,\mathrm{dm}^3$$

Hence, the sought change in volume upon heating is only $V_2 - V_1 = 0.005\,\mathrm{dm}^3$.

Subproblem (b) deals with the case of heating liquid water at a constant volume (Fig. 3.2b). Although we have seen that the effect of thermal expansion is only small for condensed phases, heating the latter at a constant volume can involve enormous changes in pressure, as we will see. We start with Eq. (3.8)

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa} \Leftrightarrow dp = \frac{\alpha}{\kappa}\,dT; \qquad V = \text{const.}$$

Integration within the limits $p_1 = 100{,}000\,\mathrm{Pa}$ at $T_1 = 298.15\,\mathrm{K}$ and p_2—the sought pressure at $T_2 = 323.15\,\mathrm{K}$—yields

$$\int_{p_1}^{p_2} dp = \frac{\alpha}{\kappa} \int_{T_1}^{T_2} dT.$$

We obtain

$$p_2 = p_1 + \frac{\alpha}{\kappa}\,(T_2 - T_1) = 100{,}000\,\mathrm{Pa} + \frac{20 \times 10^{-5}\,\mathrm{K}^{-1}}{0.5 \times 10^{-9}\,\mathrm{Pa}^{-1}} \times 25\,\mathrm{K} = 10.1\,\mathrm{MPa}$$

Hence, the pressure increases by a factor of 100. To avoid such drastic pressure changes, technical closed water circuits, such as domestic central heating systems, are equipped with an expansion tank.

Finally, we calculate α and κ for a perfect gas in **subproblem (c)**. From Eq. (3.2) we obtain by differentiation

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} \qquad\qquad \left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2}$$

We take these derivatives and obtain from Eqs. (3.6) and (3.7) after resubstitution of $V = \frac{nRT}{p}$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{p}{nRT}\frac{nR}{p} = \frac{1}{T}$$

and

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{p}{nRT}(-1)\frac{nRT}{p^2} = \frac{1}{p}$$

Thus, for a perfect gas, the expansion coefficient is $\alpha = 3.35 \times 10^{-3}\,\mathrm{K}^{-1}$ at 298.15 K, and the compressibility is $\kappa = 1.0 \times 10^{-5}\,\mathrm{Pa}^{-1}$ at 100,000 Pa. Gases have a much larger thermal expansion coefficient than condensed phases, which, in addition, strongly depend on temperature. Gases also have a much higher compressibility than condensed phases: if you keep the outlet of a bicycle tire inflator shut, you can compress the air a small amount. However, human forces are not able to do the same with liquid water.

Problem 3.3 (Perfect Gas vs Real Gas) A high-pressure gas cell for laser spectroscopy experiments is filled with pure methane. At a temperature of 300 K, the pressure is 6 MPa.

a. Determine the gas density in $\mathrm{mol\,cm^{-3}}$, assuming perfect gas behavior of CH_4.
b. At 300 K, the second virial coefficient of methane is $-42.23\,\mathrm{cm^3\,mol^{-1}}$. Determine the gas density in the cell. Judging from your results, is the real gas behavior of CH_4 under the given conditions dominated more by the repulsive or by the attractive part of the intermolecular interaction?
c. To obtain accurate results, the third virial must generally be included in the calculation. For methane at 300 K, its value is $2{,}410\,\mathrm{cm^6\,mol^{-2}}$. Use an iterative procedure or a cubic equation solver to determine the gas density in the cell.

Solution 3.3 This is a practical problem from the laboratory: the determination of the gas density from a simple measurement of pressure and temperature. For such applications, the model of the perfect gas gives only an approximate result, but it is easy to handle. For the solution of **subproblem (a)** we start with Eq. (3.2) and obtain the gas density in question

$$\frac{n}{V} = v^{-1} = \frac{p}{RT} = 2.405 \times 10^{-3}\,\mathrm{mol\,cm^{-3}}, \tag{3.18}$$

or 1.445×10^{21} particles per cm^3. Note that the gas density is simply the inverse of the molar volume.

In **subproblem (b)** we use the virial equation Eq. (3.4), but we only consider the second virial coefficient, which is related to pair interactions between molecules.

Hence, we obtain

$$p = \frac{RT}{v} + \frac{RTB}{v^2}$$

This can be written as a quadratic equation

$$\frac{p}{RT}v^2 - v - B = 0,$$

with the two solutions

$$v_{1/2} = \frac{1 \pm \sqrt{1 + \frac{4pB}{RT}}}{\frac{2p}{RT}}$$

The solution with the negative sign yields a vanishing molar volume in the limit $B \to 0$. It is thus not meaningful in the sense of our problem. The solution with the positive sign yields a molar volume of $368.0\,\mathrm{cm^3\,mol^{-1}}$. Hence, the gas density under consideration of the second virial coefficient is $2.717 \times 10^{-3}\,\mathrm{mol\,cm^{-3}}$ or 1.636×10^{21} particles per $\mathrm{cm^3}$.

To discover whether or not the repulsive or attractive nature of the intermolecular interaction is more important under the given conditions, we compare the molar volumes that we have calculated: if molecular interactions are neglected, i.e., in the approximation of the perfect gas, we obtain $v = 415.8\,\mathrm{cm^3\,mol^{-1}}$ from Eq. (3.18). If we take molecular interactions into account by considering the second virial coefficient, we obtain a smaller value of $368.0\,\mathrm{cm^3\,mol^{-1}}$. Imagine for a moment that we were able to switch the molecular interaction on and off. If we were to switch it off, a constant number of molecules would fill a larger volume. Then, if we were to switch it on again, the molar volume would shrink, i.e., the average distance between the molecules would be *smaller*. Thus, we conclude that under the chosen conditions, the molecular interaction among methane molecules is attractive, not repulsive. It is convenient to define the so-called **compression factor** $z = \frac{pv}{RT}$, which is less than 1 if attractive interactions are dominant, exactly 1 for vanishing interactions, and greater than 1 if repulsive interactions are dominant.

In **subproblem (c)** we include the third virial coefficient in the calculation:

$$p = \frac{RT}{v}\left(1 + \frac{B}{v} + \frac{C}{v^2}\right) \tag{3.19}$$

Note that the sum in the bracket is simply the compression factor z. Because an analytic solution is tedious, we determine the molar volume iteratively. Systematically, this could be done using Newton's method (see appendix Sect. A.3.19). But even a *trial and error* procedure starting from the best guess value $v = 368\,\mathrm{cm^3\,mol^{-1}}$ yields the result with just five functional evaluations of Eq. (3.19), as demonstrated in Table 3.1.

Table 3.1 Iterative determination of the molar volume of methane based on the virial equation

v (cm^3 mol^{-1})	z	p (MPa)	Deviation (MPa)
368	0.90304	6.121	+0.121
380	0.90556	5.944	−0.056
375	0.90452	6.017	+0.017
377	0.90490	5.987	−0.013
376	0.90473	6.002	+0.002

Hence, the molar volume of methane is 376 cm^3 mol^{-1}, determined with an accuracy of 1 cm^3 mol^{-1}. Our final result for the gas density is 2.660×10^{-3} mol cm^{-3}. It is instructive to compare our results with experimental values for methane under these conditions. The true experimental molar volume of methane at 300 K and 0.6 MPa is 376.2 cm^3 mol^{-1} [1], and the experimental compression factor is 0.90496. This shows that at a moderate pressure of 6 MPa, the inclusion of the third virial coefficient is sufficient for an accurate description of the p–V–T behavior of methane. Omission of the third virial coefficient, however, consistent with the neglect of three body interactions, gives a result that deviates by about 2% from the experimental value.

Problem 3.4 (Van der Waals Isotherms, Maxwell Construction) The critical temperature of nitrogen N_2 is 126.1 K, and the critical pressure is 35 bar.

a. Plot the van der Waals isotherms of nitrogen at 100, 126, 150, and 300 K.
b. Apply the Maxwell construction to the 100 K isotherm to obtain the vapor pressure of N_2 predicted by the van der Waals model.

Solution 3.4 This exercise deals with the van der Waals model of real gases, which to some extent is capable of explaining the coexistence of the gas phase with a condensed phase and the *critical point* (see Fig. 3.1). How good is the van der Waals model in predicting such properties in a concrete example? Before we move on to the solution, we recall the qualitative behavior of the pressure as a function of volume under isothermal conditions below the critical temperature where gas liquefaction is possible. Consider a gas in a sealed vessel (Fig. 3.3). By means of a moveable piston, the gas is more and more compressed, and the pressure increases. If the volume goes below a certain value, the gas is partially liquefied, and coexistence of the gas and the liquid is observed. Under these conditions, the pressure within the vessel is the vapor pressure p_v of the substance. If the gas is completely liquefied, the pressure increases considerably, because a condensed phase is barely compressible (see Problem 3.2).

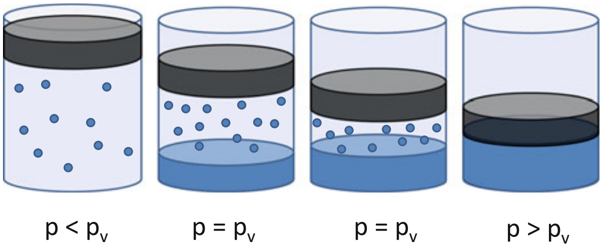

Fig. 3.3 The different stages of gas liquefaction at constant temperature

Moving on to the solution of the **subproblem (a)**, we use Eq. (3.3) to obtain the relation

$$p(v) = \frac{RT}{v - b} - \frac{a}{v^2} \tag{3.20}$$

for 1 mol of nitrogen, for which we shall plot isotherms at 100, 126, 150, and 300 K. At a constant temperature, Eq. (3.20) is the mathematical representation of a van der Waals isotherm. It has a pole for $v = b$, and thus involves a finite volume of the molecules. The two parameters a and b need to be determined from the critical data of nitrogen, the critical temperature $T_c = 126.1\,\mathrm{K}$, and the critical pressure provided $p_c = 3.5\,\mathrm{MPa}$ (Fig. 3.1). Above the critical temperature, no coexistence of the gas phase and the liquid phase is possible, and a supercritical phase is formed. The relation between the critical data and the van der Waals parameters is obtained from the analysis of the *critical isotherm*, $p(v) = \frac{RT_c}{v-b} - \frac{a}{v^2}$. The textbook result is

$$T_c = \frac{8\,a}{27\,R\,b} \tag{3.21}$$

$$p_c = \frac{a}{27\,b^2} \tag{3.22}$$

Division of these equations yields

$$b = \frac{RT_c}{8p_c} = 3.744 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$$

and

$$a = \frac{27\,R\,T_c\,b}{8} = 0.133\,\mathrm{Pa\,m^6\,mol^{-2}}.$$

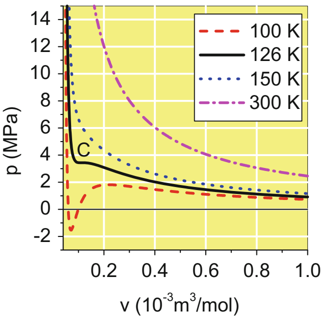

Fig. 3.4 Van der Waals isotherms of N_2 at various temperatures. C is the critical point

The van der Waals isotherms, computed with these values for the temperatures in question are shown in Fig. 3.4. The 126 K isotherm is the critical isotherm. It has the *critical point* as an inflection point.[1] The isotherms at 150 and 300 K show monotonic behavior. The 100 K isotherm has a minimum and a maximum, which does *not* reflect the real behavior of a gas described above.

To obtain a more realistic description within the van der Waals model, the **Maxwell construction** shall be applied in **subproblem (b)**. It is illustrated in Fig. 3.5, where the 100 K isotherm is again shown. The horizontal line intersecting the isotherm at the three points A, B, and C indicates a certain constant pressure $\bar{p}$, which within the model will be interpreted as the vapor pressure p_v at the given temperature, if the enclosed area between A and B has the same absolute value as the enclosed area between B and C. Mathematically, these areas are related to the integrals

$$\begin{aligned} W_{AB} &= \int_{v_A}^{v_B} \left(\frac{RT}{v-b} - \frac{a}{v^2} - \bar{p} \right) dv \\ &\overset{\text{Eq. (A.35),Eq. (A.37)}}{=} RT \ln \frac{v_B - b}{v_A - b} + \frac{a}{v_B} - \frac{a}{v_A} - \bar{p}(v_B - v_A) \end{aligned} \tag{3.23}$$

and

$$W_{BC} = \int_{v_B}^{v_C} \left(\frac{RT}{v-b} - \frac{a}{v^2} - \bar{p} \right) dv = RT \ln \frac{v_C - b}{v_B - b} + \frac{a}{v_C} - \frac{a}{v_B} - \bar{p}(v_C - v_B) \tag{3.24}$$

The sum $W = W_{AB} + W_{BC}$ is the work done in a cycle starting at A along the van der Waals isotherm to the point C, and back on the constant pressure line $p(v) = \bar{p}$ to point A. For reasonable values of $\bar{p}$, W_{AB} takes negative values, whereas W_{AB} is

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[1] The condition of the inflection point to have vanishing first and second derivatives of the function $p(v)$ yields the relations between the van der Waals parameters a and b on the one hand, and the critical data p_c, T_c, and v_c on the other hand.

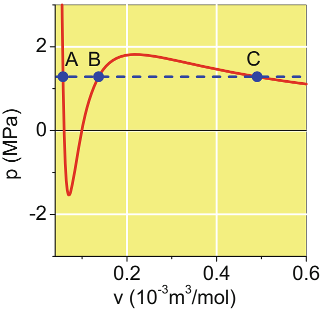

Fig. 3.5 Maxwell construction of the vapor pressure of nitrogen at 100 K. The *curved line* is the van der Waals isotherm at this temperature, the *horizontal dashed line* p = const. marks the coexistence of liquid and gas, if the enclosed areas between the intersecting points A and B, and B and C take the same value

positive, and our task is to find $\bar{p}$, which is consistent with vanishing work done in this virtual thermodynamic cycle. The problem is complicated by the fact that the determination of the intersection points v_A, v_B, and v_C for a given value $\bar{p}$ cannot be done analytically. Using an iterative procedure, we obtain $\bar{p} = 1.2843$ MPa. The related intersection points are $v_A = 0.57509 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1}$, $v_B = 0.13679 \times 10^{-3}\,\text{m}^3\,\text{mol}^{-1}$, and $v_C = 0.49053 \times 10^{-3}\,\text{m}^3\,\text{mol}^{-1}$. W_{AB} is -0.1086×10^3 J, and $W_{BC} = 0.1086 \times 10^3$ J. Thus, for a temperature of 100 K, the van der Waals model predicts the vapor pressure of nitrogen to be $p_v = 1.28$ MPa. It is instructive to compare this value with the experimental value taken from the literature [2], which is 0.76 MPa. We conclude that the van der Waals model only gives an approximate quantitative prediction of the vapor pressure of nitrogen.

