Chapter 17
Thermodynamic Equilibrium

17.1 Equilibrium Conditions

We introduced the second law of thermodynamics to formalize the statement that a system which is left to itself will approach a final stable equilibrium state. A system left completely to itself is isolated, and does not exchange heat, work or mass with its surroundings, therefore $\dot{Q} = \dot{W} = 0$; for such a system, the second law states that in equilibrium entropy will assume a maximum. While the initial state of a system typically is inhomogeneous, in equilibrium we expect homogeneous temperatures and zero velocity, since internal heat transfer will equilibrate temperature, and internal friction will dissipate all kinetic energy. If gravity can be ignored, pressure and density (in a single phase system) are homogeneous as well, else they might be inhomogeneous, as, e.g., in the barometric formula.

Below, we shall confirm these expectations by evaluating the second law for isolated systems. Thereafter, we generalize the discussion to thermodynamic equilibria of closed systems with various boundary conditions. The state of the system can be controlled from the surroundings of the system in a number of ways. When the system is in thermal contact with a temperature reservoir it will assume the temperature of the reservoir, and thus the system temperature is controlled. The system volume can be controlled by confining material into a closed box. The system pressure can be controlled by exerting a constant force on a piston that closes the system. The system's energy E is controlled when heat and work balance, i.e., $\dot{Q} = \dot{W}$, so that $\frac{dE}{dt} = 0$. Systems at controlled temperatures or pressures will exchange heat or work, and change their volume, as they approach their equilibrium state.

We shall see that, depending on the boundary conditions, different thermodynamic properties will attain a minimum or a maximum in equilibrium. However, the resulting equilibria share the same characteristics.

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17.2 Equilibrium in Isolated Systems

An isolated system does not exchange energy or mass with its surroundings. Accordingly, first and second law reduce to

$$\frac{dE}{dt}=0 \quad , \quad \frac{dS}{dt}=\dot{S}_{gen}\geq 0\,, \tag{17.1}$$

with a constant mass m in the system. Since no work is exchanged, the volume V must be constant as well. According to the second law, the state of the system will change until the entropy has reached a maximum. However, since mass and energy of the system do not change over time, at all times the process is restricted by having the initial mass and energy enclosed in the system. The approach to equilibrium is a reorganization of the local properties of the system towards the final equilibrium state.

We study the approach to equilibrium for a single phase system; heterogeneous systems will be discussed later, in Sec. 17.7. For this we have to consider the total mass, energy and entropy by integration over the full system,

$$m=\int_V \rho dV \quad , \quad E=\int_V \rho\left(u+\frac{1}{2}\mathcal{V}^2+\gamma z\right)dV \quad , \quad S=\int_V \rho s dV\,. \tag{17.2}$$

In order to avoid confusion with the Gibbs free energy, the gravitational acceleration is denoted by γ. Here, ρ, T, $\mathcal{V}$, and $u\left(\rho,T\right)$, $s\left(\rho,T\right)$ are the *local* values of the thermodynamic properties, that is, $\rho=\rho\left(\overrightarrow{r}\right)$, $T=T\left(\overrightarrow{r}\right)$ etc., where $\overrightarrow{r}$ is the location in the volume V of the system, see Sec. 2.7.

Before we proceed, we need to state the momentum vector $\overrightarrow{M}$ of the system. Typically, we are interested in systems that are globally at rest, where the overall momentum vanishes, but we might consider also systems moving with a constant velocity $\overrightarrow{v}$, so that $\overrightarrow{M}=m\overrightarrow{v}$. Since all elements of the system have their own velocity $\overrightarrow{\mathcal{V}}\left(\overrightarrow{r}\right)$, we find the total momentum by summing over the system,

$$\overrightarrow{M}=m\overrightarrow{v}=\int_V \rho\overrightarrow{\mathcal{V}}dV\;; \tag{17.3}$$

here $\overrightarrow{\mathcal{V}}$ is the local velocity vector with $\mathcal{V}=\sqrt{\overrightarrow{\mathcal{V}}\cdot\overrightarrow{\mathcal{V}}}$. As long as no forces act on the system, its momentum will be constant; total momentum vanishes for a system at rest in the observer frame, $\overrightarrow{M}=0$.

The equilibrium state is the maximum of entropy S under the constraints of given mass m, momentum $\overrightarrow{M}$, and energy E. The best way to account for the constraints is the use of Lagrange multipliers Λ_ρ, $\overrightarrow{\Lambda}_M$ and Λ_E to incorporate the constraints and maximize not S but

$$\begin{aligned}\varPhi = \int_V \rho s dV - \varLambda_\rho \left(\int_V \rho dV - m\right) - \overrightarrow{\varLambda}_M \cdot \left(\int_V \rho \overrightarrow{\mathcal{V}} dV - \overrightarrow{M}\right) \\ - \varLambda_E \left(\int_V \rho \left(u + \frac{1}{2}\mathcal{V}^2 + \gamma z\right) dV - E\right) \ . \quad (17.4)\end{aligned}$$

The maximization of $\varPhi$ will give the local values of the thermodynamic equilibrium properties $\{\rho, T, \mathcal{V}\}$ in terms of the Lagrange multipliers, which then must be determined from the given values of $\left\{m, \overrightarrow{M}, E\right\}$.

For the solution of this problem, we employ some rules of variational calculus. The condition for an extremum of the integral $\int_{x_0}^{x_1} X\left(x, y, y'\right) dx$ with $y = y\left(x\right)$ and $y' = dy/dx$, where $X\left(x, y, y'\right)$ is known, is that the first variation of the integral vanishes. This requirement results in Euler's differential equation of variational calculus, $\frac{d}{dx}\frac{\partial X}{\partial y'} - \frac{\partial X}{\partial y} = 0$ (Leonhard Euler, 1707 - 1783). The solution of Euler's equation yields the desired function $y\left(x\right)$ that maximizes the integral. Euler's equation holds also when x and y are vectors. In our case we identify $x = \overrightarrow{r}$, $y = \left\{\rho, \overrightarrow{\mathcal{V}}, T\right\}$ and

$$X = \rho\left[s - \varLambda_\mu - \overrightarrow{\varLambda}_M \cdot \overrightarrow{\mathcal{V}} - \varLambda_E \left(u + \frac{1}{2}\mathcal{V}^2 + \gamma z\right)\right] \ . \qquad (17.5)$$

