Real gases   Engel & Reid chapter 7

All real gas molecules have some volume and they interact with each other. There is a paradox in ideal gases. We always assume that they are in equilibrium but this is not possible if the molecules do not interact. The ideal gas cannot either describe the liquid phase.

The form of the molecular interaction depends on the molecules involved. Argon atoms interact differently than water molecules. There is no unique equation for real gases.

The mostly used model is the van der Waals equation

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

and another one, the Redlich-Kwong equation

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{\sqrt{T}} \frac{1}{V(V + nb)}$$

the a and b are empirical gas dependent parameters. See Table 7.4. (Appendix A). Note that parameter b is related to the molecules volume.

Virial expansion is another type of model. The coefficients B(T) and C(T) can be computed from the model potentials.

$$P = RT\left(\frac{1}{V_m} + \frac{B(T)}{V_m^2} + \frac{C(T)}{V_m^3} + \cdots\right)$$

As one can expect the ideal gas equation do not work close to the boiling point. On the left is the P-V diagrams of CO_2. The one above (a) is at 426 K and the lower at 310 K (the boiling point of CO_2 is 304 K at 76 bar.) The red curve is the ideal gas, blue the RK model and purple the vdW.

To understand better the liquid-gas behavior we need to look what happen in a pressure experiment. When gas is compressed at fixed temperature it will first stay as gas (a). Then there will be liquid in the systems (b) and (c) and finally only liquid (d).
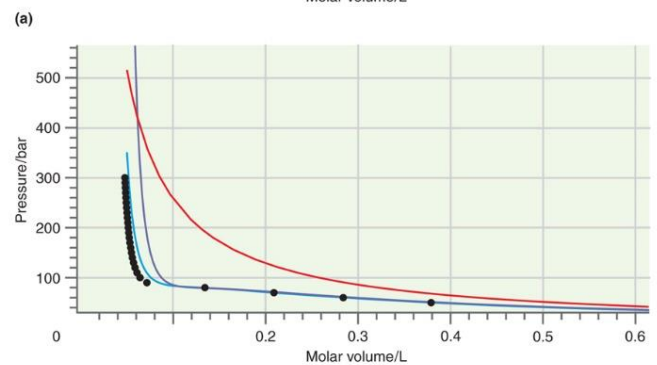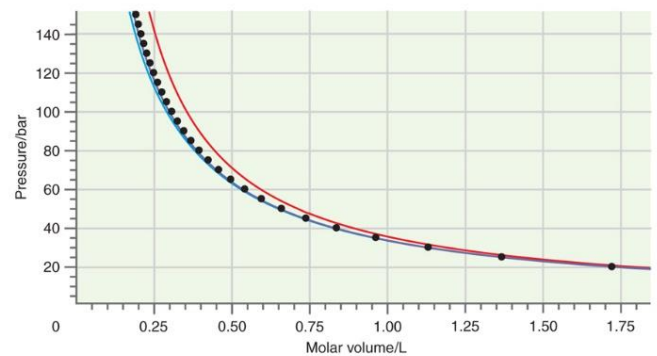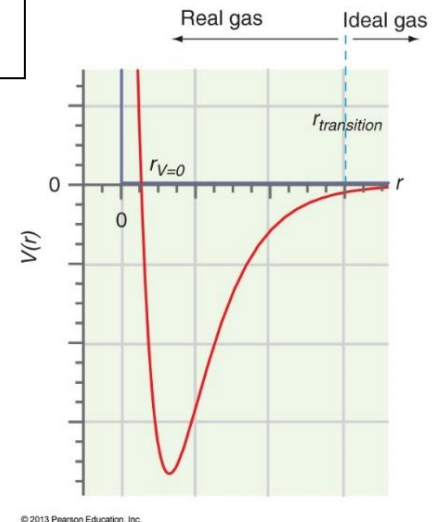
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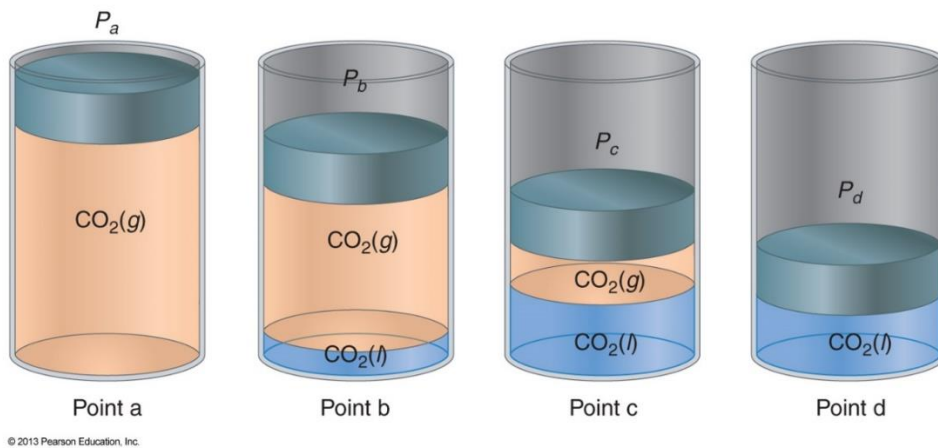
This can be done at different temperatures and a rather complex but interesting figure can be made. The examples above are at 258 K and the points are marked to the figure. There are several features here. The liquid is noted with blue and the gas-liquid coexistence with yellow.