3.3 Caloric State Variables, Entropy

In addition to the thermal state variables, the **caloric** state variables are of fundamental importance for the change of state of a system. According to the universal principle of potential energy minimization, any mechanical system left to itself tends to reduce its potential energy and thus its ability to do work. On the other hand, if the system is driven by external forces, work can be transferred to energy or to heat, or vice versa. There are, of course, many important technical applications for this, including heat engines, refrigerators, energy storage, and energy conversion.

There is a second universal principle based on the state variable entropy and the second law of thermodynamics, which predicts the direction of spontaneous processes.

3.3.1 Internal Energy, Work, and Enthalpy

The **internal energy** U corresponds to the sum of all kinetic and potential energy of the atoms and molecules of a system. Energy, defined as the ability of an object or a system to do work, changes, if work is done. By this, a *change* of a system's internal energy, dU, may be related to a certain amount of work δW done by it. Less obviously, there is also a change in internal energy, if an amount of heat δQ is transferred from or to the system:

$$\boxed{dU = \delta Q + \delta W} \tag{3.25}$$

This is the **First law of thermodynamics**. If a system undergoes a change of state without the transfer of heat to the surroundings, the process is called **adiabatic**. In contrast, if the temperature is constant during the change of state, it is called **isothermal**. If work is done during a change of state under isothermal conditions, there is usually a transfer of heat with the surroundings.

As a state variable, the value of the internal energy depends on other state variables, e.g., on T and V, but not on the way in which the system reached this state. This is expressed by the symbol dU for the total differential, in contrast to the infinitesimal changes in heat and work, which generally do depend on the way in which a change of state is performed.

Again, a change in the internal energy of a system depends on its material properties. If U is assumed as a function of temperature and volume,[2] $U = U(T, V)$, the total differential can be written:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{3.26}$$

The derivative

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V} \tag{3.27}$$

is called the **constant volume heat capacity** of the system. The derivative

$$\boxed{\Pi = \left(\frac{\partial U}{\partial V}\right)_T} \tag{3.28}$$

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[2] Because there is always an equation of state that relates p, T, and V, it does not make sense to assume U to be a function of all thermal state variables.

is called the **internal pressure**. As a result of the assumption of non-interacting point masses, the model of the perfect gas does not involve any dependence of the internal energy on system volume. Hence, its internal pressure is zero and internal energy depends only on temperature. In contrast, there is nonzero internal pressure in the model of van der Waals.

Based on the mechanical definition of work related to force F and distance s, $dW = Fds$, in addition to the definition of pressure $p = \frac{F}{A}$ as the quotient of force F acting on an area A, the work done on a system upon a change in volume from V_1 to V_2 is defined as

$$\boxed{W = -\int_{V_1}^{V_2} p\,dV} \tag{3.29}$$

If W is negative, work is done by the system at the expense of its internal energy or the transfer of heat according to Eq. (3.25). If W is positive, work is done to the system.

As the internal energy is the sum of all kinetic and potential energy among the atoms and molecules that constitute a system, the amount of energy needed to create this system at a certain temperature is U. If the system has a certain volume V, an additional amount of work pV is necessary to give it room by displacing the surroundings at an external pressure p. Hence, the work necessary to create a system and give it room is the **enthalpy**,

$$\boxed{H = U + pV.} \tag{3.30}$$

The differential

$$dH = dU + d(pV) = \delta Q - p\,dV + p\,dV + V\,dp = \delta Q + V\,dp$$

Shows the practical importance of the enthalpy: The heat δQ_p which is exchanged by a system with its surroundings at a constant pressure ($dp = 0$), directly corresponds to the change in enthalpy: $\delta Q_p = dH$. Similarly, the heat δQ_V exchanged under isochoric conditions ($dV = 0$) corresponds to the change in internal energy: $\delta Q_V = dU$. The two situations are illustrated in Fig. 3.6. Thus, the measurement of transferred heats in *calorimetric* experiments gives direct access to changes in U and H.

From the total differential of the enthalpy

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp, \tag{3.31}$$

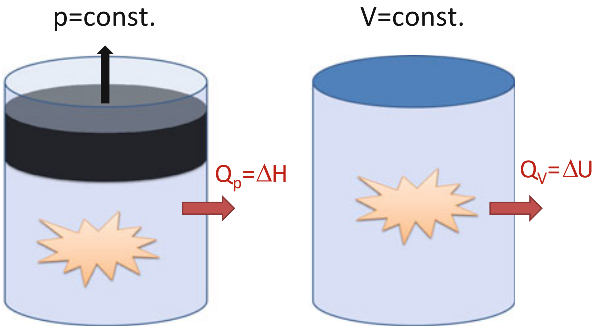

Fig. 3.6 Heat transfer of a system undergoing a change of state with its surroundings. Under isobaric conditions (*left*), the transferred heat corresponds to the change in enthalpy. Under isochoric conditions (*right*), the transferred heat corresponds to the change in internal energy

the **isobaric heat capacity**

$$\boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p} \tag{3.32}$$

is derived as a further material property.

3.3.2 *Reversible and Irreversible Changes of State, the Second Law and Entropy*

The first law of thermodynamics alone leaves a wealth of observations unexplained. One example is the transfer of heat. If two subsystems at different temperatures are brought into contact with each other, heat is always transferred from the subsystem at a higher temperature to the subsystem at a lower temperature, until the temperature of the two subsystems are equal. The reverse process is not observed spontaneously, although, using a cooling machine, for example, it is possible to transfer heat from a system at a lower temperature to a system at a higher temperature, at the expense of doing work. A spontaneous heat transfer from a hot object to a cold one is a typical example of an **irreversible process**. Another example is the spontaneous expansion of a gas. For example, consider a perfect gas: if its internal energy does not depend on volume, for what reason does it tend to expand freely into the whole accessible volume? Again, at the expense of doing work, the spontaneous free expansion of a perfect gas can be reversed by a process of compression.

It is the merit of Clausius to have figured out another state variable that can be used to predict the direction of a spontaneous change of state: the **entropy** S of a system. According to Clausius, entropy is defined by

$$\boxed{dS = \frac{\delta Q_{\mathrm{rev}}}{T}} \tag{3.33}$$

where δQ_{rev} is the infinitesimal heat transferred reversibly to a system at a temperature T.

According to the **Second law of thermodynamics**, the entropy in an isolated system tends toward a maximum:

$$dS \geq 0 \tag{3.34}$$

In the limiting case of a reversible process, $\Delta S = 0$. At this point, it is worth noting that the calculation of ΔS in an irreversible process requires the consideration of a reversible equivalent thermodynamic process. For n moles of a perfect gas undergoing a change of state either from a temperature T_1 to T_2, from a volume V_1 to V_2, or from pressure p_1 to p_2, the change in entropy is

$$\boxed{\Delta S = n\,c_v\,\ln\frac{T_2}{T_1} + n\,R\,\ln\frac{V_2}{V_1} = n\,c_p\,\ln\frac{T_2}{T_1} - n\,R\,\ln\frac{p_2}{p_1}} \tag{3.35}$$

where c_v is the constant volume molar heat capacity, and c_p is the isobaric molar heat capacity of the perfect gas. A similar equation also holds for a van der Waals gas (see Problem 3.8). The inspection of Eq. (3.35), although strictly only valid for a perfect gas, is the key to a general understanding of the direction of irreversible processes: the entropy of a gas increases, if $V_2 > V_1$, because in this case $\ln\frac{V_2}{V_1} > 0$. This is the explanation for the above- mentioned spontaneous free expansion of gases.

3.3.3 Adiabatic Changes of State of a Perfect Gas

If a perfect gas undergoes an adiabatic reversible change of state, pressure, temperature, and volume change according to Poisson's equations:

$$\boxed{p_1\,V_1^{\gamma} = p_2\,V_2^{\gamma}} \tag{3.36}$$

$$\boxed{T_1\, V_1^{\gamma-1} = T_2\, V_2^{\gamma-1}} \tag{3.37}$$

$$\boxed{p_1^{1-\gamma}\, T_1^{\gamma} = p_2^{1-\gamma}\, T_2^{\gamma}} \tag{3.38}$$

where $\gamma = \frac{c_p}{c_v}$ is the **heat capacity ratio**. Equation (3.37) will be derived in Problem 3.9.

3.3.4 The Thermodynamic Potentials

Apart from the internal energy and enthalpy, there are two further essential caloric quantities, the **Gibbs free energy**

$$\boxed{G = H - T\,S,} \tag{3.39}$$

and **Helmholtz free energy**

$$\boxed{A = U - T\,S.} \tag{3.40}$$

The definition of the free energies is that A and G are Minimized, either because of H and U being minimized or because of the entropy S being maximized. In that sense, the two above-mentioned principles energy minimization and entropy maximization are combined into one. It can be shown that there is another condition for the direction of a spontaneous change of a system: at constant pressure and temperature, the direction of spontaneous change of a system is such that G is minimized:

$$dG_{p,T} \leq 0 \tag{3.41}$$

At a constant volume and temperature, A is minimized:

$$dA_{V,T} \leq 0 \tag{3.42}$$

If a process is reversible, $dG_{p,T} = 0$ or $dA_{V,T} = 0$ respectively. These relations are not restricted to isolated systems, they hold for each subsystem separately. Further analysis shows that the Gibbs free energy G is the maximum non-expansion work that can be obtained from a closed system at a constant pressure and temperature. Similarly, A is the maximum work that can be done by a closed system.

Table 3.2 Compilation of thermodynamic potentials

Thermodynamic potential	Natural variables	Differential
Internal energy U	S, V	$dU = T\,dS - p\,dV$
Enthalpy $H = U + pV$	S, p	$dH = T\,dS + V\,dp$
Free energy $A = U - TS$	T, V	$dA = -S\,dT - p\,dV$
Free enthalpy $G = H - TS$	T, p	$dG = -S\,dT + V\,dp$

The thermodynamic potentials U, H, A, and G are summarized in Table 3.2 along with their natural variables.

The thermodynamic potentials, in combination with the Schwarz integrability condition for state functions, provide the extremely useful **Maxwell relations** among thermodynamic state functions:

$$\frac{\partial^2 U}{\partial S\,\partial V} = \frac{\partial^2 U}{\partial V\,\partial S} \Leftrightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{3.43}$$

$$\frac{\partial^2 H}{\partial S\,\partial p} = \frac{\partial^2 H}{\partial p\,\partial S} \Leftrightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{3.44}$$

$$\frac{\partial^2 A}{\partial T\,\partial V} = \frac{\partial^2 A}{\partial V\,\partial T} \Leftrightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{3.45}$$

$$\frac{\partial^2 G}{\partial T\,\partial p} = \frac{\partial^2 G}{\partial p\,\partial T} \Leftrightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{3.46}$$

3.3.5 Problems

Problem 3.5 (Molar Heat Capacities of a van der Waals Gas)
Derive an expression for $c_p - c_v$ for a van der Waals gas.

Solution 3.5 This exercise is an instructive example of how relations between material properties can be derived using the thermodynamic schemes of calculation. Before we start, we recall the textbook result for the difference in molar heat capacities c_p and c_v of a *perfect gas*:

$$c_p - c_v = R. \tag{3.47}$$

For a van der Waals gas, we expect a similar expression to hold that contains the two van der Waals parameters a and b. Moreover, we expect that the sought expression is identical to Eq. (3.47) in the limit $a \to 0$ and $b \to 0$. We start our derivation considering the first law (Eq. (3.25)) for 1 mol of a substance, according to which $\delta q_p = du + p\,dv$ is the transferred heat at a constant pressure.[3] Using the total differential for the molar internal energy (cf. Eq. (3.26)), this can be written as

$$\delta q_p = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv + p\,dv$$

The first term on the right-hand side contains the constant volume heat capacity (see Eq. (3.27)). Hence,

$$\delta q_p = c_v\,dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right]\left(\frac{\partial v}{\partial T}\right)_p dT,$$

and thus, introducing the constant pressure heat capacity $c_p\,dT = \delta q_p$,

$$c_p = c_v + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right]\left(\frac{\partial v}{\partial T}\right)_p. \tag{3.48}$$

The expression in square brackets containing the internal pressure can be simplified by considering:

$$T\,ds = du + p\,dv = c_v\,dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right]dv. \tag{3.49}$$

Here, we have considered once more the total differential for the molar internal energy using the expression from Table 3.2 with the molar entropy s and the molar volume v as natural variables. Therefore,

$$\left[\left(\frac{\partial u}{\partial v}\right)_T + p\right] = T\left(\frac{\partial s}{\partial v}\right)_T \overset{\text{Eq. (3.45)}}{=} T\left(\frac{\partial p}{\partial T}\right)_V \tag{3.50}$$

follows, where we have made use of one of the Maxwell relations. Thus, Eq. (3.48) simplifies to

$$c_p = c_v + T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p \tag{3.51}$$

So far, our intermediate result (3.51) is general, as we have not yet specified an equation of state to replace the derivatives of the thermal state variables. Using Eq. (3.20), it is straightforward to get $\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$. However, $\left(\frac{\partial v}{\partial T}\right)_p$ cannot be evaluated directly, as the van der Waals equation (3.20) cannot be solved for v. The

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[3] For the use of lower letters for molar quantities, see Sect. 3.1.

trick is to consider the total differential dp, which is zero at a constant pressure: $dp \overset{!}{=} 0 = \left(\frac{\partial p}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial v}\right)_T dv$. Therefore,

$$\left(\frac{\partial v}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_T} \tag{3.52}$$

follows, and moreover

$$c_p - c_v \overset{\text{Eq. (3.51)}}{=} -T\frac{\left(\frac{\partial p}{\partial T}\right)_v^2}{\left(\frac{\partial p}{\partial v}\right)_T} = \frac{R}{1 - \frac{2a(v-b)^2}{RTv^3}} \tag{3.53}$$

As expected above, our result agrees with the expression for a perfect gas, if we set the van der Waals parameters at zero. Moreover, $c_p - c_v \to R$ for $v \to \infty$, i.e., for a dilute van der Waals gas, the difference $c_p - c_v$ is the same as for a perfect gas.