In this particular case the integrand X is independent of $y' = \left\{\frac{d\rho}{d\mathbf{r}}, \frac{d\overrightarrow{\mathcal{V}}}{d\mathbf{r}}, \frac{dT}{d\mathbf{r}}\right\}$, so that Euler's equation reduces to

$$\frac{\partial X}{\partial y} = \left\{\frac{\partial X}{\partial \rho}, \frac{\partial X}{\partial \overrightarrow{\mathcal{V}}}, \frac{\partial X}{\partial T}\right\} = 0 \ , \qquad (17.6)$$

or, in detail,

$$\begin{aligned}\frac{\partial X}{\partial \rho} = \left[s - \varLambda_\rho - \mathbf{\Lambda}_M \cdot \overrightarrow{\mathcal{V}} - \varLambda_E \left(u + \frac{1}{2}\mathcal{V}^2 + \gamma z\right)\right] \\ + \rho\left[\left(\frac{\partial s}{\partial \rho}\right)_T - \varLambda_E \left(\frac{\partial u}{\partial \rho}\right)_T\right] = 0 \ , \quad (17.7)\end{aligned}$$

$$\frac{\partial X}{\partial \overrightarrow{\mathcal{V}}} = \rho\left[-\overrightarrow{\varLambda}_M - \varLambda_E \overrightarrow{\mathcal{V}}\right] = 0 \ . \qquad (17.8)$$

$$\frac{\partial X}{\partial T} = \rho\left[\left(\frac{\partial s}{\partial T}\right)_\rho - \varLambda_E \left(\frac{\partial u}{\partial T}\right)_\rho\right] = 0 \ , \qquad (17.9)$$

We proceed with evaluating these three conditions to find the equilibrium state. For convenience, we begin with the middle equation, (17.8), which gives immediately that the velocity is homogeneous in equilibrium,

$$\vec{\mathcal{V}} = -\frac{\vec{\Lambda}_M}{\Lambda_E} \,. \tag{17.10}$$

For the case of a system at rest, where

$$0 = \vec{M} = \int_V \rho \vec{\mathcal{V}} dV = -\frac{\vec{\Lambda}_M}{\Lambda_E} \int_V \rho dV = -\frac{\vec{\Lambda}_M}{\Lambda_E} m \,, \tag{17.11}$$

this implies that in equilibrium all local elements are at rest,

$$\vec{\mathcal{V}} = \vec{\Lambda}_M = \vec{M} = 0 \,. \tag{17.12}$$

To evaluate the last condition, (17.9), we recall that the Gibbs equation $Tds = du - \frac{p}{\rho^2} d\rho$ gives $\left(\frac{\partial s}{\partial T}\right)_\rho = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_\rho$. Hence, the condition becomes

$$\left(\frac{\partial s}{\partial T}\right)_\rho - \Lambda_E \left(\frac{\partial u}{\partial T}\right)_\rho = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_\rho - \Lambda_E \left(\frac{\partial u}{\partial T}\right)_\rho = 0 \,. \tag{17.13}$$

It follows that in equilibrium the temperature is homogeneous, and equal to the inverse Lagrange multiplier,

$$T = \frac{1}{\Lambda_E} \,. \tag{17.14}$$

To evaluate the first condition, (17.7), we insert the above results for Λ_E, $\mathbf{\Lambda}_M$, $\vec{\mathcal{V}}$ and use again the Gibbs equation, which gives $\left(\frac{\partial s}{\partial \rho}\right)_T - \frac{1}{T}\left(\frac{\partial u}{\partial \rho}\right)_T = -\frac{p}{T\rho^2}$. After some reordering, we find

$$g = u - Ts + \frac{p}{\rho} = -T\Lambda_\rho - \gamma z \,, \tag{17.15}$$

where g is the Gibbs free energy, and γ is gravitational acceleration. With the temperature homogeneous, and the constant Lagrange multiplier Λ_ρ, this is an implicit equation for the equilibrium density, which appears as an argument in the Gibbs free energy $g(\rho, T)$, or, alternatively, it is an equation for pressure p, if we write $g(p, T)$. Often we consider systems in which the potential energy can be ignored. For such systems, the Gibbs free energy is homogeneous, $g(\rho, T) = -T\Lambda_\rho$. Homogeneous Gibbs free energy and temperature implies that density and pressure are homogeneous as well. Phase equilibrium will be discussed in Sec. 17.9.

In summary, maximizing entropy in the isolated system yields that the system is fully at rest, $\mathcal{V} = 0$, has homogeneous temperature, $T = 1/\Lambda_E$, and, in the gravitational field, has inhomogeneous density and pressure, given implicitly by $g(T, \rho) = -T\Lambda_\rho - \gamma z$. What remains is to determine the Lagrange multipliers $\Lambda_E = 1/T$ and Λ_ρ, which follow from the given values of mass

$m = \int_V \rho dV$ and energy $E = \int_V \rho \left[u\left(T,\rho\right) + \gamma z\right] dV$ in the system. Their detailed values depend on the size and geometry of the system.

17.3 Barometric and Hydrostatic Formulas

To gain insight into the influence of potential energy, we evaluate (17.15) for ideal gases and incompressible fluids. For an ideal gas, the Gibbs free energy is $g\left(\rho,T\right) = h\left(T\right) - T\left(s^0\left(T\right) - R\ln\frac{\rho RT}{p_0}\right)$. Using this in (17.15) and solving for density gives the barometric formula,

$$\rho = \rho^0 \exp\left[-\frac{\gamma z}{RT}\right] , \tag{17.16}$$

where $\rho^0 = \frac{p_0}{RT}\exp\left[-\frac{\Lambda_\rho}{R} - \frac{h(T) - Ts^0(T)}{RT}\right]$ is the density at reference height $z = 0$. The ideal gas law gives the corresponding expression for pressure as $p = p^0\exp\left[-\frac{\gamma z}{RT}\right]$, where $p^0 = \rho^0 RT$ is the pressure at $z = 0$.

For incompressible fluids, $\rho = const.$, and internal energy and entropy depend only on temperature, so that the Gibbs free energy is $g\left(T,p\right) = u\left(T\right) + \frac{p}{\rho} - Ts\left(T\right)$. Using this in (17.15) and solving for pressure gives the hydrostatic pressure formula,

$$p = p^0 - \rho\gamma z , \tag{17.17}$$

where $p^0 = \rho T\left[s\left(T\right) - u\left(T\right)/T - \Lambda_\rho\right]$ is the pressure at reference height $z = 0$.