Note that temperatures above 304.12 K for CO_2 there is no gas-liquid coexistence at any pressure or no liquid phase. This temperature is called the **critical temperature**. There is also critical pressure and volume. Together these values are called the critical point. See Table 7.2. (Appendix A). In this table there are some critical constants of some substances.
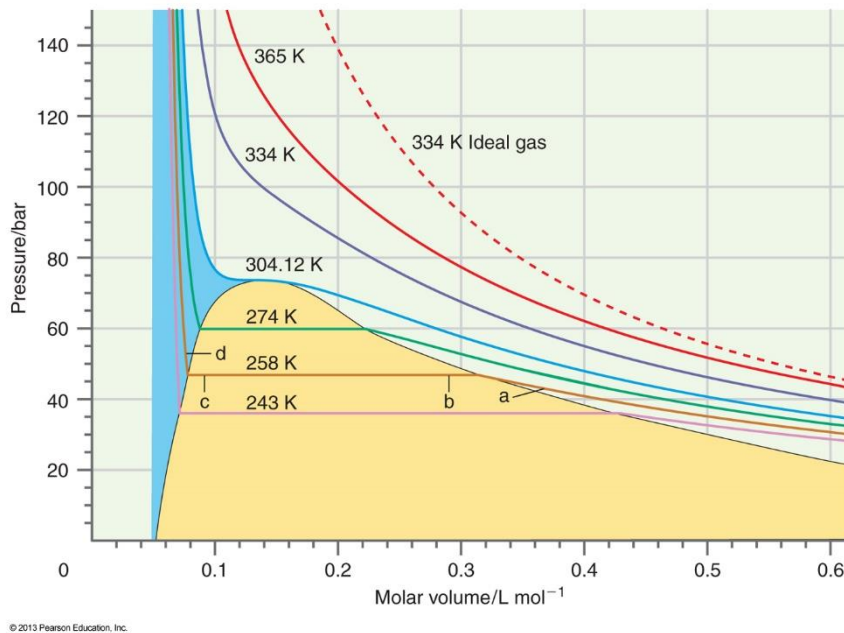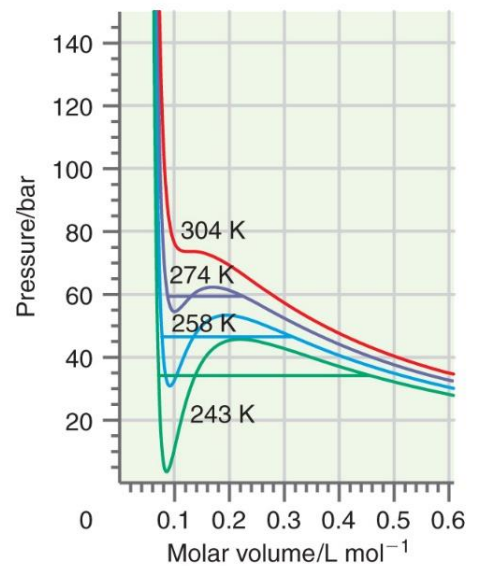

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Figure 7.2 Isotherms of CO_2

Go through example 7.1

Find out what is the critical temperature, pressure and volume in the van der Waals equation; $T_c = \frac{8a}{27Rb}$, $P_c = \frac{a}{27b}$ and $V_{m,c} = 3b$. These relations can be used to determine the parameters a and b:

$b = \frac{RT_c}{8P_c}$ and $a = \frac{27R^2T_c^2}{64P_c}$. There are some parameters of different materials in Table 7.4 (Appendix A)