Problem 3.6 (Work and Mechanical Equilibrium) A gas cylinder with a total volume of $V = 1\,\text{dm}^3$ is divided initially by a movable piston into two equal volumes, V^0_{Ar} and V^0_{Ne}. V^0_{Ar} contains argon at 1 bar, V^0_{Ne} is filled with neon at 3 bar. Assume perfect gas behavior for both gases and isothermal conditions at $T = 298\,\text{K}$.

a. Explain why the system is not in mechanical equilibrium and calculate the volume of both gases after the piston has reached its equilibrium position.
b. For both gases, determine the expansion/compression work if the piston moves reversibly into its equilibrium position.

Solution 3.6 This problem deals with the case of an isothermal change of state of a system of two perfect gases, separated from each other. The initial situation is depicted in Fig. 3.7. In **subproblem (a)** we explain why the system is not in *mechanical* equilibrium. The latter is established, if the net force acting on the piston is zero. The force $\mathbf{F_2} = -F_2\,\mathbf{e_z}$ is directed downward (in a negative z-direction), $\mathbf{F_1} = +F_1\mathbf{e_z}$ points upward in a positive z-direction. Because the initial pressures are different, $p^0_{\text{Ar}} \neq p^0_{\text{Ne}}$, we can prove that there is a net force acting on the piston with area A:

$$\mathbf{F} = \mathbf{F_1} + \mathbf{F_2} = p^0_{\text{Ar}} A\,\mathbf{e_z} - p^0_{\text{Ne}} A\,\mathbf{e_z} = (p^0_{\text{Ar}} - p^0_{\text{Ne}})A\,\mathbf{e_z} \neq 0 \tag{3.54}$$

Hence, mechanical equilibrium is not established, and the piston moves in the direction that increases the volume filled with neon, until the pressure in both

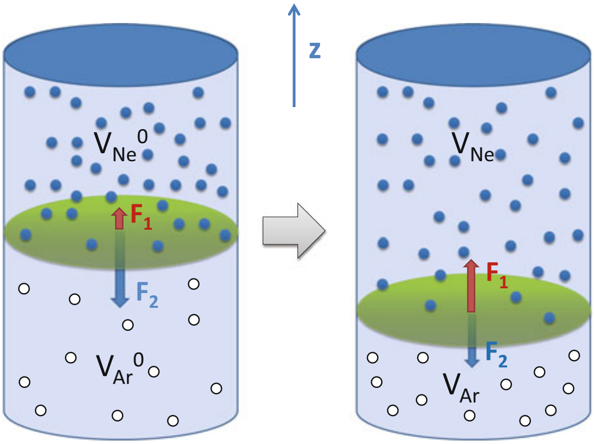

Fig. 3.7 Isothermal expansion of neon and compression of argon, separated by a piston that is free to move in a *z* direction. Mechanical equilibrium is established, if the forces acting on the piston balance each other

volumes is the same:

$$p_{\mathrm{Ne}} \overset{!}{=} p_{\mathrm{Ar}} \tag{3.55}$$

This is the condition for mechanical equilibrium that we use to calculate the final volumes of the two perfect gases:

$$\frac{n_{\mathrm{Ne}}RT}{V_{\mathrm{Ne}}} \overset{!}{=} \frac{n_{\mathrm{Ar}}RT}{V_{\mathrm{Ar}}}$$

We make use of the fact that the total volume $V = V_{\mathrm{Ar}} + V_{\mathrm{Ne}}$ of the gases is unchanged if the piston moves, and, moreover, $n_{\mathrm{Ne}} = 3n_{\mathrm{Ar}}$. Hence the condition for mechanical equilibrium is simplified to

$$\frac{3}{V - V_{\mathrm{Ar}}} = \frac{1}{V_{\mathrm{Ar}}}$$

which can be solved for V_{Ar}: the result is $V_{\mathrm{Ar}} = \frac{V}{4} = 0.25\,\mathrm{dm}^3$. Accordingly, $V_{\mathrm{Ne}} = \frac{3V}{4} = 0.75\,\mathrm{dm}^3$. We note that the equilibrium pressure on both sides of the piston is 2 bar, i.e., the average of the initial pressures.

In **subproblem (b)** we calculate the work done by the expansion of neon and the compression of argon. We make use of Eq. (3.29) and consider that the piston moves *reversibly*, i.e., at each of its positions, the pressure can be calculated by the equation of state: $p_{\mathrm{Ne}} = \frac{n_{\mathrm{Ne}}RT}{V_{\mathrm{Ne}}}$, and $p_{\mathrm{Ar}} = \frac{n_{\mathrm{Ar}}RT}{V_{\mathrm{Ar}}}$:

$$W_{\mathrm{Ne}} = -n_{\mathrm{Ne}}RT \int_{V_{\mathrm{Ne}}^0}^{V_{\mathrm{Ne}}} \frac{dV}{V} = -p_{\mathrm{Ne}}^0 V_{\mathrm{Ne}}^0 \ln \frac{V_{\mathrm{Ne}}}{V_{\mathrm{Ne}}^0}$$

$$W_{\mathrm{Ne}} = -3 \times 10^5\,\mathrm{Pa} \times \frac{1}{2} \times 10^{-3}\,\mathrm{m}^3 \ln \frac{0.75}{0.5} = -60.8\,\mathrm{J}$$

$$W_{\mathrm{Ar}} = -n_{\mathrm{Ar}}RT \int_{V_{\mathrm{Ar}}^0}^{V_{\mathrm{Ar}}} \frac{dV}{V} = -p_{\mathrm{Ar}}^0 V_{\mathrm{Ar}}^0 \ln \frac{V_{\mathrm{Ar}}}{V_{\mathrm{Ar}}^0}$$

$$W_{\mathrm{Ar}} = -1 \times 10^5\,\mathrm{Pa} \times \frac{1}{2} \times 10^{-3}\,\mathrm{m}^3 \ln \frac{0.25}{0.5} = +34.7\,\mathrm{J}$$

Consistent with the compression of argon, the work done on argon, W_{Ar}, is positive. Accordingly, W_{Ne} is negative.

At the end of this problem it is worth reflecting on the significance of mechanical equilibrium in the context of thermodynamics. Although we are dealing with *changes* of state, we usually characterize these changes by an initial state, a final state, and perhaps intermediate states. Even if these states are not states of thermodynamic equilibrium, they may still be states of mechanical equilibrium in which the mechanical forces are balanced exactly. We deal with an example in Problem 3.7. Furthermore, mechanical equilibrium is a precondition for thermodynamic equilibrium.[4] Therefore, states of mechanical equilibrium are, for example, important for the discussion of reversible and irreversible changes of state. An example is presented in Problem 3.9.

Problem 3.7 (Adiabatic Reversible Expansion/Compression)
A gas cylinder with a total volume of $V = 1\,\mathrm{dm}^3$ is divided initially by a movable piston into two equal volumes, V_{Ar}^0 and V_{Ne}^0. V_{Ar}^0 contains argon at 1 bar, V_{Ne}^0 is filled with neon at 3 bar. Assume perfect gas behavior for both gases. The initial temperature of the two gases is $T^0 = 298\,\mathrm{K}$. Assume adiabatic conditions, i.e., that no heat is exchanged, neither between the gases, nor between the gases and the surroundings. For both gases, the constant volume heat capacity is $c_v = \frac{3}{2}R$

a. Calculate the volume, the temperature, and the pressure of both gases, after the piston has moved reversibly into its equilibrium position.
b. Calculate the work and the change in entropy for both gases.
c. What is the temperature of the gases and the entropy change if the piston is suddenly removed?

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[4] Thermodynamic equilibrium between two systems involves thermal, mechanical, and also chemical equilibrium.

Solution 3.7 This problem is an extension of Problem 3.6. Starting from the same initial conditions (see Fig. 3.7), we calculate the volume of the two gases, neon and argon, separated by a piston, if the latter moves reversibly and *adiabatically* instead of isothermally into its equilibrium position. What is different? If no heat exchange occurs, neon does expansion work at the expense of losing internal energy, and cools down. Conversely, argon, which is compressed, heats up. Hence, the final temperature of both gases is different. Furthermore, we cannot assume that the final equilibrium pressure on both sides of the piston will be the average of the initial values, as in Problem 3.6. Our solution is again based on the condition for mechanical equilibrium, Eq. (3.55), but we use Eq. (3.36) for reversible adiabatic changes of state:

$$p_{\mathrm{Ne}}^{0}\, V_{\mathrm{Ne}}^{0,\gamma} = p_{\mathrm{Ne}}\, V_{\mathrm{Ne}}^{\gamma} \tag{3.56}$$

$$p_{\mathrm{Ar}}^{0}\, V_{\mathrm{Ar}}^{0,\gamma} = p_{\mathrm{Ar}}\, V_{\mathrm{Ar}}^{\gamma} \tag{3.57}$$

$\gamma = \frac{c_p}{c_v} = \frac{5/2}{3/2} = \frac{5}{3}$ is the heat capacity ratio. Thus, by using Eq. (3.55), the condition is

$$\frac{p_{\mathrm{Ne}}^{0}\, V_{\mathrm{Ne}}^{0,\gamma}}{V_{\mathrm{Ne}}^{\gamma}} \overset{!}{=} \frac{p_{\mathrm{Ar}}^{0}\, V_{\mathrm{Ar}}^{0,\gamma}}{V_{\mathrm{Ar}}^{\gamma}}$$

Because $V_{\mathrm{Ne}}^{0} = V_{\mathrm{Ar}}^{0}$, and $V = V_{\mathrm{Ar}} + V_{\mathrm{Ne}}$, we can eliminate V_{Ar}:

$$\frac{p_{\mathrm{Ne}}^{0}}{V_{\mathrm{Ne}}^{\gamma}} = \frac{p_{\mathrm{Ar}}^{0}}{(V - V_{\mathrm{Ne}})^{\gamma}}$$

This expression can be solved for V_{Ne}:

$$V_{\mathrm{Ne}} = V \frac{\left(\frac{p_{\mathrm{Ne}}^{0}}{p_{\mathrm{Ar}}^{0}}\right)^{\frac{1}{\gamma}}}{1 + \left(\frac{p_{\mathrm{Ne}}^{0}}{p_{\mathrm{Ar}}^{0}}\right)^{\frac{1}{\gamma}}} = 1\,\mathrm{dm}^3\, \frac{3^{\frac{3}{5}}}{1 + 3^{\frac{3}{5}}} = 0.66\,\mathrm{dm}^3$$

Thus, $V_{\mathrm{Ar}} = V - V_{\mathrm{Ne}} = 0.34\,\mathrm{dm}^3$. Neon expands, but the final volume is smaller for adiabatic conditions than in the isothermal case treated in Problem 3.6a. The equilibrium pressure on both sides of the piston is

$$p_{\mathrm{Ar}} = p_{\mathrm{Ar}}^0 \left(\frac{V_{\mathrm{Ar}}^0}{V_{\mathrm{Ar}}} \right)^{\gamma} = 1.8932\,\mathrm{bar},$$

the same pressure is obtained for p_{Ne}. Note that the equilibrium pressure differs from our result for the isothermal case (Problem 3.6). Finally, we calculate the temperature of both gases using the equation of state for the perfect gas, and the initial temperature $T^0 = 298\,\mathrm{K}$:

$$T_{\mathrm{Ne}} = \frac{p_{\mathrm{Ne}} V_{\mathrm{Ne}}}{n_{\mathrm{Ne}} R} = \frac{p_{\mathrm{Ne}} V_{\mathrm{Ne}}}{\frac{p_{\mathrm{Ne}}^0 V_{\mathrm{Ne}}^0}{R T^0} R} = \frac{p_{\mathrm{Ne}} V_{\mathrm{Ne}}}{p_{\mathrm{Ne}}^0 V_{\mathrm{Ne}}^0} T^0 = 247.9\,\mathrm{K}$$

$$T_{\mathrm{Ar}} = \frac{p_{\mathrm{Ar}} V_{\mathrm{Ar}}}{p_{\mathrm{Ar}}^0 V_{\mathrm{Ar}}^0} T^0 = 384.7\,\mathrm{K}$$

As expected, neon has cooled down after its expansion, and the compressed argon has heated up markedly.

In **subproblem (b)** we shall calculate the work and the change in entropy for both gases. For an adiabatic change of state, the work can be calculated from the first law (Eq. (3.25)) with the assumption $\delta Q = 0$. Therefore,

$$W_{\mathrm{Ne}} = \Delta U_{\mathrm{Ne}} = n_{\mathrm{Ne}}\, c_v \left(T_{\mathrm{Ne}} - T_{\mathrm{Ne}}^0 \right) = \frac{p_{\mathrm{Ne}}^0 V_{\mathrm{Ne}}^0}{R T_{\mathrm{Ne}}^0} \frac{3R}{2} \left(T_{\mathrm{Ne}} - T_{\mathrm{Ne}}^0 \right) = -37.8\,\mathrm{J}$$

and

$$W_{\mathrm{Ar}} = \Delta U_{\mathrm{Ar}} = n_{\mathrm{Ar}}\, c_v \left(T_{\mathrm{Ar}} - T_{\mathrm{Ar}}^0 \right) = \frac{p_{\mathrm{Ar}}^0 V_{\mathrm{Ar}}^0}{R T_{\mathrm{Ar}}^0} \frac{3R}{2} \left(T_{\mathrm{Ar}} - T_{\mathrm{Ar}}^0 \right) = +21.8\,\mathrm{J}$$

The total work done is therefore $W = W_{\mathrm{Ne}} + W_{\mathrm{Ar}} = 16\,\mathrm{J}$, which will be further discussed below. The entropy change in the gases, undergoing an adiabatic reversible change of state, is zero: $\Delta S_{\mathrm{Ne}} = 0$, $\Delta S_{\mathrm{Ar}} = 0$.

In **subproblem (c)** the piston is suddenly removed from its equilibrium position, as indicated in Fig. 3.8. The gases spontaneously expand into the whole volume V, which is an irreversible process.[5] In addition, there is an equilibration of temperature by a transfer of heat from argon at 384.7 K to neon at 247.9 K. We determine the final temperature of the gases after equilibration, and, in addition, the entropy changes involved with this irreversible process. In the first step, we calculate the final temperature T_f in two ways. The first method is to regard the determination of the final temperature as a problem of heat transfer: as no heat is exchanged with the

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[5] For a rather elementary analysis of the mixing of gases based on statistics, see Problem 8.2.