17.4 Thermodynamic Stability

The equilibrium state determined in the previous sections should be stable, which means that, indeed, it should be a maximum of the integral Φ as defined in (17.4). This requires that the second variation of Φ must be negative. In our case, where the integrand X depends only on y, this requires negative values for the second derivatives $\partial^2 X/\partial y^2$ at the location of the maximum. With the help of the Gibbs equation, the second derivatives can be written as

$$\frac{\partial X}{\partial\rho\partial\rho} = \left[\frac{1}{T} - \Lambda_E\right]\left[2\left(\frac{\partial u}{\partial\rho}\right)_T + \rho\left(\frac{\partial^2 u}{\partial\rho^2}\right)_T\right] - \frac{1}{\rho T}\left(\frac{\partial p}{\partial\rho}\right)_T ,$$

$$\frac{\partial^2 X}{\partial\overrightarrow{\mathcal{V}}^2} = -\rho\Lambda_E ,$$

$$
\begin{aligned}
\frac{\partial^2 X}{\partial T^2} &= \rho\left[\frac{1}{T} - \varLambda_E\right]\left(\frac{\partial^2 u}{\partial T^2}\right)_\rho - \frac{\rho}{T^2}\left(\frac{\partial u}{\partial T}\right)_\rho , \\
\frac{\partial^2 X}{\partial \rho \partial T} &= \frac{\partial^2 X}{\partial T \partial \rho} = \left[\frac{1}{T} - \varLambda_E\right]\left(\frac{\partial u}{\partial T}\right)_\rho , \\
\frac{\partial X}{\partial \rho \partial \vec{\mathcal{V}}} &= \frac{\partial X}{\partial \vec{\mathcal{V}} \partial \rho} = -\vec{\varLambda}_M - \varLambda_E \vec{\mathcal{V}} , \\
\frac{\partial X}{\partial T \partial \vec{\mathcal{V}}} &= \frac{\partial X}{\partial \vec{\mathcal{V}} \partial T} = 0 .
\end{aligned}
\tag{17.18}
$$

These must now be evaluated at the equilibrium state, $T = 1/\varLambda_E$ and $\vec{\mathcal{V}} = -\vec{\varLambda}_M/\varLambda_E$, where they must be negative. With the definitions of isothermal compressibility κ_T (16.37) and the specific heat at constant volume c_v (16.20), the resulting conditions can be written as

$$
\begin{aligned}
\frac{\partial X}{\partial \rho \partial \rho}_{|eq} &= -\frac{1}{\rho T}\left(\frac{\partial p}{\partial \rho}\right)_T = -\frac{1}{\rho^2 T \kappa_T} < 0 , \\
\frac{\partial^2 X}{\partial \vec{\mathcal{V}}^2}_{|eq} &= -\frac{\rho}{T} < 0 , \\
\frac{\partial^2 X}{\partial T^2}_{|eq} &= -\frac{\rho}{T^2}\left(\frac{\partial u}{\partial T}\right)_\rho = -\frac{\rho}{T^2} c_v < 0 ;
\end{aligned}
\tag{17.19}
$$

all mixed derivatives vanish in equilibrium. With the mass density being positive, thermodynamic stability thus requires that isothermal compressibility, specific heat, and thermodynamic temperature are positive,

$$
\kappa_T > 0 \quad , \quad c_v > 0 \quad , \quad T \geq 0 . \tag{17.20}
$$

These conditions imply that the volume decreases when pressure is increased isothermally, and that the temperature rises when heat is added to the system. While this matches our daily experience, it is nevertheless remarkable that it is guaranteed by the second law as a universal principle, valid for all materials.

17.5 Equilibrium in Non-isolated Systems

Non-isolated systems exchange work or heat with their surroundings. For the study of their equilibria, we use the first and second law in their global forms,

$$
\frac{d}{dt}\left(U + E_{pot}\right) = \dot{Q} - p_B \frac{dV}{dt} \quad , \quad \frac{dS}{dt} - \frac{\dot{Q}}{T_B} = \dot{S}_{gen} \geq 0 , \tag{17.21}
$$

which are valid when the system exchanges work only via a piston. Here, p_B is the pressure at the piston boundary, and the system exchanges heat only at boundary temperature T_B; we shall consider only cases with homogeneous pressure and temperature at the system boundary. For simplicity, we ignore kinetic energy, which can be incorporated as in the previous sections, with the same result that all elements of the system will be at rest in equilibrium.

For all systems discussed below, if single phase systems are considered, the respective maximization or minimization requirements are mathematically very similar to the maximization of entropy as discussed above.

In cases where the homogeneous boundary temperature T_B is prescribed, the role of the Lagrange multiplier Λ_E is assumed by the boundary temperature T_B, and thus the homogeneous equilibrium temperature of the system is $T = T_B$.

In cases where the piston pressure is prescribed, the pressure condition $g\,(p, T) = -T\Lambda_\rho - \gamma z$ must be compatible with the pressure prescribed at the piston. If gravity can be ignored, this gives $g\,(p, T) = g\,(p_B, T) = -T\Lambda_\rho$, hence homogeneous pressure $p = p_B$. In cases with gravity, since we have assumed homogeneous piston pressure, this implies horizontal piston and $g\,(p, T) = g\,(p_B, T) - \gamma\,(z - z_B)$, where z_B is the height of the piston.

17.5.1 Adiabatic and Isochoric System

For an adiabatic system, we have $\dot{Q} = 0$ and thus

$$\frac{d}{dt}\left(U + E_{pot}\right) = -p_B\frac{dV}{dt} \quad , \quad \frac{dS}{dt} \geq 0\ . \tag{17.22}$$

Entropy grows in an adiabatic process, until it reaches a maximum in equilibrium. We note that for an isochoric process, where $V = const.$, or $\frac{dV}{dt} = 0$, the total energy $E = U + E_{pot}$ stays constant as well. Thus, we have in particular

$$S \Longrightarrow \text{Maximum and } U + E_{pot} = const. \ \text{ for } \ \dot{Q} = 0,\ V = const. \tag{17.23}$$

Indeed, this is the case of a fully isolated system as discussed above, which does not exchange heat and work with its surroundings. The equilibrium state for this case follows from maximizing entropy under constraints of given values for mass m and energy $U + E_{pot}$.

17.5.2 Adiabatic and Isobaric System

A Legendre transform gives an alternative form of the first law,

$$\frac{d}{dt}\left(U + p_BV + E_{pot}\right) = V\frac{dp_B}{dt}\ , \tag{17.24}$$

and we conclude that

$$S \Longrightarrow \text{Maximum and } U + p_B V + E_{pot} = const. \text{ for } \dot{Q} = 0,\ p_B = const. \tag{17.25}$$

Note that $H = U + pV$ is the enthalpy. The equilibrium state for this case follows from maximizing entropy under constraints of given values for mass m and $U + p_B V + E_{pot}$.

17.5.3 Isentropic and Isochoric System

For the discussion of non-adiabatic systems, we eliminate the heat $\dot{Q}$ between the first and the second law, to find

$$\frac{d}{dt}\left(U + E_{pot}\right) - T_B \frac{dS}{dt} + p_B \frac{dV}{dt} = -T_B \dot{S}_{gen} \leq 0\ . \tag{17.26}$$

It follows that in a process with constant entropy and constant volume, where $\frac{dS}{dt} = \frac{dV}{dt} = 0$, the total energy will assume a minimum in equilibrium,

$$E = U + E_{pot} \Longrightarrow \text{Minimum for } S = const.,\ V = const. \tag{17.27}$$

The equilibrium state for this case follows from minimizing energy $U + E_{pot}$ under constraints of given values for mass m and entropy S. Note that entropy is difficult to control, and thus this case is typically not encountered in applications.

