



THERMODYNAMICS OF PHASE CHANGE

| | |
|-----------------------------------------------------------|----|
| Phase changes | 1 |
| Phase rule | 2 |
| Clapeyron equation | 2 |
| Discontinuities in the phase change. Vapour fraction..... | 5 |
| Closed system evolutions..... | 7 |
| Open system evolutions | 8 |
| Metastable states | 9 |
| Vaporization kinetics | 11 |
| Exergy | 13 |
| Type of problems | 14 |

PHASE CHANGES

We said in [Chapter 4: Thermodynamic Potentials and Properties](#), that when a system reaches an unstable state it splits itself into different phases with different properties but in equilibrium with each other. [Chapter 5: Control Volume](#), was just a halt to change our view-point and see how the balance equations change when we let mass flows through the frontier of our system. Now we proceed with the thermodynamics of simple compressible system, and we analyse phase changes in a pure chemical substance, as already introduced in Chapter 4.

Only phase changes in pure small-molecule substances are considered (i.e. usual gases, water and other simple inorganic liquids, small-chain hydrocarbons, metals and other inorganic solids), but not glasses, polymers and composites. It is interesting, however, to look at how, for instance, honey (or milk, oil, wax) boils and solidifies, or at how wax melts (or paper, wood, teflon, concrete, and so on). Furthermore, we focus on the liquid/vapour phase change, covering other phase changes occasionally; solid/solid allotropic transformations are not mentioned at all. Glasses are substances (inorganic as silicates or organic as plastics) that solidify from a molten state into an amorphous solid (i.e. without crystalline order); see [Thermal effects on materials](#). Phase changes in mixtures are also covered in [Chapter 7: Mixtures](#) and [Solutions](#).

It is also important to mention that although we only deal here with phase changes of aggregation in a pure substance (the first phase transitions discovered), other thermodynamic phase changes occur in Nature, as the change from normal electrical conductivity to superconductivity (with or without magnetic field), the change from paramagnetism to ferromagnetism, the change from normal viscosity to superfluidity in ^4He , etc. The second phase transition discovered was the ferromagnetic-paramagnetic transition at high temperature, when J. Hopkinson described in 1890 the disappearance of magnetism in hot iron. Later on, electrical superconductivity was discovered in 1911 by Kamerlingh Onnes, in mercury.

We only deal with phase changes at equilibrium conditions, and do not consider the kinetics of the change, dominated by mass diffusion and [nucleation](#) processes.

Besides, it must be mentioned that there is a whole field in Thermodynamics, not covered here, that deals with the critical region, i.e. the neighbourhood of critical points. The existence of a critical temperature above which a gas cannot be condensed by increasing pressure was first pointed out in 1822 by Cagniard de la Tour, studied in detail by D. Mendel ev in 1860, and fully described by T. Andrews in 1869 in terms of the isothermal behaviour with pressure of carbon dioxide, at several temperatures; three years later, van der Waals proposed the first embracing theory for phase transition, with his famous state equation modelling both the gas and the liquid states.

PHASE RULE

The condition of equilibrium for a pure substance introduced three intensive variables ([Chapter 2: Entropy](#)): T , p and μ (the chemical potential of the substance), but they were not all independent since the Gibbs-Duhem equation, $0 = s dT - v dp + d\mu$, correlates them, thus a simple thermodynamic system has only two independent intensive variables. When there are several phases, the same equilibrium variables hold (T , p and μ), but now there is a Gibbs-Duhem equation for each of the phases, since each one has different s and v . Thus, the variance (intensive degrees of freedom) of a single phase is 2 (e.g. T and p), that of a two-phase system is 1 (only T or p), and that of a three-phase is 0 (it is a constant state without any possible variation of T or p), not being possible a four-phase system (for a pure substance). The variance of a system, or Gibbs phase rule, was analysed in more detail in [Chapter 2: Entropy](#).

CLAPEYRON EQUATION

Clapeyron equation gives the relation between T and p in a two-phase pure-substance system. It is deduced by just subtracting the two Gibbs-Duhem equations for the two phases at equilibrium. Using the notation for the liquid-to-vapour phase change, the most important in Thermodynamics, one gets:

$$\left. \begin{aligned} 0 &= s_V dT - v_V dp + d\mu \\ 0 &= s_L dT - v_L dp + d\mu \end{aligned} \right\} 0 = (s_V - s_L) dT - (v_V - v_L) dp \Rightarrow \left. \frac{dp}{dT} \right|_{sat} = \frac{h_V - h_L}{T(v_V - v_L)} = \frac{h_{LV}}{T v_{LV}} \quad (6.1)$$

after Δs has been substituted by $\Delta h/T$ based on the general relation (4.2), $dh = T ds + v dp$, and the fact that both equilibrium states (liquid and vapour) have the same pressure. The enthalpy change in a phase change, e.g. $h_{LV} = h_V - h_L$ for vaporisation, was initially named 'latent heat' by J. Black; [a list of values for melting and boiling is given aside](#). Notice that subindex 'sat', meaning 'saturated' or better 'in saturation', is used as a synonym of biphasic equilibrium, and that the loci of liquid-vapour equilibrium states is known as vapour pressure curve, being bounded by the triple point and the critical point.