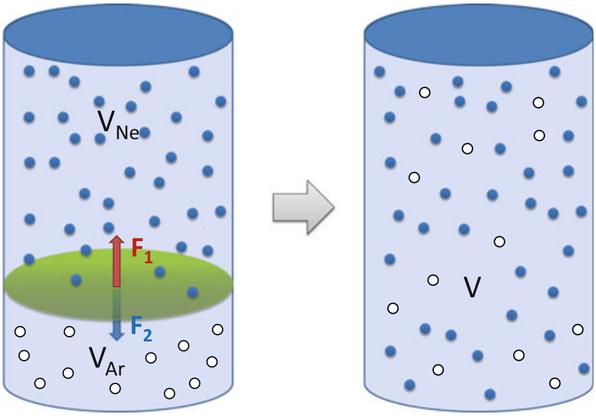

Fig. 3.8 Free expansion of neon and argon after removal of the piston

surroundings,

$$Q_{\mathrm{Ne}} + Q_{\mathrm{Ar}} = n_{\mathrm{Ne}} c_v \left(T_f - T_{\mathrm{Ne}}\right) + n_{\mathrm{Ar}} c_v \left(T_f - T_{\mathrm{Ar}}\right) = 0$$

We solve for T_f and obtain

$$T_f = \frac{n_{\mathrm{Ne}}\, T_{\mathrm{Ne}} + n_{\mathrm{Ar}}\, T_{\mathrm{Ar}}}{n_{\mathrm{Ne}} + n_{\mathrm{Ar}}} = \frac{3T_{\mathrm{Ne}} + T_{\mathrm{Ar}}}{4} = 282.1\,\mathrm{K}. \tag{3.58}$$

We note that the number of moles of neon and argon can be calculated from the initial conditions, $n_{\mathrm{Ar}} = \frac{p^0_{\mathrm{Ar}} V^0_{\mathrm{Ar}}}{RT^0} = 0.02018\,\mathrm{mol}$, and $n_{\mathrm{Ne}} = 3n_{\mathrm{Ar}}$, because $p^0_{\mathrm{Ne}} = 3p^0_{\mathrm{Ar}}$. According to Eq. (3.58) T_f is 15.9 K smaller than T^0, the initial temperature of the two gases, before the piston went into its position of mechanical equilibrium. Did we expect this? To check our result, we calculate T_f in a second way, using an argument of energy conservation. Between the initial state of the gases at temperature $T^0 = 298\,\mathrm{K}$ and the final state at T_f, the above calculated work involved with the movement of the piston was $W = 16\,\mathrm{J}$. No further was done, because, after the piston was removed, the expansion of the gases was a free expansion. As there was no heat transfer with the surroundings, we did indeed expect a cooling of the gases in the final state by

$$\Delta T = \frac{W}{\left(n_{\mathrm{Ar}} + n_{\mathrm{Ne}}\right) c_v} = \frac{16\,\mathrm{J}}{0.08072\,\mathrm{mol} \times 12.4718\,\mathrm{J\,K^{-1}\,mol^{-1}}} = 15.9\,\mathrm{K}, \tag{3.59}$$

and thus $T_f = T^0 - \Delta T = 282.1\,\mathrm{K}$, i.e., the same result as above. Finally, we can calculate the entropy change in the gases using Eq. (3.35):

$$\Delta S_{\mathrm{Ne}} = n_{\mathrm{Ne}}\, c_v \,\ln \frac{T_f}{T_{\mathrm{Ne}}} + n\, R\, \ln \frac{V}{V_{\mathrm{Ne}}} = 0.308\,\mathrm{J\,K^{-1}\,mol^{-1}} \tag{3.60}$$

$$\Delta S_{\mathrm{Ar}} = n_{\mathrm{Ar}}\, c_v \,\ln \frac{T_f}{T_{\mathrm{Ar}}} + n\, R\, \ln \frac{V}{V_{\mathrm{Ar}}} = 0.103\,\mathrm{J\,K^{-1}\,mol^{-1}} \tag{3.61}$$

As expected, the mixing of the gases leads to an increase in their entropy, emphasizing the irreversible nature of this process.

Problem 3.8 (Entropy Change and Free Expansion of a van der Waals Gas)
Initially, at a temperature T_1 and a molar volume v_1, a van der Waals gas undergoes a change of state to the final temperature T_2 and the molar volume v_2. The van der Waals gas is characterized by the two parameters a and b (cf. Eq. (3.3)).

a. Show that the change in molar entropy is

$$\Delta s = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2 - b}{v_1 - b} \tag{3.62}$$

b. A volume of $1\,\mathrm{dm^3}$ is partitioned by a wall into two equal parts, one containing 1 mol xenon (van der Waals parameters $a = 4.250\,\mathrm{dm^6\,bar\,mol^{-2}}$ and $b = 0.0511\,\mathrm{dm^3\,mol^{-1}}$), the other part being evacuated. Calculate the change in the entropy of xenon after the wall is removed and the gas undergoes a free expansion under isothermal conditions ($T = 298.15\,\mathrm{K}$). Also, calculate the change in entropy of the surroundings.

Solution 3.8 Sometimes it is quite difficult to deal with entropy changes in the correct way. An instructive case is the *free expansion* of a perfect gas. The movement of individual gas particles is completely uncorrelated, and in a process of diffusion,[6] the entirely accessible volume rapidly filled by the gas. This is an example of an irreversible process. From the atomistic point of view, the uncorrelated movement of non-interacting particles leaves a probability of finding all the particles back in the initial volume, which is so small, that it never happens in practice. Students frequently think that they have figured out a contradiction between the irreversible nature of the free expansion and the fact that there is no heat transfer with the surroundings. They argue that according to the Clausius equation, Eq. (3.33), the

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[6] A simple model of diffusion is treated in Problem 8.3.

entropy change should then be zero, and thus the expansion should be reversible. Of course, they overlook the fact that the application of Eq. (3.33) assumes that the heat is exchanged in a *reversible* process, which is not the case. The reason for the zero heat transfer in the case of a free expansion of a perfect gas is the absence of intermolecular interaction, equivalent to the fact that the internal energy of a perfect gas is only a function of temperature, not of volume.

An even more puzzling case is the free expansion of a van der Waals gas, which we deal with in this problem. Here, we have to take molecular interaction into account, which, during expansion must be overcome. Thus, under isothermal conditions, if the gas is in thermal contact with the surroundings, there will be a small heat transfer; thus, there will also be a change in entropy of the surroundings.

In **subproblem (a)** we derive a general formula for the molar entropy change in a van der Waals gas undergoing a change of state. Equation (3.62) is analogous to Eq. (3.35), which is valid for a perfect gas. Our derivation starts with Eq. (3.26). If we consider 1 mol of substance,

$$du = c_v\, dT + \Pi\, dv, \tag{3.63}$$

where Π is the internal pressure. Equating the last expression to $du = T\,ds - p\,dv$, we obtain

$$ds = c_v \frac{dT}{T} + \frac{1}{T}\left(\Pi + p\right) dv. \tag{3.64}$$

Exploiting Eq. (3.50) in Problem 3.5 and the van der Waals equation of state Eq. (3.3), we can evaluate the bracket term and obtain

$$ds = c_v \frac{dT}{T} + \frac{R}{v-b}\, dv. \tag{3.65}$$

Finally, integration of the latter equation proves Eq. (3.62):

$$\Delta s = \int_{s_1}^{s_2} ds = c_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v-b} \tag{3.66}$$

$$= c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2 - b}{v_1 - b}. \tag{3.67}$$

This equation is very similar to the corresponding expression for a perfect gas (Eq. (3.35)). Interestingly, the change in molar entropy of a van der Waals gas does not depend on the van der Waals parameter a or on the internal pressure Π, which according to Eqs. (3.50) and (3.3), is given by

$$\Pi = T\left(\frac{\partial p}{\partial T}\right)_v - p = \frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2} = \frac{a}{v^2}. \tag{3.68}$$

Equation (3.66) can be generalized for arbitrary mole numbers:

$$\Delta S = nc_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2 - nb}{V_1 - nb}. \tag{3.69}$$

In **subproblem (b)** we calculate the change in entropy ΔS for $n = 1\,\mathrm{mol}$ xenon with $a = 4.250\,\mathrm{dm^6\,bar\,mol^{-2}}$ and $b = 0.0511\,\mathrm{dm^3\,mol^{-1}}$. The initial and final volume is $V_1 = 0.5\,\mathrm{dm^3}$ and $V_2 = 1\,\mathrm{dm^3}$ respectively. In SI units, $a = 0.4250\,\mathrm{m^6\,Pa\,mol^{-2}}$ and $b = 5.11 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$. Using Eq. (3.69), the entropy change in the gas due to the isothermal expansion is

$$\Delta S_{\text{gas}} = nR \ln \frac{V_2 - nb}{V_1 - nb} \tag{3.70}$$

$$= 1\,\mathrm{mol} \times 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} \ln \frac{10^{-3} - 5.11 \times 10^{-5}}{0.5 \times 10^{-3} - 5.11 \times 10^{-5}} \tag{3.71}$$

$$= +6.223\,\mathrm{J\,K^{-1}}. \tag{3.72}$$

As expected, the entropy of the gas increases upon expansion, for a van der Waals gas as well. For comparison, the corresponding result for a perfect gas (Eq. (3.35)) would have been $+5.763\,\mathrm{J\,K^{-1}}$. Now, we are interested in the entropy change in the surroundings associated with this process, ΔS_{surr}. As discussed above, there is a low heat transfer from the surroundings to the gas upon expansion, resulting in a negative Δs_{surr}. However, is it correct to use the Clausius equation (3.33) and write

$$\Delta S_{\text{surr}} = \frac{\Delta Q_{\text{surr}}}{T} \tag{3.73}$$

at this point? Above, we have mentioned the significance of a heat transfer in a reversible process as a requirement for using the Clausius equation, but here, we assume the expansion of our van der Waals gas to be irreversible. Therefore, how can we justify Eq. (3.73)? Consider the surroundings as a system that is so large that the small heat transfer ΔQ_{surr} does not change the system temperature. The entropy change in the surroundings only depends on the amount of heat transferred. We could construct an alternative reversible thermodynamic process in a system in contact with the surroundings, leading to just the same heat transfer and thus to the same change in entropy of the surroundings. Hence, regarding the entropy change of the surroundings, it does not matter if the van der Waals gas undergoes a reversible or an irreversible change of state, as long as *only* the same heat is transferred. Next, we calculate $\Delta Q_{\text{surr}} = -\Delta Q_{\text{gas}}$ on the basis of the first law Eq. (3.25). Because in a free expansion, no work is done by the gas, ΔQ_{gas} corresponds to the change in its internal energy, $\Delta Q_{\text{gas}} = \Delta U_{\text{gas}}$. As $T = \text{const.}$,

$$dU_{\text{gas}} = \left(\frac{\partial U_{\text{gas}}}{\partial V} \right)_T dV = \Pi \, dV = \frac{an^2}{V^2} \, dV \tag{3.74}$$

After a step of integration, we obtain

$$\Delta U_{\text{gas}} = an^2 \left(\frac{1}{V_1} - \frac{1}{V_2} \right) \tag{3.75}$$

$$= 0.4250 \left(\frac{1}{0.5 \times 10^{-3}} - \frac{1}{10^{-3}} \right) \text{J} \tag{3.76}$$

$$= +425\,\text{J}. \tag{3.77}$$

Thus, following our above argument,

$$\Delta S_{\text{surr}} = \frac{\Delta Q_{\text{surr}}}{T} = -\frac{-\Delta Q_{\text{gas}}}{T} = -\frac{425\,\text{J}}{298.15\,\text{K}} = -1.425\,\text{J}\,\text{K}^{-1}. \tag{3.78}$$

Hence, the total entropy change in the total system constituted by the surroundings and the van der Waals gas is $\Delta S = \Delta S_{\text{gas}} + \Delta S_{\text{surr}} = +4.798\,\text{J}\,\text{K}^{-1}$.

Problem 3.9 (Reversible and Irreversible Adiabatic Expansion)
A cylinder with a movable piston is filled with 2 mol of a perfect gas. The initial volume is $10\,\text{dm}^3$, the initial temperature is $T_1 = 320\,\text{K}$. The constant volume molar heat capacity of the gas is $25\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$. Then, the gas expands adiabatically against a constant external pressure of $10^5\,\text{Pa}$, until mechanical equilibrium is established.

a. Calculate the final temperature and volume assuming an irreversible expansion of the gas.
b. Calculate the final temperature and volume in the case of a reversible expansion.
c. Calculate explicitly the entropy change in the gas, both for reversible and for irreversible expansion.

Solution 3.9 This exercise deals with adiabatic changes of state of a perfect gas and the differences between reversible and irreversible processes. Initially locked, a moveable piston limits the volume of the gas to $V_1 = 0.01\,\text{m}^3$. The perfect gas within the cylinder is thermally isolated from the surroundings, i.e., no heat transfer is possible. Using the equation of state (Eq. (3.2)), we can calculate the

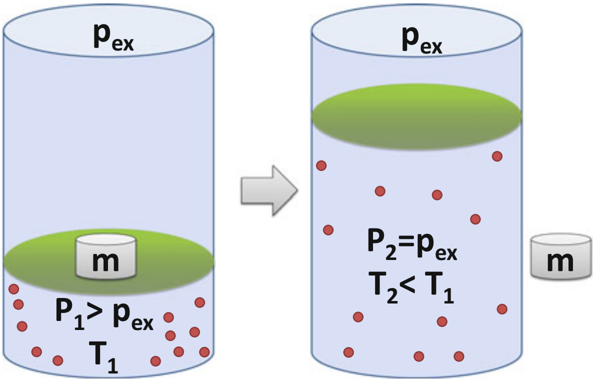

Fig. 3.9 Adiabatic irreversible expansion of a perfect gas, initiated by removing a mass from the piston. Upon expansion, the temperature of the gas is reduced

initial pressure within the cylinder,

$$p_1 = \frac{nRT_1}{V_1} \tag{3.79}$$

$$= \frac{2\,\text{mol} \times 8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1} \times 320\,\text{K}}{0.01\,\text{m}^{-1}} \tag{3.80}$$

$$= 532{,}128\,\text{Pa} \tag{3.81}$$

As this initial pressure is larger than the external pressure of $p_{\text{ex}} = 10^5$ Pa, the gas expands adiabatically as soon as the piston is unlocked. Hence, work is done upon expansion, and, according to the first law (Eq. (3.25)) and the adiabatic condition $\delta Q = 0$, the amount of work done by the gas is balanced by a reduction in its internal energy, which in turn is a function of temperature. Thus, we expect a *cooling* of the gas during expansion.