17.5.4 Isothermal and Isochoric System

By means of a Legendre transform, (17.26) can be rewritten as

$$\frac{d}{dt}\left(U - T_B S + E_{pot}\right) + S \frac{dT_B}{dt} + p_B \frac{dV}{dt} = -T_B \dot{S}_{gen} \leq 0\ . \tag{17.28}$$

It follows that in a process with constant boundary temperature and volume, where $\frac{dT_B}{dt} = \frac{dV}{dt} = 0$, the combination $E - T_B S$ assumes a minimum in equilibrium,

$$U - T_B S + E_{pot} \Longrightarrow \text{Minimum for } T_B = const.,\ V = const. \tag{17.29}$$

Recall that $U - TS = F$ is the Helmholtz free energy. The equilibrium state for this case follows from minimizing $U - T_B S + E_{pot}$ under constraint of given value for mass m.

17.5.5 Isothermal and Isobaric System

Another Legendre transform shows that for a process with constant boundary pressure and temperature ($\frac{dT_B}{dt} = \frac{dp_B}{dt} = 0$) the combination $E + p_B V - T_B S$ assumes a minimum,

$$U + p_B V - T_B S + E_{pot} \Longrightarrow \text{Minimum for } T_B = const.,\ p_B = const. \quad (17.30)$$

Recall that $U + pV - TS = H - TS = G$ is the Gibbs free energy. The equilibrium state for this case follows from minimizing $U + p_B V - T_B S + E_{pot}$ under constraint of given value for mass m.

17.5.6 Energy vs. Entropy

Temperature, volume and pressure are far easier to control than energy and entropy, and thus one normally encounters the last two cases for the computation of equilibria. For simple one-phase systems the results are straightforward: homogeneous temperature T, and, if gravity is ignored, homogeneous pressures p. More complex systems, in particular systems in several phases, and reacting and inert mixtures of several components have additional degrees of freedom that approach equilibrium values, and it is convenient to determine these equilibrium values under the assumption that thermal and mechanical equilibrium, i.e., homogeneous temperature and pressure, are established already. Then, the computation of equilibrium states typically entails to find minima of free energies, either of the Helmholtz free energy $F = U - TS$, or of the Gibbs free energy $G = H - TS$.

The free energies describe the competition between energy and entropy, with the temperature as factor to determine their relative importance. We take a look at this for the Helmholtz free energy, $F = U - TS$. The Helmholtz free energy can attain a minimum state either by making the energy U small, or by making the entropic term TS large. At low temperatures, the product TS is relatively small, thus the entropic term does not matter much, and energy is more important; states of low energies are assumed, for instance the liquid state, which is due to the attractive potential between molecules. For high temperatures, however, the entropic term TS dominates, and states of large entropy are assumed, e.g., the vapor state. For intermediate temperatures, energy and entropy find a compromise, e.g., the coexistence of vapor, which has large entropy, and liquid, which has low energy, in phase equilibrium.

17.6 Interpretation of the Barometric Formula

We discuss the barometric formula (17.16) in the context of the competition between energy and entropy, where the temperature is the deciding factor.

The barometric formula is quite interesting as a rough indicator on the behavior of planetary atmospheres. For an exact discussion, however, one should account for temperature variances within the atmosphere, and for the spherical geometry of the planets.

We consider a column of atmosphere of base area A. The number of moles in a layer of the atmosphere at height z is $dn = \frac{\rho(z)}{M} A dz$, while the total number of moles in the column is $N = m/M$, with $m = \int \rho A dz$ being the total mass in the column. The probability to find a particle in the layer at z is given by

$$\pi dz = \frac{dn}{N} = \frac{\rho(z) A dz}{m} = \frac{\gamma}{RT} \exp\left[-\frac{\gamma z}{RT}\right] dz \ . \qquad (17.31)$$

$\pi(z)$ as defined here is a probability density, which fulfills $\int_0^\infty \pi(z)\, dz = 1$. Mean value and variance of the height of a particle are

$$\bar{z} = \int_0^\infty z\pi(z)\, dz = \frac{\bar{R}T}{M\gamma} \quad , \quad \sigma = \sqrt{\int_0^\infty (z-\bar{z})^2 \pi(z)\, dz} = \frac{\bar{R}T}{M\gamma} \ . \qquad (17.32)$$

For large values of $\bar{z}$ and σ, gases are more likely to escape a planet. Obviously, $\bar{z}$ and σ grow with temperature, which explains why hot planets, e.g., Mercury, have lost their atmosphere. Moreover, $\bar{z}$ and σ are smaller for larger gravitation γ, which explains why heavier planets have more stable atmospheres: Jupiter, for instance, is a heavy gas planet. Finally, $\bar{z}$ and σ grow with decreasing molar mass M which explains why light elements are more likely to escape from the atmosphere of a planet. Indeed, there is only little helium left in Earth's atmosphere, although helium is one of the most abundant elements in the universe. A good source for helium is natural gas which was formed long ago, when Earth's atmosphere was richer in helium.

The above discussion can be seen in the context of competition between energy and entropy. When the temperature is low, the entropy is less important, and the equilibrium state has a low potential energy, $\bar{z}$ is small, and $\bar{z} = 0$ for $T = 0$. But when the temperature is high, entropy is more important, and tries to establish a state of even distribution within the accessible volume. The actual state, with exponential decay, is a compromise between the two opposing tendencies. We shall explore this competition more as we proceed.

17.7 Equilibrium in Heterogeneous Systems

The thermodynamic equilibrium conditions, e.g., system entropy assumes a maximum in isolated systems (17.23), or Gibbs free energy assumes a minimum when pressure and temperature are prescribed at the boundary (17.30), are universally valid. In this section, we evaluate the equilibrium state for a heterogeneous system, which consists of two parts in thermal and mechani-

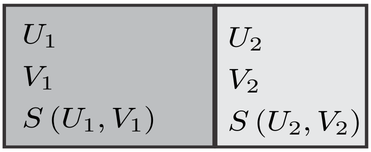

Fig. 17.1 An externally adiabatic system at constant volume, containing two different materials or phases

cal contact. To be specific, we consider an adiabatically enclosed system at constant volume that is divided into two parts as depicted in Fig. 17.1. The two parts may contain different substances, or the same substance, and they might contain different phases. The divider between the two parts can move freely, and is diathermal, i.e., heat can pass, potential and kinetic energies are ignored. Due to the boundary conditions for the system, total energy, $U = U_1 + U_2$, and total volume, $V = V_1 + V_2$ are constants, but energy and volume of the parts might change. We assume the system is in thermal equilibrium and consider small perturbations from the equilibrium state such that the energies and volumes of the two parts are

$$U_1 + \delta U \quad , \quad U_2 - \delta U \quad \text{and} \quad V_1 + \delta V \quad , \quad V_2 - \delta V \; . \tag{17.33}$$