Equation (6.1) is the general Clapeyron equation and to go any further we need to have a model for the substance. An integrated Clapeyron equation is obtained if one makes the following three simplifications: $v_L \ll v_V$, $v_V = RT/p$ and $h_{LV} = \text{constant}$, what yields:

$$\left. \frac{dp}{dT} \right|_{sat} = \frac{h_V - h_L}{T(v_V - v_L)} \xrightarrow{v_V \gg v_L, v_V = RT/p, h_{LV} = \text{const}} \ln\left(\frac{p}{p_0}\right) = \frac{-h_{LV}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (6.2)$$

which may be used if one saturated point is known (T_0, p_0 ; e.g. the normal boiling point, T_b , at $p_0 = 100$ kPa) to compute some neighbouring saturated state, far from the critical region.

Clapeyron equation (6.2) is often known as Clausius-Clapeyron equation; Émile Clapeyron, a co-worker of Carnot, proposed it around 1834 to find the variation of vaporisation enthalpy with temperature, and Rudolph Clausius reformulated it in the 1850s. The name 'Clapeyron equation' is sometimes ascribed to the ideal gas law $pV=mRT$. The p - V diagram is occasionally named Clapeyron diagram.

Based on the functional dependence of vapour pressure with temperature given by (6.2), and trying a best fit to experimental data, Charles Antoine proposed in 1888 (“Tensions des vapeurs; nouvelle relation entre les tensions et les températures”, C.R. 107, 681-684, 778-780, 836-837; 1888), an empirical fit that is used the most:

$$\ln\left(\frac{p}{p_0}\right) = A - \frac{B}{\frac{T}{T_0} + C}, \text{ with } A, B \text{ and } C \text{ tabulated usually for } T_0=1 \text{ K and } p_0=1 \text{ kPa} \quad (6.3)$$

A table with these 3 constants for usual pure substances is presented in [Thermal data tables](#).

Finally, it is worth rewriting the general Clapeyron equation in term of reduced variables (dividing T - p values with those at the critical point), obtaining:

$$\left.\frac{dp}{dT}\right|_{sat} = \frac{h_V - h_L}{T(v_V - v_L)} \Rightarrow \frac{d \ln p_R}{d \frac{1}{T_R}} = \frac{h_V - h_L}{RT_{CR}(Z_V - Z_L)} \approx 6 \text{ for many substances} \quad (6.4)$$

It is amazing that for many substances the slope of the vapour pressure curve in the $\ln p_R$ - $1/T_R$ diagram is almost constant from the triple point to the critical point. The integrated Clapeyron equation (6.2) has a constant $\ln p_R$ - $1/T_R$ slope, but that is only valid locally and far from the critical point. What happens is that the enthalpy of vaporisation (the numerator in (6.4)) varies with temperature as the difference in compressibility factor does, and both effects compensate. This fact, $d \ln p_R / d(1/T_R) \approx 6$ for most substances, is often known as Guggenheim's rule, that can be somehow tailored to a particular substance by using the [Pitzer's acentric factor](#), ω , introduced in [Chapter 4](#) and using $\ln p_R = 5.4(1 + \omega)(1 - 1/T_R)$ instead of (6.4). There are some other similar generic approximation rules worth mention. Guldberg's rule points out that the ratio of boiling to critical temperatures for most substances is around $T_b/T_{CR} \approx 0.6$. Trouton's rule points out that $h_{lv}/(RT_b) \approx 10$, which can be deduced from the two precedent rules. Watson rule establishes a generic approximation to the variation of vaporisation enthalpy with temperature, $h_{lv}/h_{lv,b} \approx [(1 - T_R)/(1 - T_b/T_{CR})]^{0.38} \approx [2.5(1 - T_R)]^{0.38}$.

[Exercise 1. Vapour pressure curve](#)

Clapeyron equations may also be applied to the solid-vapour phase change (sublimation) by changing the values of the variables accordingly. Substances with sublimation points are not common, the best known being carbon dioxide (CO_2 , with $T_{\text{subl}}=195 \text{ K}$), called dry ice, and less known acetylene (C_2H_2 , with $T_{\text{subl}}=189 \text{ K}$), sulfur hexafluoride (SF_6 , with $T_{\text{subl}}=209 \text{ K}$), uranium hexafluoride (UF_6 , with $T_{\text{subl}}=329 \text{ K}$),

arsenic (As, with $T_{\text{subl}}=887$ K), carbon (C, graphite, $T_{\text{subl}}=3910$ K), and some mercury compounds. Notice, however, that the strict meaning of sublimation-point used here, i.e. the solid-to-vapour phase-change of a pure substance with its triple-point pressure below normal pressure, $p_0=100$ kPa, is rarely followed not only in common language but in scientific literature, where sublimation is synonymous of evaporation from a solid, usually in the presence of ambient air, and thus, one talks about sublimation of iodine, I_2 , having a normal boiling point at $T_b=387$ K, sublimation of naphthalene, $C_{10}H_8$, having a normal boiling point at $T_b=491$ K, etc. Evaporation of solids in air is a general rule, forced by the gradient of chemical-potential and thus proportional to its vapour pressure, but their vapour pressure at normal temperatures is very low and, although all solids sublime, their sublimation is usually neglected except in the examples given. Water ice sublimates too, below freezing temperatures, as in a freezer. Dry ice is a strong freezing agent (easier to handle than cryogenic liquids), and is used to shrink shafts to be permanently mounted on their holes, to make ice plugs to repair water piping or LPG bottles without emptying them, etc.