In **subproblem (a)** we assume an irreversible expansion. Experimentally, this could be realized by removing a single piece of mass from the top of the piston, for example, as illustrated in Fig. 3.9. The piston then expands immediately into its equilibrium position, which is characterized by a final pressure $p_2 = p_{\text{ex}}$. To calculate the final temperature T_2 and final volume V_2 of the gas, we use the first law[7] (Eq. (3.25)) with the adiabatic condition $\delta Q = 0$:

$$dU = n\,c_v\,dT = -p_{\text{ex}}\,dV \tag{3.82}$$

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[7] Note that we cannot use Poisson's equation here, because the latter assumes a *reversible* adiabatic change of state.

We assume that work is done by the piston moving against the constant external pressure. We discuss this below in more detail. After an integration step, we obtain

$$n\,c_v\,(T_2 - T_1) = -p_{\mathrm{ex}}\,(V_2 - V_1)$$

This expression contains two unknowns, T_2 and V_2. We can eliminate V_2 using the equation of state, $p_2V_2 = nRT_2$. After solving for T_2, we obtain the result

$$T_2 = \frac{p_2V_1 + nc_vT_1}{n\,(c_v + R)} \tag{3.83}$$

$$= \frac{100{,}000\,\mathrm{Pa} \times 0.01\,\mathrm{m}^3 + 2\,\mathrm{mol} \times 25\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 320\,\mathrm{K}}{2\,\mathrm{mol} \times (25\,\mathrm{J\,K^{-1}\,mol^{-1}} + 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})} \tag{3.84}$$

$$= 255.14\,\mathrm{K} \tag{3.85}$$

The final volume is

$$V_2 = \frac{nRT_2}{p_2} = \frac{2\,\mathrm{mol} \times 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 255.14\,\mathrm{K}}{100{,}000\,\mathrm{Pa}} = 0.0424\,\mathrm{m}^3 \tag{3.86}$$

As expected, the gas has cooled down from 320 to about 255 K during expansion. The work is best calculated from this temperature difference,

$$W = n\,c_v\,(T_2 - T_1) = -3243\,\mathrm{J}. \tag{3.87}$$

Before discussing these results, we move on to **subproblem (b)**, where reversible adiabatic expansion is assumed. How could we at least approximately realize this experimentally? We can obtain *quasi reversible* processing in a step-by-step procedure, by removing small pieces of mass one by one from the piston, as illustrated in Fig. 3.10. With the limit of arbitrarily small differential masses *dm*, we would obtain reversible expansion. We check this by recalling the difference between an irreversible and a reversible change of state: if a process is irreversible, then the initial state can only be re-established by doing work. If we look at Fig. 3.9, this corresponds to lifting the single mass upward back onto the piston by doing linear work. The piston then moves down until the initial state is reached. In contrast, as illustrated in Fig. 3.10, we could simply establish the initial state by putting the small mass pieces back on the piston one by one—without doing linear work. A second intuitive criterion of reversibility is time invariance. If we record a movie of the quasi-reversible expansion in Fig. 3.10 and run the movie in reverse, we could simply see a physically meaningful process: pieces of mass are taken back onto the piston, and the piston moves gradually down step by step, i.e., the reversible compression of the gas. In contrast, a movie of the process illustrated in Fig. 3.9 run backward would show a physically absurd scene: a gas does not spontaneously reduce its volume and heat up!

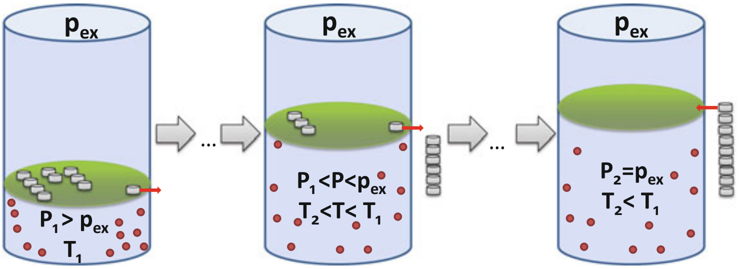

Fig. 3.10 Adiabatic quasi reversible expansion of a perfect gas by removing several small pieces of mass from the piston. In each of the intermediate steps, the gas takes different values of pressure and temperature

In the course of the reversible adiabatic expansion, the gas is permanently in a state of equilibrium, i.e., the thermal state variables are related to each other according to the equation of state: the more the piston moves up and the volume increases, the pressure is gradually reduced according to $p = \frac{nRT}{V}$. If we take this into account, the application of the first law gives

$$dU = n\,c_v\,dT = -\frac{n\,R\,T}{V}\,dV \;\Leftrightarrow\; c_v\frac{dT}{T} = -R\frac{dV}{V} \tag{3.88}$$

After integration,

$$c_v\int_{T_1}^{T_2}\frac{dT}{T} = -R\int_{V_1}^{V_2}\frac{dV}{V} \;\Leftrightarrow\; c_v\,\ln\frac{T_2}{T_1} = R\,\ln\frac{V_1}{V_2} \tag{3.89}$$

and consideration of Eq. (3.47), one of **Poisson's equations** follows:

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma} \tag{3.90}$$

where $\gamma = \frac{c_p}{c_v}$. These equations need to be used to calculate the final volume and temperature after the reversible expansion:

$$V_2 = V_1\left(\frac{p_{\text{ex}}}{p_1}\right)^{\frac{1}{\gamma}} = 0.01\,\text{m}^3\left(\frac{100{,}000\,\text{Pa}}{532{,}128\,\text{Pa}}\right)^{0.75042} = 0.0351\,\text{m}^3 \tag{3.91}$$

$$T_2 = \frac{p_{\text{ex}}\,V_2}{n\,R} = \frac{100{,}000\,\text{Pa}\times 0.0351\,\text{m}^3}{2\,\text{mol}\times 8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}} = 210.84\,\text{K} \tag{3.92}$$

Finally, the work done by the gas is

$$W = n\,c_v\,(T_2 - T_1) = -5458\,\text{J} \tag{3.93}$$

In **subproblem (c)** we deal with entropies and calculate them explicitly. We expect $\Delta S_{\text{rev}} = 0$ for the case of the reversible adiabatic expansion, and $\Delta S_{\text{irrev}} > 0$ for the irreversible adiabatic expansion, consistent with the second law and Eq. (3.34). We bear in mind that the entropy of a gas increases upon expansion, but it decreases if its temperature is reduced. Thus, there are two competing effects that govern the total change in entropy. We start with Eq. (3.35), first dealing with the case of the irreversible adiabatic expansion, and use the results for V_2 and T_2 from subproblem (a):

$$\begin{aligned}\Delta S &= n\,c_v\,\ln\frac{T_2}{T_1} + n\,R\,\ln\frac{V_2}{V_1}\\ &= 2\,\text{mol}\times\,25\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}\,\ln\frac{255.14\,\text{K}}{320\,\text{K}}\\ &\quad+2\,\text{mol}\times\,8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}\,\ln\frac{0.0424\,\text{m}^3}{0.01\,\text{m}^3}\\ &= -11.33\,\text{J}\,\text{K}^{-1} + 24.02\,\text{J}\,\text{K}^{-1} = +12.7\,\text{J}\,\text{K}^{-1}\end{aligned} \tag{3.94}$$

For the reversible adiabatic condition, we could proceed in the same way. However, starting with Eq. (3.35) and by using Eq. (3.37), we can generally prove that the entropy change in the gas is zero in the case of an adiabatic reversible expansion:

$$\begin{aligned}\Delta S &= n\,c_v\,\ln\frac{T_2}{T_1} + n\,R\,\ln\frac{V_2}{V_1}\\ &= n\,c_v\,\ln\left(\frac{V_2}{V_1}\right)^{1-\kappa} + n\,R\,\ln\frac{V_2}{V_1}\\ &= n\,(c_v\,(1-\kappa)+R)\,\ln\frac{V_2}{V_1}\\ &= n\left(c_v - c_p + c_p - c_v\right)\,\ln\frac{V_2}{V_1} = 0\end{aligned} \tag{3.95}$$

In the special case of an adiabatic reversible expansion, the entropy increase due to expansion is exactly balanced by the entropy decrease due to temperature reduction.

A summary of the results of this exercise can be found in Table 3.3 and Fig. 3.11.

Table 3.3 Comparison of reversible and irreversible expansion with regard to the final volume and gas temperature, expansion work, and entropy change

	Final temperature (K)	Final volume (m^3)	W (J)	ΔS ($\text{J}\,\text{K}^{-1}$)
Reversible expansion	210.84	0.0351	−5458	0
Irreversible expansion	255.14	0.0424	−3243	+12.7

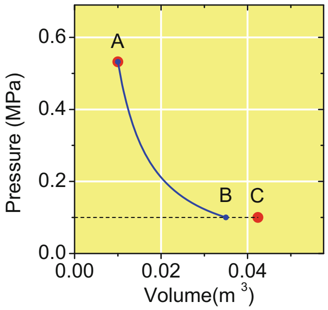

Fig. 3.11 *p*–*V* diagram of the adiabatic expansion. Point *A* is the initial state, *B* the final state of the reversible (isentropic) expansion, *C* is the final state of the irreversible case

In the isentropic, reversible adiabatic case more work is done upon expansion, consistent with stronger cooling of the gas and a smaller final volume. Thus, the final state variables of the gas do not coincide. This is also seen in the *p*–*V* diagram of the expansion in Fig. 3.11. The curve marks the reversible (isentropic) expansion, ending in the final state at point *B*. For each point between the initial and final volumes, the pressure of the gas is precisely defined according to the adiabatic line, which we could reconstruct by removing a series of infinitesimally small masses from the top of the piston, as outlined above. In contrast, the irreversible expansion lacks any intermediate states. In the *p*–*V* diagram, this case is only characterized by the two points *A* and *C* of the initial and final state.

3.4 Heterogeneous Systems and Phase Transitions

Heterogeneous systems are formed by substances in two or more different states of aggregation. To describe changes in such systems, the thermodynamic potentials in Table 3.2 are augmented by the dependency on the amount of substance of each species, and thus on the *composition of the system*:

$$dU = T\,dS - p\,dV + \sum_j \mu_j\,dn_j \tag{3.96}$$

$$dH = T\,dS + V\,dp + \sum_j \mu_j\,dn_j \tag{3.97}$$

$$dA = -S\,dT - p\,dV + \sum_j \mu_j\,dn_j \tag{3.98}$$

$$dG = -S\,dT + V\,dp + \sum_j \mu_j\,dn_j \tag{3.99}$$

The **chemical potential** μ_j of a substance in a special phase is the amount of Gibbs free energy the system gains, if dn_j mol of substance are added at constant pressure and temperature:

$$\boxed{\mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{p,T,\{n_i\}}} \tag{3.100}$$

Moreover, using the **Euler equation** $U = TS - pV + \sum_j \mu_j n_j$ it can be shown that

$$G = \sum_j \mu_j n_j, \tag{3.101}$$

i.e., the Gibbs free energy of a system is the sum of the chemical potentials of all substances in their various phases, weighted with their respective amounts of substance. The conditions for the direction of a spontaneous change, Eqs. (3.41) and (3.42), in addition to the above equations, are the basis for the description of heterogeneous systems, including *phase diagrams* and, moreover, the phenomena related to the mixing of substances, the *colligative properties*: osmotic pressure, vapor pressure reduction, the increase in the boiling point, and the lowering of the freezing point.

The *coexistence lines* in a phase diagram (see Fig. 3.1) are characterized by a *reversible* exchange of atoms or molecules between two different phases, e.g., the liquid phase and the gas phase. Because $\Delta G = \Delta H - T\Delta S = 0$ in this case, the molar entropy change involved with such a phase transition on a point of the coexistence line is

$$\boxed{\Delta s_{\mathrm{tr}} = \frac{\Delta h_{\mathrm{tr}}}{T},} \tag{3.102}$$

where Δh_{tr} is the respective molar transition enthalpy, e.g., the molar heat of vaporization. On the coexistence lines, the chemical potentials in two phases are equal. This condition is sufficient to deduce the coexistence lines in the phase diagram of a pure substance (Fig. 3.1). The **Clapeyron equation**

$$\boxed{\frac{dp}{dT} = \frac{\Delta s_{\mathrm{tr}}}{\Delta v_{\mathrm{tr}}}} \tag{3.103}$$

provides the gradient of a coexistence line on the p–T diagram, where Δv_{tr} is the change in the molar volume involved with the phase transition. For the special cases of a gas-liquid or a gas-solid phase transition, two approximations are frequently made: (1) The gas-phase is described by the equation of state for a perfect gas

(Eq. (3.2)). (2) The molar volume of the condensed phase is neglected over the molar volume of the gas phase. In this case, Eq. (3.103) together with Eq. (3.102) can be used to derive the **Clausius-Clapeyron equation** (see Problem 3.10a)

$$\frac{d\ \ln p}{dT} = \frac{\Delta h_{\mathrm{tr}}}{RT^2} \tag{3.104}$$

3.4.1 The Standard State

As material properties, transition enthalpies and entropies are quantities that depend on both temperature and pressure. For their tabulation it is convenient to *define* a suitable **standard state** of a substance:

The standard state of a substance is the state in which it is stable at a pressure of $p^{\ominus} = 10^5$ Pa.

The value of a material property at standard pressure is indicated by the superscript $\ominus$. Note that this standard state is not the only standard state used in physical chemistry. Moreover, a reference temperature of $T = 298.15$ K is usually chosen to tabulate these material properties.