This perturbation yields a change in entropy, so that the entropy of the perturbed state is $S + \delta S$. Since the perturbed state is an equilibrium state, the entropy $S = S_1\left(U_1, V_1\right) + S_2\left(U_2, V_2\right)$ is a maximum; accordingly, the perturbation in entropy must be negative, $\delta S < 0$. We have

$$S + \delta S = S_1\left(U_1 + \delta U, V_1 + \delta V\right) + S_2\left(U_2 - \delta U, V_2 - \delta V\right) \; , \tag{17.34}$$

and from Taylor expansion to first order we find

$$\delta S = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1} \delta U + \left(\frac{\partial S_1}{\partial V_1}\right)_{U_1} \delta V - \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2} \delta U - \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2} \delta V \; . \tag{17.35}$$

From the Gibbs equation $T dS = dU + p dV$ we identify $\left(\partial S/\partial U\right)_V = 1/T$ and $\left(\partial S/\partial V\right)_U = p/T$, and thus the above can be rewritten (with some reordering) as

$$0 > \delta S = \left[\frac{1}{T_1} - \frac{1}{T_2}\right] \delta U + \left[\frac{p_1}{T_1} - \frac{p_2}{T_2}\right] \delta V \; . \tag{17.36}$$

Since δU and δV can have arbitrary positive or negative values, the sign condition on δS can only be fulfilled when both terms vanish. This gives the expected equilibrium conditions for the two parts, namely that they have the same temperatures and pressures

$$T_1 = T_2 \quad \text{and} \quad p_1 = p_2 \,. \tag{17.37}$$

The above discussion can be performed for any splitting of the system, and for different substances in the subsystem. It follows that all possible subsystems have the same temperature and pressure, that is pressure and temperature are homogeneous within the system.

If potential energy, e.g., gravitation, plays a role, pressure is not homogeneous, see Sec. 17.3. Pressure distribution within one substance or phase is then given by $g\,(p,T) = -T\Lambda_\rho - \gamma z$, while the pressure is continuous at the interface between two substances or phases.

17.8 Phase Equilibrium

A particular class of equilibrium states concerns equilibria between different phases of the same substance, e.g., liquid-vapor equilibria.

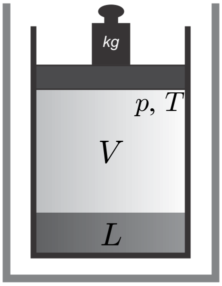

Fig. 17.2 Liquid (L) and vapor (V) phase in equilibrium at given pressure p and temperature T

Figure 17.2 shows liquid and vapor in equilibrium in a system where pressure p and temperature T are fixed at the boundaries by the given mass of the piston, and exposure to a large reservoir at T. According to (16.1) the equilibrium state of this system is determined by a minimum of the Gibbs free energy G, which is just the sum of the Gibbs free energies of the two phases. The mass $m = m_L + m_V$ within the system is constant, and thus we have

$$G = m_V g_V\,(T,p) + m_L g_L\,(T,p) = m_V g_V\,(T,p) + (m - m_V)\, g_L\,(T,p) \,. \tag{17.38}$$

The specific free energies of the individual phases, g_L and g_V, depend only on the intensive variables p and T. When thermal and mechanical equilibrium are established, T and p are homogeneous throughout both phases, and the vapor mass m_V is the only variable. The chemical equilibrium is assumed when G becomes a minimum, that is for $dG/dm_V = 0$, which gives

$$g_V(T,p) = g_L(T,p) \ . \tag{17.39}$$

Hence, in a two phase system in equilibrium, pressure, temperature *and* Gibbs free energies are homogeneous. It follows that both phases can coexist only at values for pressure and temperature (T,p) that fulfill the above condition. Solving for p gives the saturation pressure $p_{\text{sat}}(T)$, with the well known value of $p_{\text{sat}}(100\,^\circ\text{C}) = 1\,\text{atm}$ for water. Solving for T gives the saturation temperature, $T_{\text{sat}}(p)$.

In case that temperature and pressure are chosen such that the Gibbs free energies of liquid and vapor are different, the Gibbs free energy (17.38) assumes a boundary minimum with either $m_L = m$, $m_V = 0$ (compressed liquid) or $m_V = m$, $m_L = 0$ (superheated vapor). In detail we have for a specified pressure p:

$$\begin{aligned} T < T_{\text{sat}}(p) \quad &\Longrightarrow \quad g_L(T,p) < g_V(T,p) \quad \Longrightarrow \quad m_L = m,\ m_V = 0 \ , \\ T > T_{\text{sat}}(p) \quad &\Longrightarrow \quad g_L(T,p) > g_V(T,p) \quad \Longrightarrow \quad m_V = m,\ m_L = 0 \ . \end{aligned}$$

The phase change can be understood as a competition between energy and entropy. Recall that Gibbs free energy is $g = h - Ts$. For small temperatures, the entropic term $(-Ts)$ is relatively small, and energetic effects dominate. Then the Gibbs free energy is small for the liquid, where the potential energy between particles due to the molecular interaction is at a minimum, the particles are close to each other, and the volume is small. For larger temperatures, the entropic contribution becomes more important, and the Gibbs free energy becomes small for large entropies. Since vapor entropy grows with volume,[1] the vapor state prevails and the volume is large. At saturation, energetic and entropic contributions are of comparable size, and both phases coexist.

Alternatively, we have for a specified temperature T:

$$\begin{aligned} p > p_{\text{sat}}(T) \quad &\Longrightarrow \quad g_L(T,p) < g_V(T,p) \quad \Longrightarrow \quad m_L = m,\ m_V = 0 \ , \\ p < p_{\text{sat}}(T) \quad &\Longrightarrow \quad g_L(T,p) > g_V(T,p) \quad \Longrightarrow \quad m_V = m,\ m_L = 0 \ . \end{aligned}$$

Since vapor entropy grows with lower pressure[2], the entropic term will dominate even at low temperatures, if only the pressure is sufficiently small. Thus, exposing a substance to low pressure might induce phase change.

While we used liquid and vapor as example, the above derivation is not restricted to any particular phases. For any two phases to be in equilibrium, their Gibbs free energies must agree. For an example, revisit Fig. 6.4 in Chapter 6 which shows the saturation lines for water as ice, liquid, and vapor.

At the triple point, all three phases coexist in equilibrium, and their free energies must agree (S stands for solid),

$$g_V(T,p) = g_L(T,p) = g_S(T,p) \ . \tag{17.40}$$

---

[1] This can be seen from the ideal gas entropy in the form $s - s_0 = c_v \ln \frac{T}{T_0} + R \ln \frac{v}{v_0}$.

[2] This can be seen from the ideal gas entropy in the form $s - s_0 = c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0}$.