For the solid-liquid phase change, the slope of the equilibrium curve in the p - T diagram is so high that it is usually assumed that the temperature of fusion is the same at every pressure (this is used to approximate the triple point by the normal melting-point temperature and its corresponding vapour pressure). However, it can be seen from the Clapeyron equation (6.1) that the normal slope is positive because h_L-h_S is always positive and v_L-v_S is usually positive (substances contract on freezing), although the slope is negative for substances that expand on freezing, as water, silicon, germanium, gallium, bismuth, mercury, and others; in the case of pure water, it takes 13.4 MPa to freeze at -1 °C (the minimum equilibrium freezing temperature is -22 °C, at 210 MPa, but lower liquid temperatures can be obtained even at normal pressure under metastable conditions). By the way, the high pressure under an ice-skate blade is far too short to melt the ice (held at $-7..-2$ °C); the lubrication is due to a microscopic liquid layer at equilibrium on the ice surface ($10^{-10}..10^{-7}$ m thick, depending on temperature and composition), greatly enhanced by the local fusion caused by friction.

Phases and phase changes for a pure substance are named as in Fig. 6.1, jointly with a three-dimensional view of equilibrium states, or p - v - T diagram; i.e. the traditional solid, liquid and gas phases, and the phase change from one to other. Allotropic changes, in the solid state, are not considered. The supercritical region is sometimes limited to $T>T_{CP}$ and $p>p_{CP}$. The name ‘vapour’ is sometimes restricted to the gas phase in contact with its liquid phase (e.g. butane is said to be a gas out of the bottle, but a liquid-vapour mixture inside the bottle).

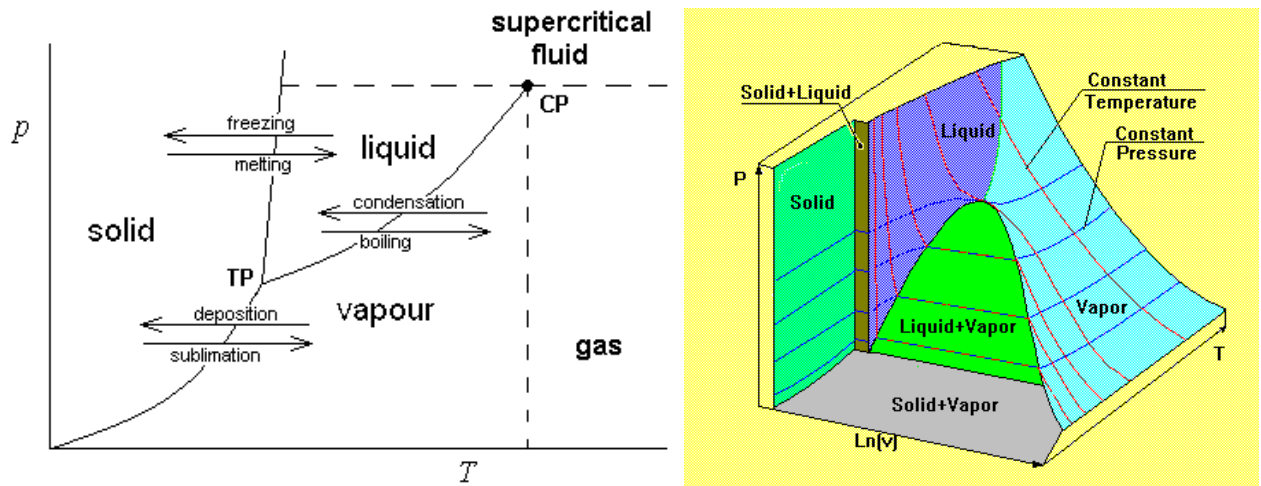


Fig. 6.1. Nomenclature for phases and phase changes for a pure substance, and p - v - T diagram.

The phase change from vapour or gas to liquid is sometimes, particularly in cryogenics, named liquefaction. The first liquefaction of a gas was made in 1780 by G. Monge (a teacher of S. Carnot), by passing compressed SO_2 through a coil tube immersed in a salt-ice mixture.

DISCONTINUITIES IN THE PHASE CHANGE. VAPOUR FRACTION

In a thermal analysis, when thermodynamic variables are plotted versus temperature at constant pressure, some of them change slope at the phase change (e.g. the Gibbs potential), others suffer a discontinuity in their values (e.g. the intensive volume, being a first derivative of the Gibbs potential), and finally others become ill-defined (e.g. the thermal expansion coefficient, being a second derivative of the Gibbs potential).

The state of equilibrium is just defined by one variable, T or p , but in order to fully define the physical state one needs to know the relative proportions of the phases. Any of the additive variables that have a discontinuity serves this purpose if its averaged value is given. The traditional way to measure the proportions is the vapour mass fraction, x , also known as vapour title or vapour quality:

$$x \equiv \frac{m_V}{m_V + m_L} \quad (6.5)$$

Some care is needed with this variable since the x 's are used for molar fractions (not mass fractions) in all but this Chapter. Besides, it only refers to one of the phases, the mass fraction of the liquid phase being $1-x$. Notice that, as a mass fraction, x is only defined in the interval $[0,1]$, although it can be extended to negative and greater-than-unity values if defined by $x \equiv (h - h_{L\text{sat}})/h_{LV}$, negative values measuring the degree of subcooling and greater-than-unity values measuring the degree of superheating.