3.4.2 Real and Ideal Mixtures

A heterogeneous system may contain more than one component, e.g., *mixtures* constituting a liquid phase, or a gas phase. If two substances A and B constitute a binary mixture, their chemical potentials change relative to the respective standard chemical potentials. In the gas phase assuming perfect gas behavior,

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\ominus} + RT\ \ln \frac{p_{\mathrm{A}}}{p^{\ominus}}. \tag{3.105}$$

An idea of how this relation can be derived gives the solution to Problem 3.11b. In the liquid phase, the respective expression is

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\star} + RT\ \ln a_{\mathrm{A}} \tag{3.106}$$

where the a_{A} is the **activity** of substance A in solution, and $\mu_{\mathrm{A}}^{\star}$ is the chemical potential of the pure substance A. The symbol $\star$ now refers to a *new standard state* of a pure substance, which is also called *Raoult's law standard state*. The activity of A is defined via its partial pressure p_{A} over the solution, related to the vapor pressure of the pure substance, $p^{\star}_{A}$:

$$\boxed{a_A = \frac{p_A}{p^{\star}_{A}}} \tag{3.107}$$

It is important to understand that the activity is a property of the solution, but it is determined indirectly by the partial pressure in the gas phase above the solution in chemical equilibrium, where the chemical potential in the solution and in the gas phase are equal. For a real solution, the activity may depend on the composition of the solution in a complicated way. In the limiting case of an *ideal solution*, the activity corresponds to the mole fraction: $a_A = x_A$, and the partial pressure of A can be calculated using **Raoult's law**:

$$\boxed{p_A = x_A \, p^{\star}_{A}} \tag{3.108}$$

In general, the relation between activity and mole fraction is

$$\boxed{a_A = x_A \, \gamma_A,} \tag{3.109}$$

where γ_A is the activity coefficient of A.

3.4.3 Problems

Problem 3.10 (Vapor Pressure of a Pure Substance)
The vapor pressure of ethylamine (CH_3–CH_2–NH_2) was measured as a function of temperature:

T (K)	250.25	259.25	267.55	278.95
p (kPa)	14.83	24.40	37.57	64.17

a. Derive the Clausius–Clapeyron equation Eq. (3.104) from the condition of equal chemical potentials in the liquid and the gas phase.
b. Determine the molar heat of vaporization, the molar entropy of vaporization, and the standard boiling point of ethylamine, assuming ideal behavior in the gas phase.

(continued)

Problem 3.10 (continued)

c. Two identical vessels with a volume of 1 dm^3 are filled with 5 and 10 g of ethylamine respectively. Then, the vessels are sealed and heated to 333 K. Calculate the internal pressure of the two vessels.

Solution 3.10 If a liquid is held in a closed vessel, it forms a gas phase above its surface, even if the vessel was initially evacuated. We have dealt with this coexistence of liquid and gas phase already in Problem 3.4, where we investigated the use of the van der Waals equation of state to estimate the vapor pressure of a gas at a given temperature. Now, we will deal with the phenomenon of vapor pressure from a different point of view: energetics. A molecule in a liquid is exerted to a much stronger intermolecular attractive interaction than in the gas phase. Thus, why does it leave the liquid phase at all, if it takes heat to bring it into the gas phase? From the viewpoint of thermodynamics, the answer is entropy. The entropy of a substance in the gaseous state is generally higher than in a condensed phase, implying a positive entropy of vaporization, ΔS_{vap}. The gain in entropy favors the transition into the gaseous state, and with increasing temperature, this effect becomes increasingly important, consistent with a lowering of the Gibbs free energy of vaporization, $\Delta G_{\text{vap}} = \Delta H_{\text{vap}} - T\,\Delta S_{\text{vap}}$. If at constant pressure and temperature there is an equilibrium between molecules leaving the gas phase and those entering the gas phase, the phase transition is reversible, consistent with a change in the system's Gibbs free energy being zero (see Eq. (3.41)). Hence, using Eq. (3.99),

$$dG = \mu_{\text{gas}}\, dn_{\text{gas}} + \mu_{\text{liq}}\, dn_{\text{liq}} = 0 \tag{3.110}$$

As $dn_{\text{gas}} = -dn_{\text{liq}}$, the condition of reversibility requires equal chemical potentials in the gas phase and the liquid phase:

$$dG = \left(\mu_{\text{gas}} - \mu_{\text{liq}}\right) dn_{\text{gas}} \overset{!}{=} 0 \quad \Leftrightarrow \quad \mu_{\text{gas}} \overset{!}{=} \mu_{\text{liq}} \tag{3.111}$$

Based on the equality of the chemical potentials, we derive the coexistence line between vapor and liquid in **subproblem (a)**. Starting with a point on the coexistence line at a given pressure and temperature, p and T, we consider the chemical potentials of the vapor and the liquid at $p + dp$ and $T + dT$, still on the coexistence line:

$$\mu_{\text{gas}}(p + dp, T + dT) = \mu_{\text{liq}}(p + dp, T + dT) \tag{3.112}$$

We can expand these chemical potentials into a power series and consider only the linear terms,

$$\mu_i(p + dp, T + dT) = \mu_i(p, T) + \left(\frac{\partial \mu_i}{\partial p}\right)_T dp + \left(\frac{\partial \mu_i}{\partial T}\right)_p dT + \cdots \tag{3.113}$$

Using the definition of the chemical potential Eq. (3.100) and the relations $\left(\frac{\partial G}{\partial T}\right)_p = -S$ and $\left(\frac{\partial G}{\partial p}\right)_T = V$, the differential quotients $\left(\frac{\partial \mu_i}{\partial p}\right)_T$ and $\left(\frac{\partial \mu_i}{\partial T}\right)_p$ are identified as the negative (partial) molar entropy s_i and the (partial) molar volume v_i of the substance in phase i respectively. Thus,

$$\mu_i(p + dp, T + dT) = \mu_i(p, T) + v_i\, dp - s_i\, dT + \cdots ,$$

and as we may consider the chemical potentials of the vapor and the liquid phase to be equal at $p + dp$ and $T + dT$ as well,

$$\mu_{\text{gas}}(p, T) + v_{\text{gas}}\, dp - s_{\text{gas}}\, dT = \mu_{\text{liq}}(p, T) + v_{\text{liq}}\, dp - s_{\text{liq}}\, dT$$

and thus, because $\mu_{\text{gas}}(p, T) = \mu_{\text{liq}}(p, T)$,

$$\frac{dp}{dT} = \frac{s_{\text{gas}} - s_{\text{liq}}}{v_{\text{gas}} - v_{\text{liq}}} = \frac{\Delta s_{\text{vap}}}{\Delta v_{\text{vap}}} \overset{\text{Eq. (3.102)}}{=} \frac{\Delta h_{\text{vap}}}{T\, \Delta v_{\text{vap}}} \tag{3.114}$$

We have now derived the Clapeyron equation. Next, we make the approximation $\Delta v_{\text{vap}} \approx v_{\text{gas}}$, i.e., we neglect the molar volume of the liquid over the molar volume of the gas phase, which is reasonable at moderate pressures. Moreover, assuming perfect gas behavior, we can express $v_{\text{gas}} = \frac{RT}{p}$ by the equation of state. Inserting this into the Clausius equation, we obtain:

$$\frac{dp}{dT} = \frac{p\, \Delta h_{\text{vap}}}{RT^2} \quad \Leftrightarrow \quad \frac{dp}{p} = \frac{\Delta h_{\text{vap}}\, dT}{RT^2}$$

Here, we have arrived at the Clausius-Clapeyron equation because $\frac{dp}{p} = d \ln p$. We go one step further and integrate the last expression, assuming that the molar heat of vaporization is independent of temperature and takes the value of the standard molar heat of vaporization, $\Delta h^{\ominus}_{\text{vap}}$. We obtain

$$\ln \frac{p}{p^{\ominus}} = -\frac{\Delta h^{\ominus}_{\text{vap}}}{R} \left(T^{-1} - T_b^{\ominus\, -1}\right) \tag{3.115}$$

As a consequence, if the molar heat of vaporization is known and one point on the coexistence line, e.g., the standard boiling point, the vapor pressure at any given temperature can be determined. Moreover, because the standard molar entropy of vaporization is $\Delta s^{\ominus}_{\text{vap}} = \frac{\Delta h^{\ominus}_{\text{vap}}}{T_b^{\ominus}}$ as a special case of Eq. (3.102), we obtain

$$\ln \frac{p}{p^{\ominus}} = -\frac{\Delta h^{\ominus}_{\text{vap}}}{R} T^{-1} + \frac{\Delta s^{\ominus}_{\text{vap}}}{R} \tag{3.116}$$

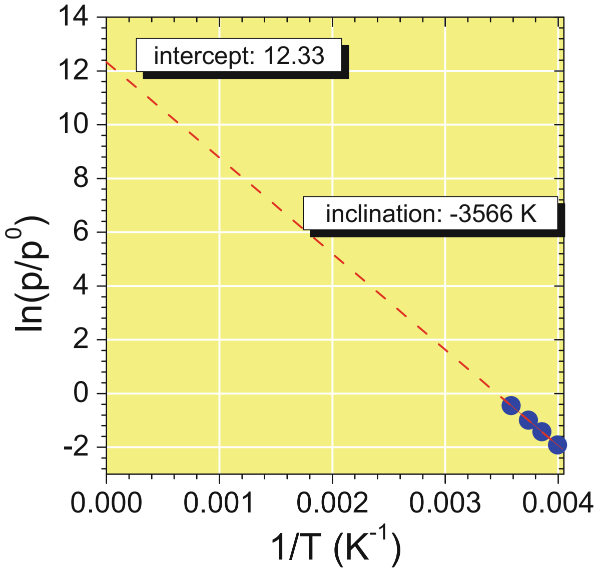

Fig. 3.12 Graphical determination of the enthalpy and entropy of vaporization from vapor pressure variation with temperature according to Eq. (3.116)

We can use this relation to determine $\Delta h^{\ominus}_{\mathrm{vap}}$ and $\Delta s^{\ominus}_{\mathrm{vap}}$ and the standard boiling point of ethylamine, as we do in **subproblem (b)**. Therefore, we plot ln $\frac{p(T)}{p^{\ominus}}$ against the reciprocal temperature, as shown in Fig. 3.12. If $\Delta h^{\ominus}_{\mathrm{vap}}$ and $\Delta s^{\ominus}_{\mathrm{vap}}$ are constant over the temperature range of tabulated data, then a linear behavior can be expected. Inspection of the diagram shows that this seems to be the case. A linear regression provides the axis intercept and the inclination of the best-fit line:

$$\frac{\Delta s^{\ominus}_{\mathrm{vap}}}{R} = 12.33 \qquad \Leftrightarrow \qquad \Delta s^{\ominus}_{\mathrm{vap}} = 102.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

$$\frac{\Delta h^{\ominus}_{\mathrm{vap}}}{R} = -3566\,\mathrm{K} \qquad \Leftrightarrow \qquad \Delta h^{\ominus}_{\mathrm{vap}} = 29.7\,\mathrm{kJ\,mol^{-1}}$$

Note that in general, Δh_{vap} and Δs_{vap} will depend markedly on temperature, if the examined temperature interval is sufficiently large. The standard boiling point can be determined in two different ways. The simplest way is based on Eq. (3.102) and yields

$$T^{\ominus}_{b} = \frac{\Delta h^{\ominus}_{v}}{\Delta s^{\ominus}_{v}} = 289.3\,\mathrm{K}. \tag{3.117}$$

The alternative way is based on the analysis of Fig. 3.12. Because at $T_b^{\ominus}$ the vapor pressure is only $p^{\ominus}$, the best-fit line intersects the line $\ln \frac{p}{p^{\ominus}} = 0$ at $\left(T_b^{\ominus}\right)^{-1} = 0.003458\,\mathrm{K}^{-1}$. We therefore obtain $T_b^{\ominus} = 289.2\,\mathrm{K}$. The discrepancy of 0.1 K can be explained by the statistical and systematic uncertainties in the experimental vapor pressure data. In **subproblem (c)** we calculate the pressure within two identical vessels, which at $T = 333\,\mathrm{K}$ contain 5 and 10 g of ethylamine respectively. This question challenges the student's ability to assess whether under given conditions a system is a *homogeneous* system or a *heterogeneous* system. The molar mass of ethylamine is $M = 45\,\mathrm{g\,mol}^{-1}$. Thus, the first vessel contains an amount of

$$n_1 = \frac{5\,\mathrm{g}}{45\,\mathrm{g\,mol}^{-1}} = 0.\bar{1}\,\mathrm{mol}. \tag{3.118}$$

The second vessel is filled with 10 g of ethylamine, which corresponds to $n_2 = 0.\bar{2}\,\mathrm{mol}$. Next, we calculate the vapor pressure of ethylamine at $T = 333\,\mathrm{K}$ using our results from subproblem (a). Apparently, the vapor pressure is

$$p_{\mathrm{vap}}(T) = p^{\ominus} \exp\left(-\frac{\Delta h_v^{\ominus}}{R}\left(\frac{1}{T} - \frac{1}{T_b^{\ominus}}\right)\right) \tag{3.119}$$

$$= 100{,}000\,\mathrm{Pa} \times \exp\left(-3566\left(\frac{1}{333} - \frac{1}{289.3}\right)\right) \tag{3.120}$$

$$= 504{,}000\,\mathrm{Pa} \tag{3.121}$$

If ethylamine in the vessel is present as a liquid phase coexisting with a gas phase, i.e., as a heterogeneous system, then the inner pressure of the vessel will be this vapor pressure of about 5 bar. Here, however, we have also take the possibility into account that the amount of ethylamine might be insufficient to establish the coexistence of liquid and vapor. If we assume that gaseous ethylamine is a perfect gas, then the nominal gas phase pressure at a given amount of substance and temperature according to the equation of state is

$$p_1 = \frac{n_1 RT}{V} = \frac{0.\bar{1}\,\mathrm{mol} \times 8.3145\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1} \times 333\,\mathrm{K}}{10^{-3}\,\mathrm{m}^3} = 308{,}000\,\mathrm{Pa} < p_{\mathrm{vap}}(T). \tag{3.122}$$

As a consequence, the 5 g of ethylamine in the first vessel is present in the gaseous state. This is also illustrated in Fig. 3.13, where the coexistence line between vapor and liquid is shown in a p–T diagram. The point p_1 resides in the area below the coexistence line, i.e., in the area of gaseous ethylamine. The pressure within the vessel is thus $p_1 = 3.08\,\mathrm{bar}$

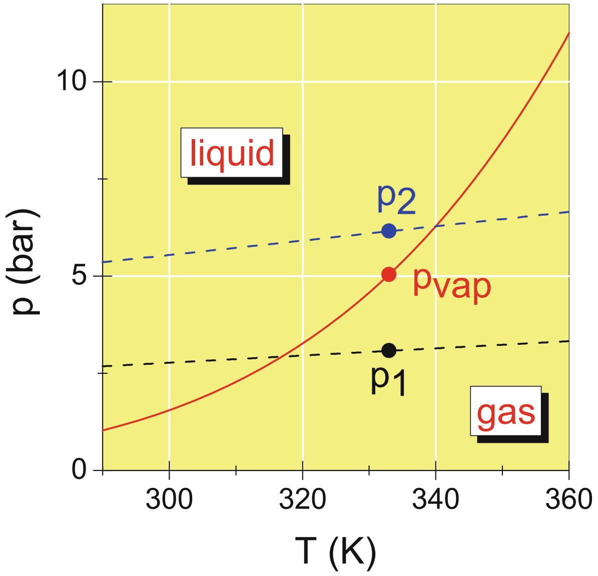

Fig. 3.13 Coexistence line $p_{\mathrm{vap}}(T)$ of gaseous and liquid ethylamine (*solid line*) according to Eq. (3.119). The *dashed lines* indicate the nominal gas pressure of 5 g (p_1) and 10 g (p_2) ethylamine in the vessel according to the perfect gas equation of state. At $T = 333$ K, $p_2 > p_{\mathrm{vap}} > p_1$

In contrast, a vessel containing 10 g of ethylamine would have a nominal gas pressure

$$p_2 = \frac{n_1 RT}{V} = \frac{0.\bar{2}\,\mathrm{mol} \times 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 333\,\mathrm{K}}{10^{-3}\,\mathrm{m^3}} = 616{,}000\,\mathrm{Pa} > p_{\mathrm{vap}}(T), \tag{3.123}$$

as also shown in Fig. 3.13. Therefore, a fraction of ethylamine condenses and forms a liquid phase coexisting with gaseous ethylamine. In this case, the pressure within the vessel is thus the vapor pressure $p_{\mathrm{vap}} = 5.04$ bar.