These are two conditions for T, p and thus there is only one pair of values T_{tr}, p_{tr} at which three phases can coexist, the triple point (e.g., for water: $T_{tr} = 0.01\,°\mathrm{C}$, $p_{tr} = 611\,\mathrm{Pa}$).

The conditions derived above describe the thermodynamic equilibrium of two phases, which is not always attained. Some substances can exist for very long periods in metastable states, outside of equilibrium. A typical example is tin, which below 13.2 °C is stable as a semiconductor phase, and is metallic above. However, the phase transition does only occur at much lower temperatures. Another example is carbon, for which the stable phase at room temperature is graphite, while diamond is metastable, which obviously does not diminish its value, both as a gem, and for toolmaking.

17.9 Example: Phase Equilibrium for the Van der Waals Gas

We consider the van der Waals equation (16.48) for its ability to describe phase equilibrium.

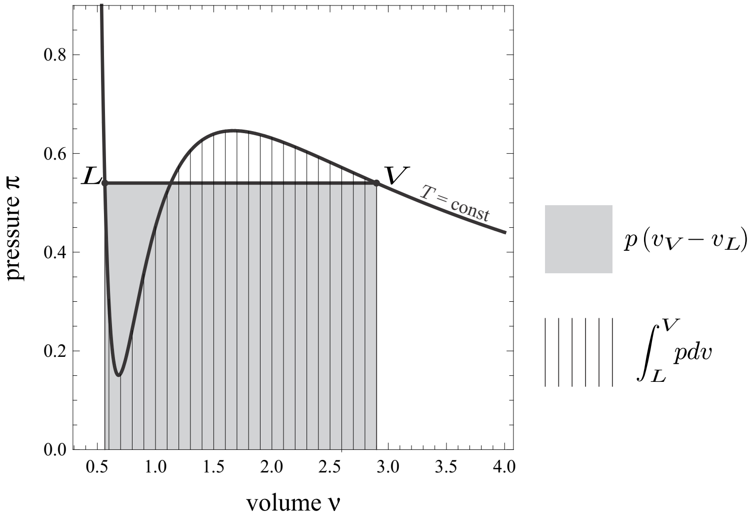

Fig. 17.3 Phase equilibrium for van der Waals gas

Figure 17.3 shows the sketch of an undercritical isotherm for the van der Waals gas, which is not monotonous, but exhibits an unstable region where $\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \leq 0$ (so that the isotherm has a positive slope). Instead of following the curve, the gas can split into two phases: L (liquid) and V (vapor) as indicated. The question is, where the connecting line which determines the saturation pressure should be drawn. The answer comes from evaluation of (17.39) which can be written as

$$g_L = g_V \quad \text{or, with } g = f + pv \text{, as} \quad f_L - f_V = p\left(v_V - v_L\right) \ , \tag{17.41}$$

where p is the common pressure of the two phases, i.e., the saturation pressure.

The difference in Helmholtz free energy can be reformulated as

$$f_L - f_V = -\underset{\text{isotherm}}{\int_L^V} \left(\frac{\partial f}{\partial v}\right)_T dv = \underset{\text{isotherm}}{\int_L^V} p dv \ , \tag{17.42}$$

where we used that $f\left(T, v\right)$ is a potential, see (16.11). Thus the condition for the saturation pressure reads

$$\underset{\text{isotherm}}{\int_L^V} p dv = p\left(v_V - v_L\right) \ . \tag{17.43}$$

This is Maxwell's equal area rule, which states that the areas below the $\mathcal{S}$-shaped van der Waals curve and the straight line connecting vapor and liquid, as shown in the figure, must be equal.

The evaluation of this condition leads to transcendental equations which must be solved numerically. Figure 17.4 shows, in dimensionless variables, some isotherms and the computed vapor dome in the p-v-diagram.

17.10 Clapeyron Equation

The Clapeyron equation describes the slope of the saturation curve. The two phases, and the corresponding properties are denoted as phase $'$ and phase $''$, respectively. To find the Clapeyron equation, we consider a point $\{p_{\text{sat}}, T\}$ on the saturation curve, and an adjacent point on the curve $\{p_{\text{sat}} + dp_{\text{sat}}, T + dT\}$. For the Gibbs free energy of the latter, for one phase, we find by Taylor expansion

$$\begin{aligned} g'\left(p_{\text{sat}} + dp_{\text{sat}}, T + dT\right) &= g'\left(p_{\text{sat}}, T\right) + \left(\frac{\partial g'}{\partial p_{\text{sat}}}\right)_T dp_{\text{sat}} + \left(\frac{\partial g'}{\partial T}\right)_{p_{\text{sat}}} dT \\ &= g'\left(p_{\text{sat}}, T\right) + v' dp_{\text{sat}} - s' dT \ , \end{aligned} \tag{17.44}$$

where we have used (16.13). We consider the corresponding equation for phase $''$ as well,

$$g''\left(p_{\text{sat}} + dp_{\text{sat}}, T + dT\right) = g''\left(p_{\text{sat}}, T\right) + v'' dp_{\text{sat}} - s'' dT \tag{17.45}$$

and take the difference,

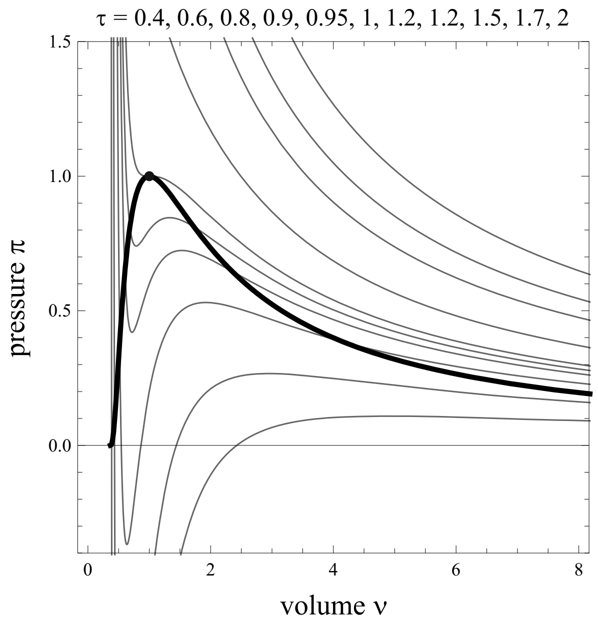

Fig. 17.4 Van der Waals isotherms and two phase region in the $\pi - v$-diagram

$$\begin{aligned} & g''\left(p_{\text{sat}} + dp_{\text{sat}}, T + dT\right) - g'\left(p_{\text{sat}} + dp_{\text{sat}}, T + dT\right) \\ & \qquad = g''\left(p_{\text{sat}}, T\right) - g'\left(p_{\text{sat}}, T\right) + \left(v'' - v'\right) dp_{\text{sat}} - \left(s'' - s'\right) dT \ . \end{aligned}$$

Since both points are on the saturation curve, the differences of the free energies vanish on both sides, and we find the Clapeyron equation[3]

$$\frac{dp_{\text{sat}}}{dT} = \frac{s'' - s'}{v'' - v'} = \frac{1}{T} \frac{h'' - h'}{v'' - v'} \ . \tag{17.46}$$

$h'' - h'$ is the heat of phase change, for instance the heat of evaporation or the heat of melting.