Any specific variable (i.e. extensive variable by unit of mass) for the whole two-phase system is defined like for the enthalpy:

$$h \equiv \frac{H}{m} = \frac{m_V h_V + m_L h_L}{m_V + m_L} = x h_V + (1-x) h_L = h_L + x h_{LV} \quad (6.6)$$

i.e. the same applies for s , u , v , g , ϕ , etc. Concerning the values of functions in the liquid phase and on the vapour phase (e.g. h_L and h_V) it is imperative to be aware that only one reference state can be chosen for all Thermodynamics of phase change

of them. Thus, if one applies the perfect liquid model to the liquid and the perfect gas model to the vapour, one may write $h_L - h_{L0} = c_L(T - T_0) + (p - p_0)/\rho_L$ and $h_V - h_{V0} = c_p(T - T_0)$, but both h_{L0} and h_{V0} cannot be chosen as zero because $h_{V0} - h_{L0} = h_{LV0}$. The reference state is a free choice to the user; a liquid-state reference is preferable to work with positive numbers most of the time, but several different temperatures are still in use. We advocate for $h=0$ and $s=0$ at the liquid state at the triple point, although there are other choices in the literature, like setting $h=0$ and $s=0$ at the liquid state at the normal boiling point, or ASHRAE setting $h=0$ and $s=0$ for saturated liquid at $T=-40$ °C ($=-40$ °F); mind that IIR reference setting is not zero but $h=200$ kJ/kg and $s=1$ kJ/(kg·K) for saturated liquid at $T=0$ °C.

Notice that the thermal capacity of a biphasic single-component system is infinite since $c_p = \partial h / \partial T|_p$ and at $p = \text{constant}$ the system increases h with $dT=0$. The sound speed in a liquid-vapour mixture is much smaller than those of the pure phases, particularly for small vapour fractions, as can be explained from Eq. (4.14), $c = 1/(\rho\kappa_s)^{1/2}$, because mixture density, ρ , approaches liquid density, whereas mixture compressibility, κ_s , approaches that of the gas. And the same occurs in multicomponent liquid-gas mixtures.

Once a reference is taken, e.g. the liquid state at the triple point; the value for a vapour state may be composed in the three different manners sketched in Fig. 6.2, that with the perfect-substance models give, for the enthalpy: 1) $h_V - h_0 = h_{LV0} + c_p(T - T_0)$, 2) $h_V - h_0 = c_L(T_1 - T_0) + h_{LV1} + c_p(T - T_1)$ and 3) $h_V - h_0 = c_L(T - T_0) + h_{LV}$. Any path should give the same result (under the accuracy of the model) since they are state functions, but the first is shorter if the vaporisation enthalpy at the triple point is known (e.g. $h_{LV0} = 2.50$ MJ/kg for water) and the second only needs the vaporisation enthalpy at the boiling point that is ready available (e.g. $h_{LV0} = 2.26$ MJ/kg for water).

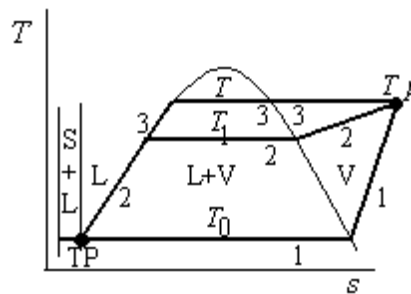


Fig. 6.2. Usual reference state for energies and entropies (liquid state at the triple point, TP), and the three possible paths to compute a vapour-region value from that reference point.

Notice also that mean variables do not measure any local state but the weighted average according to the mass proportions of the phases, as seen in (6.6). When two-phase states of a system are represented in a thermodynamic diagram, the point corresponding to those mean variables should be interpreted as auxiliary points that show the proportion of the two phases, whose properties, constant along an isobar (or isotherm), are those at the extremes of the isobar, as shown in Fig. 6.3. The linear application between an specific variable like h in (6.6) and x is known as the lever rule (i.e. the amount of each phase is proportional to the distance to the other extreme).

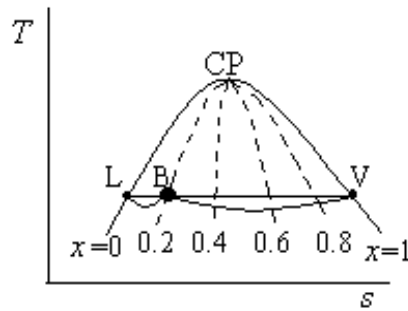


Fig. 6.3. A biphasic state B corresponds to the averaged properties (in this case specific entropy) of the coexisting phases: liquid, L, and vapour, V.

The two bounds to the two-phase region, are known as the saturated liquid curve ($x=0$) and the saturated vapour curve ($x=1$). Mixed states inside the two-phase region, below the $x=1$ curve, are known sometimes as wet vapour states, and those beyond $x=1$ superheated vapour states.

The vaporisation enthalpy monotonically decreases from the triple point to the critical point where it cancels, what can easily be appreciated in a $p-h$ diagram on the width of the two-phase region (e.g. for water, $h_{LV}=2500$ kJ/kg at 273 K, $h_{LV}=2260$ kJ/kg at 373 K and $h_{LV}=0$ at 647 K).