Problem 3.11 (Molar Gibbs Free Energies of Solids and Gases, Conversion of Graphite to Diamond)

At 298 K the molar standard Gibbs free energy of graphite is zero, whereas the corresponding value for diamond is +2.9 kJ mol^{-1}. The densities of graphite and diamond are 2.3 and 3.5 g cm^{-3} respectively.

(continued)

Problem 3.11 (continued)

a. For both forms of carbon, calculate the molar Gibbs free energy of formation at a pressure of 10 bar and 298 K. Assume that diamond and graphite are incompressible solids.
b. At 298 K, the molar standard Gibbs free energy of gaseous CO_2 is $-394.4\,\mathrm{kJ\,mol^{-1}}$. Assume perfect gas behavior and calculate the molar Gibbs free energy of formation of $CO_2(g)$ at a pressure of 10 bar. What do you conclude concerning the pressure dependence of the free Gibbs energy of gaseous and condensed phases?
c. Calculate the minimum pressure, at which diamond is the stable form of carbon.

Solution 3.11 In this exercise, we deal with the relative stability of two forms of carbon, diamond and graphite. We deal with the relationship between the Gibbs free energy of a substance as a function of pressure, its structure, and the phase diagram.

Graphite is the stable form of carbon under normal atmospheric pressure. As an element in its standard state, by definition, its *standard* molar Gibbs free energy of formation is zero.[8] Diamond, however, can be formed if a high pressure is exerted on carbon. Its crystal structure is more compact and thus its density is higher than that of graphite.

In **subproblem (a)**, we seek the function $g(p)$ of diamond and graphite and we treat them as incompressible solids. From Eq. (3.99),

$$\left(\frac{\partial g}{\partial p}\right)_T = v \tag{3.124}$$

where v is the molar volume, which is related to the density ρ and the molar mass M: $\rho = \frac{M}{v}$. Integration yields

$$g(p) = g(p^\ominus) + v\int_{p^\ominus}^{p} dp = g(p^\ominus) + v(p - p^\ominus) = g(p^\ominus) + \frac{M}{\rho}(p - p^\ominus) \tag{3.125}$$

For graphite with $g(p^\ominus) = 0$ and $\rho = 2300\,\mathrm{kg\,m^{-3}}$, the molar free Gibbs energy takes a value of

$$g(10^6\,\mathrm{Pa}) = 0 + \frac{12\times10^{-3}\,\mathrm{kg\,mol^{-1}}}{2300\,\mathrm{kg\,m^{-3}}}\left(10^6 - 10^5\right)\,\mathrm{Pa} = +4.7\,\mathrm{J\,mol^{-1}}. \tag{3.126}$$

For diamond with $g(p^\ominus) = 2900\,\mathrm{J\,mol^{-1}}$, we obtain a value of $2903.1\,\mathrm{J\,mol^{-1}}$.

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[8] See the definition of the enthalpy of formation in Sect. 4.1.1 at page 71.

Table 3.4 Molar Gibbs free energies of graphite, diamond, and CO_2 at standard pressure and at $p = 10^6$ Pa

Substance	State	$g(p^\ominus)$	$g(10^6\,\text{Pa})$	Δg
C (Graphite)	Solid	0	$+4.7 \times 10^{-3}$	$+4.7 \times 10^{-3}$
C (Diamond)	Solid	+2.9000	+2.9031	$+3.1 \times 10^{-3}$
CO_2	Gaseous	−394.4	−388.7	+5.7

All values are given in kJ mol^{-1}

In **subproblem (b)** we consider the function $g(p)$ for CO_2 treated as a perfect gas:

$$g(p) = g(p^\ominus) + \int_{p^\ominus}^{p} v(p)\, dp \tag{3.127}$$

Using the equation of state, $v(p) = \frac{RT}{p}$.

$$g(p) = g(p^\ominus) + RT \int_{p^\ominus}^{p} \frac{dp}{p} = g(p^\ominus) + RT \ln \frac{p}{p^\ominus} \tag{3.128}$$

For CO_2 with $g^\ominus = -394.4\,\text{kJ mol}^{-1}$, we obtain a value of $g(10^6\,\text{Pa}) = -388.7\,\text{kJ mol}^{-1}$. In Table 3.4, all results are summarized:

Although the molar Gibbs free energy of solids changes only weakly to the order of a few J mol^{-1} under a moderate change in pressure, the Gibbs free energy of a perfect gas changes markedly to the order of several kJ mol^{-1}. This general trend allows a different treatment of gases and condensed phases in the thermodynamic characterization of the chemical equilibrium in Chap. 4.

In **subproblem (c)** we calculate the pressure at which diamond becomes the stable form of carbon. Looking at our tabulated results, we recognize that the molar Gibbs free energy of diamond increases slightly more weakly than that of graphite, if the pressure is increased. Thus, at a certain pressure p_{eq}, the molar Gibbs free energies of diamond and graphite are equal. For $p > p_{\text{eq}}$, diamond becomes the stable form of carbon, indicated by the lower value of $g(p)$. The situation is illustrated in the schematic phase diagram in Fig. 3.14. To evaluate p_{eq}, we use our above results and consider the transition

$$\text{graphite} \rightarrow \text{diamond} \qquad |\Delta g(p) = g_{\text{diamond}}(p) - g_{\text{graphite}}(p)$$

with the change in molar Gibbs free energy

$$\Delta g(p) = g^\ominus_{\text{diamond}} - g^\ominus_{\text{graphite}} + \Delta v\,(p - p^\ominus), \tag{3.129}$$

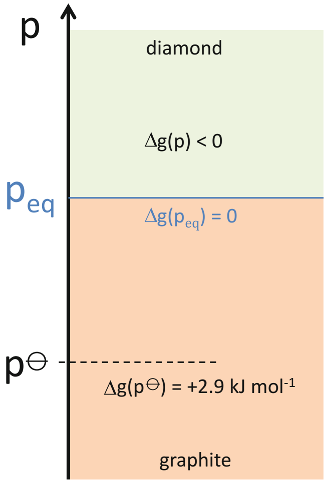

Fig. 3.14 Schematic phase diagram of carbon with the phase boundary between graphite and diamond

and the change in molar volume $\Delta v = v_{\mathrm{diamond}} - v_{\mathrm{graphite}}$. With the different densities of diamond and carbon given, we obtain

$$\begin{aligned}\Delta v &= \frac{M}{\rho_{\mathrm{diamond}}} - \frac{M}{\rho_{\mathrm{graphite}}}\\ &= 12 \times 10^{-3}\,\mathrm{kg\,mol^{-1}} \left(\frac{1}{3500} - \frac{1}{2300}\right) \mathrm{m^3\,kg^{-1}}\\ &= -1.79 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}\end{aligned}$$

On the coexistence line between diamond and graphite, i.e., at $p = p_{\mathrm{eq}}$, the transition between the two carbon phases is reversible. Therefore, the molar Gibbs free energy of the phase transition is zero: $\Delta g \overset{!}{=} 0$. In this special case, Eq. (3.129) yields

$$p_{\mathrm{eq}} = \frac{p^{\ominus}\Delta v - \Delta g^{\ominus}}{\Delta v} = \frac{10^5\,\mathrm{Pa} \times (-1.79 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}) - 2900\,\mathrm{J\,mol^{-1}}}{(-1.79 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}})}$$

and our result for p_{eq} is 1.62 GPa. Experimentally, the transition from graphite to diamond is observed at pressures above 2 GPa.

Problem 3.12 (Ideal Solutions)
The main components of liquid petroleum gas (LPG) are propane and butane in seasonally varying compositions. Assuming that propane and butane constitute an ideal mixture, calculate the maximum acceptable mole fraction

(continued)

Problem 3.12 (continued)
of propane, for which at a temperature of 50 °C the internal pressure of a tank containing LPG does not exceed a value of 12 bar. The molar standard heats of vaporization of pure propane and butane are 19.0 and 22.4 kJ mol^{-1} respectively. The standard boiling points of propane and butane are 231.1 and 272.7 K respectively.

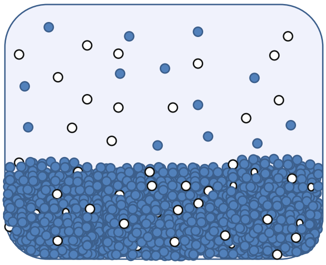

Fig. 3.15 A tank containing a binary solution of a more volatile substance indicated by *white balls*, and a less volatile species (*blue balls*), which is in excess. In the gas phase, the more volatile component is enriched

Solution 3.12 In middle Europe, the summer composition of LPG fuels is about 40 mass-% propane and 60 mass-% n-butane, and vice versa in winter. At the filling station, a compressor has to work against the tank internal pressure. Hence, to guarantee successful filling, the internal pressure should not exceed the maximum pressure of the compressor, $p_{\text{max}} = 12\,\text{bar}$ in this problem. In summer, the temperature of a car tank may easily reach 50 °C. At this temperature, the vapor pressure of *pure* butane and propane is calculated using the Clausius Clapeyron law (Eq. (3.115)). For butane, with $\Delta h^{\ominus}_{\text{vap, butane}} = 22.4\,\text{kJ mol}^{-1}$ and $T^{\ominus}_{b,\,\text{butane}} = 272.7\,\text{K}$

$$p^{\star}_{B} = p^{\ominus}\exp\left(-\frac{\Delta h^{\ominus}_{\text{vap, butane}}}{R}\left(\frac{1}{T}-\frac{1}{T^{\ominus}_{b,\,\text{butane}}}\right)\right) = 4.74\,\text{bar}.$$

For propane with $\Delta h^{\ominus}_{\text{vap, butane}} = 19.0\,\text{kJ mol}^{-1}$ and $T^{\ominus}_{b,\,\text{butane}} = 231.1\,\text{K}$, a value of 16.94 bar results. Consistent with the higher enthalpy of vaporization and the lower standard boiling temperature, propane is more volatile than butane. The situation is illustrated in Fig. 3.15. Propane (C_3H_8) and n-butane (C_4H_{10}) are hydrocarbons with similar chemical properties. The assumption of an ideal mixture is thus reasonable and justifies the application of Raoult's law (Eq. (3.108)), by which we calculate the total pressure in the gas phase

$$p = x_B\,p^{\star}_{B} + x_P\,p^{\star}_{P} \tag{3.130}$$

For $p = p_{\max}$ and $x_B = 1 - x_P$, we obtain an expression for the maximum acceptable mole fraction of propane:

$$x_P = \frac{p_{\max} - p_B^\star}{p_P^\star - p_B^\star} = \frac{12 - 4.74}{16.94 - 4.74} = 0.595$$

Hence, at least in summer, the fraction of propane should not exceed 60%. From this result, and the molar masses of propane and butane (44.1 and 58.1 g mol^{-1}), the maximum acceptable mass fraction of propane is 53%.

Problem 3.13 (Vapor Pressure Reduction)
At 293 K, the vapor pressure of the solvent diethyl ether (C_2H_5–O–C_2H_5) is 586 hPa. After the addition of 20 g of an unknown nonvolatile compound in 1 kg of diethyl ether, the vapor pressure is reduced to 583 hPa. Assume an ideal mixture of diethyl ether and the unknown compound, for which an elementary analysis yields mass fractions of 41.4% carbon, 5.5% hydrogen, 9.6% nitrogen, and 43.8% oxygen. Determine the molar mass and the molecular formula of the unknown compound.

Solution 3.13 The lowering of the vapor pressure of a solvent in the mixture with another substance is one of four **colligative properties**.[9] These are used in analytics to determine the molar mass of a solute. Combined with results from an elementary analysis providing the relative abundances of chemical elements, the molecular formula of an unknown compound can be determined. In this problem, we consider $m_\mathrm{X} = 20$ g of an unknown compound (denoted X), which is dissolved in $m_\mathrm{D} = 1000$ g diethyl ether. This causes a lowering of the vapor pressure of diethyl ether from $p_\mathrm{D}^* = 586$ hPa to $p_\mathrm{D} = 583$ hPa. Moreover, elementary analysis of X yields mass fractions $f_\mathrm{C} = 0.414$ for carbon, $f_\mathrm{H} = 0.055$ for hydrogen, $f_\mathrm{N} = 0.096$ for nitrogen, and $f_\mathrm{O} = 0.438$ for oxygen. We determine the molar mass and the molecular formula. As stated in the text of the problem, the unknown substance X and the solvent are assumed to constitute an ideal binary mixture. We can thus use Raoult's law Eq. (3.108) to obtain the mole fraction of diethyl ether:

$$x_\mathrm{D} = \frac{p_\mathrm{D}}{p_\mathrm{D}^*} = \frac{583\,\mathrm{hPa}}{586\,\mathrm{hPa}} = 0.99488 \tag{3.131}$$

The mole fraction for X results from the condition

$$x_\mathrm{D} + x_\mathrm{X} = 1. \tag{3.132}$$

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[9] The other colligative properties are the elevation of the boiling point, the depression of the freezing point, and osmotic pressure.