17.11 Example: Estimate of Heat of Evaporation

The Clapeyron equation can be used to find an estimate for the vapor pressure curve. We consider liquid-vapor equilibrium, where the Clapeyron equations reads

$$\frac{dp_{\text{sat}}}{dT} = \frac{1}{T} \frac{h_{LV}}{v_V - v_L} \ , \tag{17.47}$$

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[3] Note that $g' = g''$ implies $h'' - h' = T\left(s'' - s'\right)$.

with the heat of evaporation $h_{LV} = h_V - h_L$. To proceed, we assume that the specific volume of the vapor phase (V) is far larger than the volume of the liquid phase (L), so that $v_V - v_L \simeq v_V$. Moreover, we assume that the vapor can be described by the ideal gas law, so that $v_V = RT/p$. Both assumptions are reasonably accurate at pressures not too far from the triple point. The equation then reduces to the Clausius-Clapeyron equation

$$\frac{1}{p_{\text{sat}}} \frac{dp_{sat}}{dT} = \frac{h_{LV}}{RT^2} \,,$$

which can be integrated with the further assumption that the heat of evaporation h_{LV} is constant, to give

$$\ln \frac{p_{\text{sat}}(T_2)}{p_{\text{sat}}(T_1)} = \frac{h_{LV}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \,. \tag{17.48}$$

We use this equation to estimate the heat of evaporation at 7.5 °C from measurements of saturation pressures and volumes. From steam tables we find the following data:

$$\begin{aligned} T_1 &= 278.15\,\text{K} \,, \;\; p_{\text{sat}}(T_1) = 0.8721\,\text{kPa} \,, \;\; v_V(T_1) = 147.12 \tfrac{\text{m}^3}{\text{kg}} \,, \\ T_2 &= 283.15\,\text{K} \,, \;\; p_{\text{sat}}(T_2) = 1.2276\,\text{kPa} \,, \;\; v_V(T_2) = 106.38 \tfrac{\text{m}^3}{\text{kg}} \,. \end{aligned}$$

With $R = 0.462 \frac{\text{kJ}}{\text{kg K}}$ we find $h_{LV}(7.5\,°\text{C}) = 2488.18 \frac{\text{kJ}}{\text{kg}}$, which is reasonably close to the exact value of $2515 \frac{\text{kJ}}{\text{kg}}$.

17.12 Example: Ice Skating

Another interesting application is the discussion of ice flows and ice skating. We consider the solid-liquid equilibrium at temperatures not too far from $0\,°\text{C} = 273.15\,\text{K}$, where $h_{SL} = 333.7 \frac{\text{kJ}}{\text{kg}}$, $v_L = 0.001 \frac{\text{m}^3}{\text{kg}}$ and $v_S = 0.001085 \frac{\text{m}^3}{\text{kg}}$. Since the solid, i.e., the ice, has a larger volume than the liquid, the melting curve has a negative slope,

$$\frac{dp_{\text{sat}}}{dT} = \frac{1}{T} \frac{h_{SL}}{v_L - v_S} = -142 \frac{\text{bar}}{\text{K}} \,. \tag{17.49}$$

Due to the density anomaly of water, ice swims on water. Would this not be so, ponds and lakes would freeze completely in cold climates (ice would form on the top, and sink), and no life could survive. Thus, the anomaly is of some importance to our ecosystem. Note also that, considering its low molar mass, water condenses at rather high temperatures (100 °C at $p = 1\,\text{atm}$; compare to saturation temperature of oxygen (O_2) of $-218.8\,°\text{C}$); this is due to the strong attractive intermolecular forces between water molecules (hydrogen bonds).

Coming back to (17.49), we conclude that in order to lower the melting temperature by 1 °C, the pressure must be increased by 142 bar. In other words, to melt ice of −10 °C the pressure must be increased by 1420 bar. Due to the weight of the ice, the pressure inside glaciers is quite high, and the slow flow of glaciers might be attributed to this effect, but also to plastic deformation.

Quite often, however, melting under pressure is used to explain the physics of ice skating, but this is not a valid explanation. Indeed, high pressures would break the ice before it could melt. The contact area for the skates would have to be very small, to bring these high pressures on the ice. As most people know, ice is very slippery even with street shoes, which have a large contact area. Also one would expect a strong dependence of the skating ability on temperature, since higher pressures are required for melting at lower temperatures. Moreover, since no liquid water exist below −23 °C, skating would not be possible at temperatures below that. Canadian students report that they skated without problems at temperatures below −30 °C.

Today, it is believed that the slipperiness of ice is due to a molecular layer of water molecules at the surface which are not fixated in the lattice structure of the ice. There seems to be no stable configuration with an energetic minimum for the surface molecules, and they dangle about. This molecular layer behaves almost like liquid water, and thus ice is slippery.[4]

Problems

17.1. Barometric Formula
Atmospheric air can be considered as an ideal gas with $R = 0.287 \frac{\mathrm{kJ}}{\mathrm{kg\,K}}$.

1. Balance the forces on a layer of the atmosphere of thickness dz to show that $\frac{dp}{dz} = -\rho g$.
2. Consider an isothermal atmosphere and compute $p(z)$ with $p(z = 0) = p_0 = 1 bar$.
3. In reality, the temperature of the atmosphere is decreasing with height according to

$$T(z) = T_0 \left(1 - \frac{\gamma z}{T_0}\right) \quad \text{where} \quad \gamma = \frac{0.65\,\mathrm{K}}{100\,\mathrm{m}}\,,\ T_0 = 288\,\mathrm{K}\,,$$

   (valid for $0 \leq z \leq 10,000\,\mathrm{m}$). Compute $p(z)$ for this case (again with $p(z = 0) = p_0$).
4. In your last result, consider the limit $\gamma \longrightarrow 0$ and show that you obtain the same result as in ii.).

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[4] See: S.C. Colbeck, Pressure melting and ice skating, Am. J. Phys. **63**, 888-890 (1995). Wettlaufer & Dash, Melting Below Zero, Scientific American Magazine, February 2000.

5. Plot the two curves, and discuss—what pressures are predicted for Mt. Baker, Mt. Everest?

17.2. Three-Phase Equilibrium

Consider a phase mixture of solid, liquid and vapor in equilibrium, in a closed system at constant pressure and temperature. Minimize the Gibbs free energy to find the equilibrium condition (17.40).