Phase change problems occur in many natural and artificial processes: the hydrological cycle, casting, welding, soldering, boilers, freezers, cooling towers, etc.

[Exercise 2. Butane bottle](#)

Closed system evolutions

As a closed system, i.e. keeping invariant the total mass, a two-phase system may be processed at constant volume (by heating or cooling), at constant pressure (and thus temperature; e.g. heating or cooling it in a cylinder-piston arrangement), adiabatically (by a quick compression or expansion), or in any more general way.

Notice that heating a liquid inside a fully-filled rigid container does not give way to a boiling process (except in the rare case of a thermal expansion anomaly); it just increases the pressure up to the mechanical or thermal structural limit of the container, without change of phase; similar to when heating a gas at constant volume. Cooling at constant volume eventually gives way to a liquid/vapour transition in a fully-filled liquid container, and to a vapour/liquid transition in a gas container.

At constant mass and volume, a two-phase system increase or decrease its temperature and pressure when heated or cooled, respectively, but it is not so evident what happens to the liquid level, since on heating, for instance, the liquid expands and the level rises at the same time that some liquid is vaporised (to increase the pressure) and the level falls; which effect is preponderant depends on the value of the thermal expansion coefficient.

[Exercise 3. Level change with temperature](#)

When a two-phase system is suddenly expanded, the liquid phase starts immediately to boil-off, and the vapour phase usually condenses a little (heavy-molecule substances may expand along the gas phase), both immediately reaching the equilibrium temperature at the new pressure, so that, neglecting the entropy of dispersion of one phase in the other as is always done, the process may be considered isentropic. However, when a two-phase system is suddenly compressed, the liquid phase immediately adapts to the new pressure without any temperature variation, whereas the vapour phase gets compressed adiabatically with a large temperature increase, so that afterwards there is an entropy increase by heat exchange between both phases.

The phase change from a condensed phase to a gas can explode a closed container. This is easy to understand for cryogenic fluids (e.g. liquid nitrogen, or dry ice); the unavoidable heat flow from the warmer ambient transforms the condensed mass into a gas, dramatically increasing the internal pressure (that is why cryogenic containers should always be open to the atmosphere, releasing the [boil-off](#) gas). The same occurs in tanks with normal liquids (e.g. water) kept at temperatures higher than their boiling point at ambient pressure (e.g. if a tank with liquid water at 200 ° C, at >1.5 MPa, burst, a sudden boiling in the whole liquid mass occurs, generating an expanding shock wave of steam). This type of process is known as [BLEVE](#) (Boiling Liquid Expanding Vapour Explosion), and it is particularly harmful if the substance is flammable).

Open system evolutions

The most frequent control volume systems operate in a one-inlet one-exit steady configuration; two-phase systems may be biphasic at the entrance, at the exit or at both sides. Typical problems are the throttling of a saturated liquid, the expansion of a vapour in a turbine, the mixing of some liquid and vapour streams of the same substance, etc.

[Exercise 4. Peabody throttling](#)

In a flash chamber, non-saturated liquid is throttled into a chamber kept at lower pressure by an ejector or vacuum pump. A portion of the liquid flashes into vapour that, in the gravity field, settles upwards (a demister may help to avoid drops carry over), and can be extracted separately (flash separators) or locally condensed on cold coils and the drops collected on a plate and extracted with a liquid pump (flash distillators). The latter is used a lot to purify the solvent in a liquid mixture, as for desalting seawater (liquid seawater enters a flash chamber, and two other liquid streams are extracted: brine and distillate).

Some unsteady control volumes are also of interest to phase-change processes, as when mass (liquid or vapour) is added or extracted from a two-phase reservoir, or when steam is used to heat up some water mass (a typical example being milk steaming in coffee machines).

Two-phase bottled compressed gases are routinely used as a source of gas (e.g. camping gas), or as a source of liquid spray (e.g. insecticides). A quasi-steady process develops when a small constant mass flow rate of vapour goes out of a two-phase bottle; its energy balance is $d(m_{LE}L + m_{VE}V)/dt = \dot{Q} - \dot{m} h_V$, and, using the perfect substance models one finally gets a relation between the necessary heat input and the mass flow rate:

$$\dot{Q} = \dot{m} h_{LV} \left(1 + \frac{v_L}{v_{LV}} \right) \approx \dot{m} h_{LV} \quad (6.7)$$

The temperature (and consequently the pressure) in the interior decreases (due to the vaporisation energy) until at steady state this heat flux is furnished by heat transfer from the environment across the wall of the bottle, at the same rate.

Exercise 5. Butane supply from a bottle

When vapour is let out of a two-phase vessel, it is usually throttled (without doing work) to the supply pressure, always in the gas phase and with negligible temperature change. If the vapour were expanded doing external work, as in a turbine, it might get fogged (enter the two-phase region again). However, in the case of the liquid phase being let out of a vessel (through a valve in the bottom), the liquid will get bubbly even if just throttled, decreasing its temperature according to the decrease in pressure, what may be used for refrigeration.

Exercise 6. Self-refrigeration in a propane vessel

METASTABLE STATES

Metastable states are non-equilibrium states that appear stable under some circumstances, because the ambient noise has not enough energy or time to force a transition, but that under a sizeable perturbation, they evolve to a widely different equilibrium state (e.g. think on the effect of a <1 mJ spark on a H₂/O₂ mixture, or the trigger in a hot or cold pad).