Thus,

$$x_\mathrm{X} = 1 - x_\mathrm{D} = 5.12 \times 10^{-3}. \tag{3.133}$$

Using the definition of the mole fraction in Eq. (2.8) at page 11 we obtain

$$x_\mathrm{X} = \frac{n_\mathrm{X}}{n_\mathrm{X} + n_\mathrm{D}} \tag{3.134}$$

where n_X and n_D are the amounts of X and diethyl ether respectively. We can solve this equation for the value of X:

$$n_\mathrm{X} = \frac{x_\mathrm{X}}{1 - x_\mathrm{X}} n_\mathrm{D} = \frac{x_\mathrm{X}}{x_\mathrm{D}} \frac{m_\mathrm{D}}{M_\mathrm{D}} \tag{3.135}$$

Here, we have expressed n_D using the given mass of the solvent and its molar mass, $M_\mathrm{D} = 74\,\mathrm{g\,mol^{-1}}$, determined from the given molecular formula of diethyl ether. If we combine

$$n_\mathrm{D} = \frac{m_\mathrm{X}}{M_\mathrm{X}} \tag{3.136}$$

with Eq. (3.135), we obtain an expression for the molar mass of X:

$$M_\mathrm{X} = m_\mathrm{X} \frac{x_\mathrm{D}}{x_\mathrm{X}} \frac{M_\mathrm{D}}{m_\mathrm{D}} = \frac{20\,\mathrm{g}}{1000\,\mathrm{g}} \frac{0.99488}{5.12 \times 10^{-3}} \times 74\,\mathrm{g\,mol^{-1}} = 288\,\mathrm{g\,mol^{-1}}. \tag{3.137}$$

The given mass fractions of the elements can now be exploited to determine the molecular formula of the unknown substance: if Z_C is the number of carbon atoms in X and $M_\mathrm{C} = 12\,\mathrm{g\,mol^{-1}}$ is the elemental atomic weight of carbon, the following relation holds:

$$Z_\mathrm{C} M_\mathrm{C} = f_\mathrm{C} M_\mathrm{X}. \tag{3.138}$$

As a consequence, the number of carbons is

$$Z_\mathrm{C} = f_\mathrm{C} \frac{M_\mathrm{X}}{M_\mathrm{C}} = 0.414 \frac{288}{12} = 9.9 \approx 10. \tag{3.139}$$

In the same way, we obtain

$$Z_\mathrm{H} = f_\mathrm{H} \frac{M_\mathrm{X}}{M_\mathrm{H}} = 0.055 \frac{288}{1} = 15.8 \approx 16, \tag{3.140}$$

$$Z_\mathrm{N} = f_\mathrm{N} \frac{M_\mathrm{X}}{M_\mathrm{N}} = 0.096 \frac{288}{14} = 1.97 \approx 2, \tag{3.141}$$

$$Z_O = f_O \frac{M_X}{M_O} = 0.438 \frac{288}{16} = 7.9 \approx 8. \tag{3.142}$$

We therefore conclude that the molecular formula of the unknown compound is $C_{10}H_{16}N_2O_8$.

Problem 3.14 (Spontaneous Freezing of Supercooled Water)
Using the second law of thermodynamics, show that the freezing of 1 mol of liquid water at a temperature of 250 K is a spontaneous change of state. The standard molar heat of fusion is $6.008\,\mathrm{kJ\,mol^{-1}}$, and the constant pressure molar heat capacities of liquid water and ice are 75.3 and $37.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

Solution 3.14 According to the second law, a change of state in an isolated system is spontaneous, if the total entropy change is positive. To apply the second law, we calculate the entropy change involved with the freezing of supercooled water and thereby show that this process is indeed spontaneous. This can be quite tedious, because upon the process of freezing, the supercooled water exchanges heat with the surroundings. Our analysis of entropy changes thus has to include not only the entropy change of the water, but also the entropy change of the surroundings:

$$\Delta S = \Delta S_{\mathrm{water}} + \Delta S_{\mathrm{surroundings}} \tag{3.143}$$

Moreover, the application of the Clausius formula Eq. (3.33) requires reversible heat transfers: for the calculation of ΔS, we therefore have to replace the direct freezing at 250 K by (a) the heating of the supercooled water to the standard temperature of fusion $T_f^\ominus$, (b) the reversible freezing of the water at $T_f^\ominus$, and (c) the cooling of the frozen ice from $T_f^\ominus$ to 250 K, as outlined in Fig. 3.16. The property of entropy to be a state function guarantees that the sum of entropy changes in the steps (a), (b), and (c) in Fig. 3.16 corresponds to the entropy change of the entire irreversible process, indicated as the dashed line in Fig. 3.16. For $n = 1\,\mathrm{mol}$, the entropy change of water is

$$\Delta S_{\mathrm{water}} = \int_{250\,\mathrm{K}}^{T_f^\ominus} \frac{n\,c_p(\mathrm{liq.})\,dT}{T} - \frac{n\,\Delta h_f^\ominus}{T_f^\ominus} + \int_{T_f^\ominus}^{250\,\mathrm{K}} \frac{n\,c_p(\mathrm{ice})\,dT}{T}. \tag{3.144}$$

The first integral corresponds to the virtual entropy change of heating the water from the temperature $T_1 = 250\,\mathrm{K}$ to $T_f^\ominus$. The second term is the entropy change involved with the reversible freezing of water at $T_f^\ominus$, according to Eq. (3.102). The negative sign takes into account that the latent heat of freezing is the negative of the given molar heat of fusion, $\Delta h_f^\ominus = 6008\,\mathrm{J\,mol^{-1}}$. The third term, finally, gives the entropy change of cooling the frozen ice from $T_f^\ominus$ to 250 K. After the evaluation of

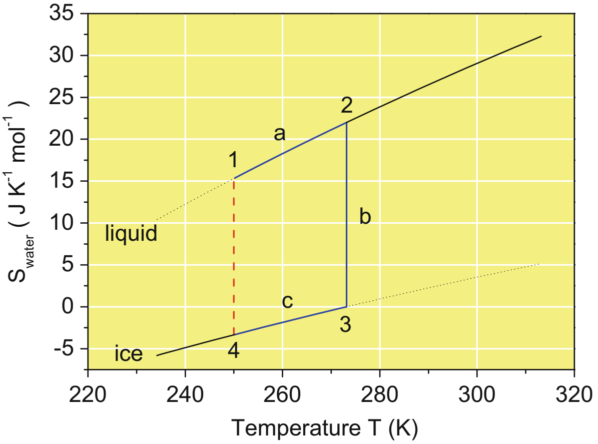

Fig. 3.16 Temperature dependence of the entropy of liquid water and ice as a function of temperature (schematic). The entropy change involved with the freezing of supercooled water at 250 K (*dashed line*) is the same as the alternative route (*solid line*) consisting of heating of liquid water to the standard temperature of fusion at 273.15 K (*a*), reversible freezing (*b*), and cooling the ice down to 250 K (*c*)

the integrals,

$$\Delta S_{\text{water}} = n\,c_p(\text{liq.})\,\ln\frac{T_f^{\ominus}}{T_1} - \frac{n\,\Delta h_f^{\ominus}}{T_f^{\ominus}} + n\,c_p(\text{ice})\,\ln\frac{T_1}{T_f^{\ominus}} \tag{3.145}$$

$$= +6.669\,\text{J K}^{-1} - 21.995\,\text{J K}^{-1} - 3.339\,\text{J K}^{-1}\,. \tag{3.146}$$

As expected from the diagram in Fig. 3.16, ΔS_{water} corresponding to the difference in S_{water} between point 4 and point 1 is negative. Next, we focus on the entropy changes in the surroundings involved with steps a, b, and c respectively. We presume that the surroundings constitute a huge heat reservoir, so that arbitrary amounts of heat can be exchanged with the surroundings without a change in its temperature, which is $T_1 = 250\,\text{K}$. Then, we can calculate the entropy changes of the surroundings, as we have done in Problem 3.8 (Eq. (3.73)) and obtain

$$\Delta S_{\text{surroundings}} = -\frac{n\,c_p(\text{liq.})(T_f^{\ominus} - T_1)}{T_1} + \frac{n\,\Delta h_f^{\ominus}}{T_1} - \frac{n\,c_p(\text{ice})(T_1 - T_f^{\ominus})}{T_1} \tag{3.147}$$

$$= -6.973\,\text{J K}^{-1} + 24.032\,\text{J K}^{-1} + 3.491\,\text{J K}^{-1} \tag{3.148}$$

The first term corresponds to the entropy change of the surroundings, if the heat $n\,c_p(\text{liq.})(T_f^{\ominus} - T_1)$ necessary to heat the liquid water to $T_f^{\ominus}$ is transferred from the surroundings to the water in step (a). The second term is the gain of entropy if the latent heat released by the water upon freezing is transferred to the surroundings in step (b). The third term, finally, is the gain of entropy of the surroundings due to the heat released by the frozen ice when it is cooled back to the lower temperature T_1. Thus, summing up all entropy changes using Eq. (3.143), we obtain an increase in total entropy of $\Delta S = +1.885\,\mathrm{J\,K^{-1}}$. Using the second law, we conclude that the cooling of supercooled water at 250 K is a spontaneous process.

Problem 3.15 (Freezing of Atmospheric Water Droplets to Cubic or Hexagonal Ice)

The molar Gibbs free energy of a substance with a surface area A is

$$g = h - Ts + \gamma A \tag{3.149}$$

where h and s are the molar enthalpy and entropy respectively, and γ is the surface tension or surface energy. Consider small water droplets of supercooled atmospheric water at a temperature of 200 K. Calculate the range of droplet radii for which freezing to cubic ice is thermodynamically favorable over freezing to hexagonal ice. For both forms of ice, assume a density of $0.93\,\mathrm{g\,cm^{-3}}$, and $h_{\text{cubic}} - h_{\text{hexagonal}} = 35\,\mathrm{J\,mol^{-1}}$. The surface energies are $\gamma_{\text{cubic}} = 22\,\mathrm{mJ\,m^{-2}}$ and $\gamma_{\text{hexagonal}} = 31\,\mathrm{mJ\,m^{-2}}$ respectively. Assume equal molar entropies of cubic and hexagonal ice. (Literature reference: G. P. Johari, J. Chem. Phys. **122**, 194504 (2005).)

Solution 3.15 Multi-phase systems necessarily have phase boundaries: surfaces. As the chemical environment at an interface is generally different , the molecules experience a different bonding at the interface compared with the bulk. As a consequence, the total energy of a finite piece of matter also depends on its surface area. The dependency of the thermodynamic potentials on the surface area is considered via the surface energy γ per unit area, equivalent to a *surface tension*. For larger systems, surface effects on the thermodynamic properties can often be neglected. However, for objects on the *nano* scale, such as the very small atmospheric water droplets considered in this problem, the surface energy may influence, among other things, the ice crystallization properties of such droplets. From the viewpoint of thermodynamics, water crystallizes in the form that under given conditions has the lower Gibbs free energy of formation. Presuming the same molar entropy of cubic and hexagonal ice, water crystallizes as hexagonal ice if we neglect the influence of the interface, because, as stated in the text of the problem, its molar enthalpy is $35\,\mathrm{J\,mol^{-1}}$ smaller than that of cubic ice. Let us consider a water droplet with a radius of r, a volume $V(r) = \frac{4\pi}{3} r^3$, a surface area $A(r) = 4\pi r^2$, and mole number $n(r) = \frac{\rho}{M} V(r)$. $M = 18\,\mathrm{g\,mol^{-1}}$ is the molar mass of water, and $\rho = 0.93\,\mathrm{g\,cm^{-3}}$ is the density. The Gibbs free energy of a droplet of hexagonal ice is

$$G_{\text{hexagonal}}(r) = n(r)\,h_{\text{hexagonal}} - n(r)\,T\,s_{\text{hexagonal}} + \gamma_{\text{hexagonal}}\,A(r) \tag{3.150}$$

For a droplet of cubic ice of the same radius,

$$G_{\text{cubic}}(r) = n(r)\,h_{\text{cubic}} - n(r)\,T\,s_{\text{cubic}} + \gamma_{\text{cubic}}\,A(r) \tag{3.151}$$

If the entropies of cubic and hexagonal ice are the same as stated above,

$$G_{\text{cubic}} - G_{\text{hexagonal}} = n(r)\,\left(h_{\text{cubic}} - h_{\text{hexagonal}}\right) + \left(\gamma_{\text{cubic}} - \gamma_{\text{hexagonal}}\right)\,A(r) \tag{3.152}$$

$$= \frac{4\pi\rho}{3M} r^3\,\left(h_{\text{cubic}} - h_{\text{hexagonal}}\right) + 4\pi r^2\,\left(\gamma_{\text{cubic}} - \gamma_{\text{hexagonal}}\right) \tag{3.153}$$

We use this expression to determine the *critical radius* at which cubic and hexagonal water droplets of the same radius have the same Gibbs free energy ($G_{\text{cubic}}(r_{\text{crit.}}) - G_{\text{hexagonal}}(r_{\text{crit.}}) = 0$):

$$r_{\text{crit.}} = -\frac{3M}{\rho}\frac{\left(\gamma_{\text{cubic}} - \gamma_{\text{hexagonal}}\right)}{\left(h_{\text{cubic}} - h_{\text{hexagonal}}\right)} \tag{3.154}$$

$$= -\frac{3 \times 18 \times 10^{-3}\,\text{kg mol}^{-1}}{930\,\text{kg m}^{-3}}\,\frac{(22-31) \times 10^{-3}\,\text{J m}^{-2}}{35\,\text{J mol}^{-1}} \tag{3.155}$$

$$= 14.9 \times 10^{-9}\,\text{m} \tag{3.156}$$

The critical radius for a water droplet is only about 15 nm. If $r > r_{\text{crit.}}$, the Gibbs free energy of hexagonal ice is lower than that of cubic ice, and the droplet crystallizes in the hexagonal crystal structure. For $r < r_{\text{crit.}}$, thermodynamics supports crystallization in the cubic form of ice.

References

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2. Friedman AS, White D (1950) J Am Chem Soc 72:3931–3932