17.3. Solid Carbon

Pure carbon in solid form can appear in different crystal lattices, as graphite ($\bar{h}_f^0 = 0\frac{\mathrm{kJ}}{\mathrm{mol}}$, $\bar{s}_f^0 = 5.75\frac{\mathrm{kJ}}{\mathrm{kmol\,K}}$) or as diamond ($\bar{h}_f^0 = 1.89\frac{\mathrm{kJ}}{\mathrm{mol}}$, $\bar{s}_f^0 = 2.38\frac{\mathrm{kJ}}{\mathrm{kmol\,K}}$). Here, $\bar{h}_f^0$, $\bar{s}_f^0$ denote enthalpy and entropy of formation, that is the values of enthalpy and entropy at standard conditions ($T_0 = 298\,\mathrm{K}$, $p_0 = 1\,\mathrm{atm}$).

1. Experience shows that both forms exist at standard conditions, but thermodynamically only one is stable—is it graphite or diamond? State your argument.
2. The mass density of graphite is $2.25\frac{\mathrm{kg}}{\mathrm{litre}}$ and that of diamond is $3.52\frac{\mathrm{kg}}{\mathrm{litre}}$. When the pressure is increased to $1.6 \times 10^4\,\mathrm{bar}$, is your answer to the previous question the same? Explain.
3. At which pressure are graphite and diamond in equilibrium (at T_0)?

17.4. Stirred Water

A rigid adiabatic container contains 1 litre of water at 20 °C. The water was briefly stirred with a propeller, so that the average velocity is $15\frac{\mathrm{m}}{\mathrm{s}}$. Consider only the time after stirring (but not the water motion) has stopped. Under the conditions of this process, water can be described as an ideal incompressible liquid $\left(v = v_0 = 0.001\frac{\mathrm{m}^3}{\mathrm{kg}}\right)$ with constant specific heat $c_p = c_w = 4.18\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$.

1. Show that incompressibility implies $c_p = c_v = c_w$.
2. Combine the 1st and 2nd law of thermodynamics to show that, while the water still moves after stirring stops, it comes to rest over time, and the rest state is the equilibrium state, that is the kinetic energy will go to zero. Hint: Use the Gibbs equation, and account for adiabatic process and incompressibility.
3. Determine the increase of temperature between the stirred state and the final rest state when the system is adiabatic.

17.5. Approximate Equation for Saturation Pressure

In order to find an approximate equation for the saturation pressure of a substance, assume that the liquid can be considered as an incompressible liquid, and the vapor as an ideal gas.

1. For the liquid (f) show first that incompressibility implies that the specific heats at constant pressure and constant volume are the same. Next, assume

constant specific heat c_f and incompressibility and find internal energy, enthalpy and entropy by integration. Show that

$$u_f = c_f\left(T - T_0\right) \quad , \quad h_f = c_f\left(T - T_0\right) \quad , \quad s_f = c_f \ln \frac{T}{T_0} \ .$$

The assumption of incompressibility is not sufficient to obtain the relation for h_f. What contribution is missing, and why (or when) can it be ignored?

2. Consider vapor (g) as an ideal gas with constant specific heats, and show that specific enthalpy and entropy are given by

$$h_g = c_p\left(T - T_0\right) + h_{fg}\left(T_0\right) \quad , \quad s_g = c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_{\text{sat}}\left(T_0\right)} + \frac{h_{fg}\left(T_0\right)}{T_0} \ ;$$

   c_p is the specific heat of the vapor, $h_{fg}\left(T_0\right)$ is the specific heat of evaporation at reference temperature T_0, and $p_{\text{sat}}\left(T_0\right)$ is the saturation pressure at T_0. Discuss the choice of integrating constants and give clear arguments why $h_{fg}\left(T_0\right)$ appears in both relations.
3. Find an expression for the heat of evaporation $h_{fg}\left(T\right)$.
4. Use the condition for phase equilibrium $g_f\left(T, p_{\text{sat}}\left(T\right)\right) = g_g\left(T, p_{\text{sat}}\left(T\right)\right)$ to find an equation for the saturation pressure $p_{\text{sat}}\left(T\right)$.
5. Use data for water and chose $T_0 = 273.15\,\text{K}$ to make a table with values of saturation pressure and heat of evaporation for several temperatures. Compare to tabled data: When an error of 5% is acceptable, what is the maximum temperature for which the approximation can be used?
6. An equation that is regularly used, and gives a better fit, is the Antoine equation

$$\log p_{\text{sat}}\left(T\right) = A - \frac{B}{C + T} \ .$$

   Use data for water at 0.01 °C, 50 °C, and 100 °C to obtain the constants A, B, C. You may use a computer program to find the constants. Plot the saturation pressure as function of T, and make a list of values for temperatures up to the critical temperature 374.14 °C. Compare with tabulated data.

17.6. Heat of Evaporation

Use the Clausius-Clapeyron equation together with the Antoine equation for water (see previous problem) to find a relation for the heat of vaporization, $h_{fg}\left(T\right)$. Assume that the liquid volume can be ignored against the vapor volume, and that the vapor can be described as an ideal gas. Plot $h_{fg}\left(T\right)$ over T, and compare with tabulated data. Discuss the result.

17.7. Property Data: Interpolation

For a thermodynamic computation you need the Gibbs free energy, the entropy, and the enthalpy of liquid water at a temperature of 97.5 °C and a pressure of 1 atm. In an old and incomplete table you find the following data:

compressed liquid:

$$g(95\,^\circ\mathrm{C}, 1\,\mathrm{atm}) = -62\frac{\mathrm{kJ}}{\mathrm{kg}}\ ,$$

saturated vapor:

$$g_g(100\,^\circ\mathrm{C}) = -68.5\frac{\mathrm{kJ}}{\mathrm{kg}}\ ,\ \ p_{sat}(100\,^\circ\mathrm{C}) = 1\,\mathrm{atm}\ .$$

Use only this data to determine (a) $g(97.5\,^\circ\mathrm{C}, 1\,\mathrm{atm})$, (b) $s(97.5\,^\circ\mathrm{C}, 1\,\mathrm{atm})$ and (c) $h(97.5\,^\circ\mathrm{C}, 1\,\mathrm{atm})$.

17.8. Phase Equilibrium of a Van der Waals Gas
Use Maxwell's equal area rule to construct the two phase region for the dimensionless van der Waals equation. For given temperature τ you need to determine saturation pressure $\pi_{sat}(\tau)$ and saturation volumes $\upsilon_f(\tau)$ and $\upsilon_g(\tau)$. It is best to prescribe a value for υ_f and then find the corresponding values for τ, π_{sat}, and υ_g.

1. Write down the equations you need to solve the problem.
2. The equations are transcendental and thus must be solved numerically. Use one of the convenient mathematics programs like Mathematica, Maple, Matlab, etc. to solve the problem.
3. Plot the two-phase region and some isothermal curves in a p-v-diagram.
4. Plot the saturation curve in the p-T-diagram.

17.9. Homogeneity
Solve problems 4.15 and 4.16.