In order to trigger the phase change, some jump in chemical potential must be applied, like the activation energy in combustion processes. To be more precise, consider phase changes from the liquid state at constant pressure. Liquids may be superheated above their boiling point without changing to vapour (as often happens in microwave ovens), and undercooled below their freezing temperature (as easily done with distilled water in a test tube). Notice that we are using the words undercooling, subcooling, and supercooling, as synonyms.

Vapours may also be undercooled below their condensation temperature, but solids are very difficult to superheat over their melting temperature. Similarly, at constant temperature, the pressure in a liquid may be decreased below its equilibrium bubbling pressure, even to negative pressures as in tall tree sap (in 1850, Berthelot subjected purified water to 5 MPa of tension), along metastable states, LL' in Fig. 6.4, and vapours compressed above their condensing pressure along metastable states VV' in Fig. 6.4. However, states along L'V' are always mechanically unstable (they would had $\kappa < 0$) and cannot be got in practice. The loci of L' and V' for different isotherms is known as the spinodal curves (spinode, Gr. cusp), liquid spinodal for L' and vapour spinodal for V'.

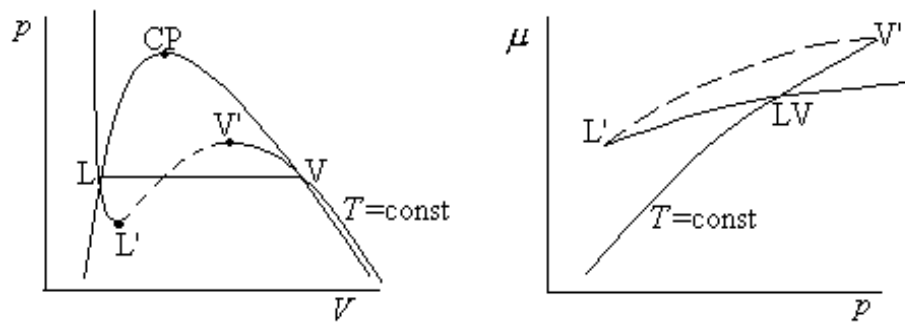


Fig. 6.4. An analytical isotherm $T=\text{const}$. (e.g. a van der Waals one) and the real discontinuities: a jump in the specific volume (straight line LV in the p - v diagram), and a change of slope in specific Gibbs potential (chemical potential, μ). Vapour states from V to V', and liquid states from L to L', called metastable states, can be obtained under controlled conditions of small perturbations in very pure substances.

The μ - p diagram in Fig. 6.4, that may be built from the p - v diagram by means of the Gibbs-Duhem equation, $0 = -s dT + v dp + d\mu$ ($\mu = \mu_0 - \int v dp$ along an isotherm), also gives an indication of the extra energy metastable states need to overpass the barrier of unstable states (dashed line). By the way, it is also seen that, for an analytical isotherm, the points corresponding to the phase change are those of equal chemical potential, those that verify $\int v dp = 0$, or $\int (p - p_{LV}) dv = 0$, i.e. when the two areas between the curve and the straight line in the p - v diagram of Fig. 6.4 are of equal area, what is known as Maxwell's rule.

Quick processes are prone to develop metastable states, as when a vapour expands in a nozzle, where it may go without phase change down to pressures below the transition one and suddenly condense in an abrupt isenthalpic jump (generally associated with the chock wave in the diverging side of a supersonic nozzle. Conversely, metastable states are prone to develop fast processes; consider the difficulty in freezing a pan with water in a fridge (ice starts at the boundaries, and take a lot of time); if, however, the liquid were undercooled to say -5°C (very difficult with tap water, but not so with distilled water, which may be cooled down to -42°C under extreme care), upon a small perturbation, a sudden freezing takes place (with a temperature increase up to 0°C due to the release of the fusion enthalpy); you can compute the amount of ice formed, by an energy balance. Flash vaporization is advantageously used in superheated fuel injectors too.

Metastable states may be classified in terms of the equilibrium line done through, and the direction:

- Through solid-liquid equilibrium line
 - Superheated solid. It is difficult to keep a substance in the solid state when heated over its melting point; that is why melting-point measurements are more accurate than freezing point ones.
 - Subcooled liquid. As said above, it is not difficult to cooled a liquid below its freezing temperature without it changing to the solid state. There is a lot of supercooled water in small droplets on middle and high clouds in the atmosphere (posing a risk to aviation because the metastable liquid droplets freeze on contact with the plane and spoil aerodynamic lift).
- Through liquid-vapour equilibrium line
 - Superheated liquid. As said above, it is not difficult to get superheated liquid water (at $>100^\circ\text{C}$) in a microwave oven, and see it 'explode' by sudden boiling when a tea-bag or sugar is

added. A sudden pressure loss in a liquid container or piping usually yields metastable liquid states too.

- Subcooled vapour. A classical example is the Wilson cloud chamber used for detecting particles of ionizing radiation.
- Through solid-vapour equilibrium line. These changes rarely yield metastable states.

The degree of a metastable state (e.g. degree of superheating, or degree of undercooling) can be measured as the temperature departure from the equilibrium line at constant pressure, or as the pressure departure from the equilibrium line at constant temperature.

Material properties of metastable phases (e.g. density, thermal capacity...) are simple extrapolation of their stable-state properties (e.g. thermal expansion of supercooled water (also named sub-cooled water) is negative with positive slope of $\partial\alpha/\partial T$, with $\alpha=-1.5\cdot 10^{-3}$ 1/K at -30 °C and $\alpha=1.2\cdot 10^{-3}$ 1/K at 150 °C and 100 kPa). However, one must be careful with phase-change relations like $\Delta s=\Delta h/T$, which only hold for equilibrium transitions; for metastables transitions, the transition enthalpy must be supplemented with the difference in thermal capacities from the stable and the metastable phases times the undercooling or overheating.

It seems that the first metastable states were recognised by Fahrenheit in 1714 when studying the freezing of water (he reported different undercooling degrees, depending on the cooling rate). The first theory of metastable states is due to Gibbs (1878).

Creation of a new phase requires a new local arrangement of matter (the nucleation process) which demands some activation energy that builds up on metastable states. Fluid-to-fluid phase-transitions in pure substances are the vaporization of a liquid (boiling) and the condensation of a vapour (e.g. in steam condensers). When a solid phase is involved, the direction of change cause great differences between the melting or vaporization of a solid, in one hand, and the solidification of a liquid or deposition of a vapour, on the other hand, particularly when the nascent solid is in crystalline form instead of amorphous. When mixtures are considered, the phase changes and their nucleation processes become more complicated (e.g. condensation from supersaturated solutions, constitutional supercooling), and new liquid-to-liquid phase changes might appear. The formation of solid phases is studied in the science of crystal growth, so important in materials science and in natural frosting (including the common case in cloud formation).

Vaporization kinetics

The growth of a different phase at the expense of another phase (as the growth of bubbles from a boiling liquid, or the growth of droplets from a condensing vapour), usually takes place at pre-existing nucleation sites (either in the heterogeneities of the container walls, or at the heterogeneities of suspended particles within the fluid), because the nucleation process in a clean fluid within smooth walls is most difficult. In the latter case, named homogeneous nucleation, the nuclei are created by large equilibrium fluctuations, which are proportional to fluid compressibility. Small nuclei, however, are unstable if their size is below a critical radius $r_{cr}=2\sigma/\Delta p$ (σ being the liquid-vapour interface tension, and Δp the underpressure), so that a large fluctuation driven by a high superheating or undercooling is required for homogeneous nucleation.

Consider the vaporization process taking place when a liquid in a reservoir is depressurised below its vapour pressure at the initial temperature; this is the best way to avoid temperature gradients and a quick phase transition (if heating were done, gradients would be proportional to heating speed). In any case, there is a correspondence between superheating and depressurization, $\Delta p/\Delta T=(h_{lv}/(T v_{lv}))$, dictated by Clapeyron's equation. The depressurization process is isenthalpic because it is adiabatic (sudden), and without work exchange with the surroundings. The initial liquid state may be a compressed-liquid state (as in Fig. 1), a saturated liquid (state 's' in the saturated liquid line), or a (metastable) superheated liquid state. The final state may be point 2 in Fig. 6.5 in the normal case of partial vaporization (the two phases may later segregate under gravity), or total vaporization at point 3 for deep-enough depressurizations. The required vaporization enthalpy is obtained from the internal energy of the superheated liquid, leaving a colder two-phase state.

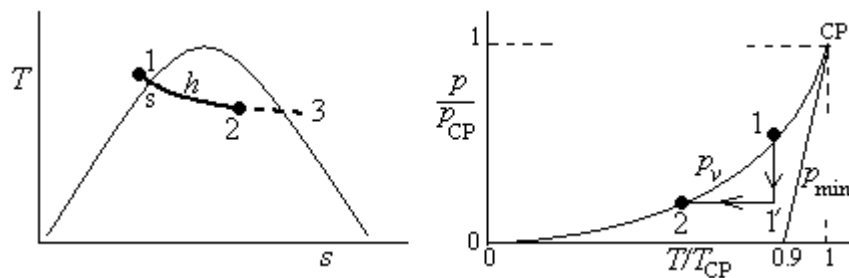


Fig. 6.5. Liquid flashing by sudden depressurization: a) isenthalpic evolution in the $T-s$ diagram; b) metastable evolution in the phase diagram: the liquid at state 1 undergoes a depressurization at constant temperature without phase change (1 to 1'), and then a flash cooling at constant pressure (1' to 2); p_{min} corresponds to spinodal points (L' in Fig. 6.4), marking the depressurization depth required to get homogeneous nucleation.

Many experiments have been carried out with a pressurized liquid in a vertical test tube (from 1 mm to 300 mm in diameter) that is suddenly opened to vacuum (or to ambient pressure, depending on liquid volatility). If the liquid has been degasified, the rarefaction pressure wave reaches the liquid bottom in less than 1 ms, but homogeneous nucleation cannot take place except close to the critical point temperatures (when the spinodal line (p_{min} in Fig. 6.5) would be crossed, and boiling can only start at the free surface (providing the glass wall is clean enough), with a fuzzy bubbling that ejects droplets and produces a two-phase downstream flow. Within about 10 ms, a vaporization front develops and attains a steady propagation downward the liquid, with a speed of order 1 m/s (0.1..10 m/s) depending on the liquid substance and the depressurization (or superheat), but independent of the tube diameter. The upstream liquid remains quiescent and at the initial temperature (except for a cooled boundary layer close to the advancing front), in a metastable equilibrium. The front is more or less planar but clearly unsteady and random in detail, with several millimetres in thickness; the typical droplet size is about 1 mm. The developed two-phase flow consists of vapour as the continuous phase and small liquid droplets as the dispersed phase, 10..100 μm in size, some times in chain-like streaks. Exit pressure is dictated by downstream details (usually a hole with choked flow).

This travelling vaporization wave is very similar to the laminar deflagration wave in premixed combustion, with similar speeds, proportional to the square root of thermal diffusivity in both cases, etc.

The depressurization process just described has been applied to many engineering problems, like the safety analysis of loss of coolant accidents in pressurised water nuclear reactors, and some natural processes like volcano eruptions (when hot lava, under pressure by overlying rock, is released).

EXERGY

Exergy, i.e. the minimum work that must be applied to arrive at a given thermodynamic state from a reference ambient (or the maximum work obtainable from a system not in equilibrium with the environment), was introduced in [Chapter 3: Exergy](#), and extended to open systems in [Chapter 5. Control volume](#) (it is further extended to multicomponent systems in [Chapter 7: Mixtures](#), and to reactive systems in [Chapter 9: Chemical reactions](#). Here, for processes with a phase change of a pure substance, the general exergy balance is:

$$\Delta\Phi = \Delta(E + p_0V - T_0S) = W_u + \sum \left(1 - \frac{T_0}{T_i}\right) Q_i + \int \left(1 - \frac{T_0}{T}\right) dQ - T_0 S_{gen} + \sum_{\text{aberturas}} \int \psi_e \dot{m}_e dt \quad (6.8)$$

where $\Delta(E + p_0V - T_0S)$ is the exergy-change of a given mass (relative to an infinite environment at p_0 and T_0), W_u is the exergy input through the walls as useful work ($W_u = W + p_0\Delta V$), $(1 - T_0/T_i)Q_i$ is the exergy input as heat through the walls from heat sources at T_i (notice the Carnot efficiency, and that for the environment $(1 - T_0/T)dQ < 0$), $-T_0S_{gen} < 0$ too (this term and the preceding one are exergy losses), and finally ψ_e is the specific flow exergy through an opening, $\psi = h - T_0s$.

As an example, imagine we have a liquid-vapour equilibrium of a pure substance with vapour mass-fraction x_1 , at temperature T_1 and pressure p_1 , and that we want to completely vaporise the system at constant pressure, i.e. to get $x_2 = 1$ at $p_2 = p_1$ (notice that thence, for a pure substance, $T_2 = T_1$ too). Find the necessary heat input, and the minimum exergy input, for the two cases: a) a steady-flow process, and b) a control mass process.

For a steady flow process, the energy balance is $\Delta h = q + w$ (neglecting kinetic and potential energy), and the exergy balance (without external heat sources) is $\Delta\psi = \Delta h - T_0\Delta s = 0 - w_u - (1 - T_0/T)q + T_0s_{gen}$. The heat input needed (with $w = 0$) is thence $q = \Delta h = (1 - x_1)h_{LV1}$, whereas the exergy increase, making use of the general equation $dh = Tds + vdp$ and thus $\Delta s = \Delta h/T$, is $\Delta\psi = \Delta h - T_0\Delta s = \Delta h - T_0\Delta h/T_1 = \Delta h(1 - T_0/T_1)$. Notice that this minimum work needed is always smaller than the heat needed in absence of work, both, for $T_0 < T_1$, and for $T_0 > T_1$, and that the exergy input is zero if $T_1 = T_0$ (the free-available heat from the environment may change the vapour fraction at no cost).

For a control mass, i.e. in a cylinder-piston-system at constant pressure, the energy balance is $\Delta U = Q + W$ (neglecting kinetic and potential energy), and the exergy balance (without external heat sources) is $\Delta\Phi = \Delta U + p_0\Delta V - T_0\Delta S$. The heat input needed is thence $Q = \Delta U - W = \Delta U + p_1\Delta V = \Delta H = m(1 - x_1)h_{LV1}$, whereas the exergy increase is $\Delta\Phi = \Delta U + p_0\Delta V - T_0\Delta S = \Delta H - p_1\Delta V + p_0\Delta V - T_0\Delta S$, and making use again of $\Delta S = \Delta H/T_1$, we finally get $\Delta\Phi = \Delta H(1 - T_0/T_1) + (p_0 - p_1)\Delta V$. Notice again that this minimum work needed is always smaller than the heat needed in absence of work, for any combination of $T_0 <> T_1$ and $p_0 <> p_1$.

TYPE OF PROBLEMS

Besides housekeeping problems of how to deduce one particular equation from others, the types of problems in this chapter are:

1. Find the new state and the energy variation when a two-phase reservoir is heated or cooled.
2. Find the mass flow rate escaping from a two-phase reservoir when the heat input is prescribed or viceversa (this is of interest in boilers).
3. Find the new state and when a steady flow of liquid is depressurised.
4. Find the new state and the work output when a steady flow of vapour is expanded and some condensate appears.

[Back to Index](#)