Note that the van der Waals (or the Redlich-Kwong) equation of state do not describe correctly the liquid-gas coexistence. It will produce unphysical decrease of pressure when compressing the system. Sensible results can be obtained with the Maxwell construction in which a straight line is drawn in the oscillatory part such that the positive and negative areas are the same.
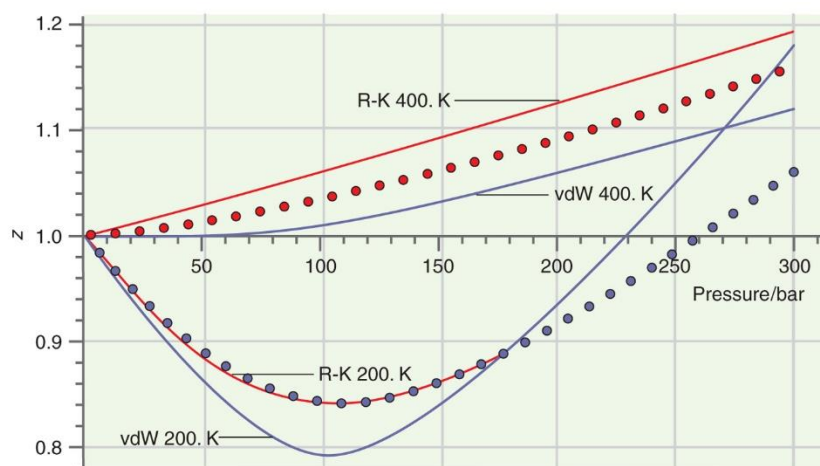

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Compression factor   Engel & Reid chapter 7.3

We see form the figure 7.2 that the ideal gas law gives too high pressure compared to experiments. We can define the compression factor as

$$z = \frac{V_m}{V_m^{ideal}} = \frac{PV_m}{RT}$$

where V_m is the measured molar volume. Interestingly at low temperatures the z is often smaller than 1 whereas at high temperatures >1.

At low temperatures, the attractive interaction cause the less than 1 z values. At high temperatures the repulsive potential dominates. Note that the pressures are rather high, up to 300 bar.

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Figure 7.5: data for N_2.

The Boyle temperature is the temperature which the initial slope of z is 0 (See Table 7.3 some values). The Boyle temperature of N_2 is 327 K. Figure 7.6. below shows that the behavior depends form gas to gas (here T = 400 K). Note oxygen Boyle temperature is 400 K.

Question: does the ideal gas law describe air well around 300 K and pressures up to ca. 100 bar. Is the situation better or worse at 350 K.

Even the gas molecules have interactions around Boyle temperature they cancel each other and the ideal gas law is "better" than it should be.
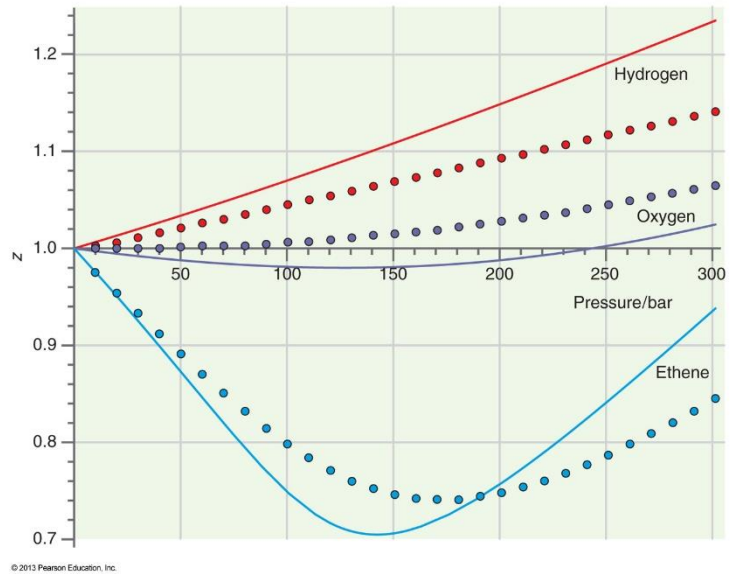

Figure 7.6: data for O_2, ethane and H_2 at 400 K (dots are experiments and lines from a van der Waals model)

Corresponding states	Engel & Reid chapter 7.4

The gas behavior depends quite much form gas to gas but is there some universality in them? There is. We can use reduced temperature, pressure and molar volume by scaling them with the critical values:

$$T_r = \frac{T}{T_c}, \ P_r = \frac{p}{P_c}, \ V_{m,r} = \frac{V_m}{V_{m,c}} \ .$$

The reduced van der Waals equation is very convenient (the derivation is in the book)

$$P_r = \frac{8T_r}{3V_{m,r} - 1} - \frac{3}{V_{m,r}^2}$$

this does not depend on the gas parameter a and b. It is valid for ALL gases. This is a rather surprising result, and we need to see how this work with real data. See the Figure 7.6 below. The agreement is very good. (Well, water is not there. That might differ from the universal curves.)

The data shows that most liquids behave quite similarly. This has also strong predictive power. One can predict properties of several gases with the same model. The main material parameters are the T_c, P_c and $V_{m,c}$.
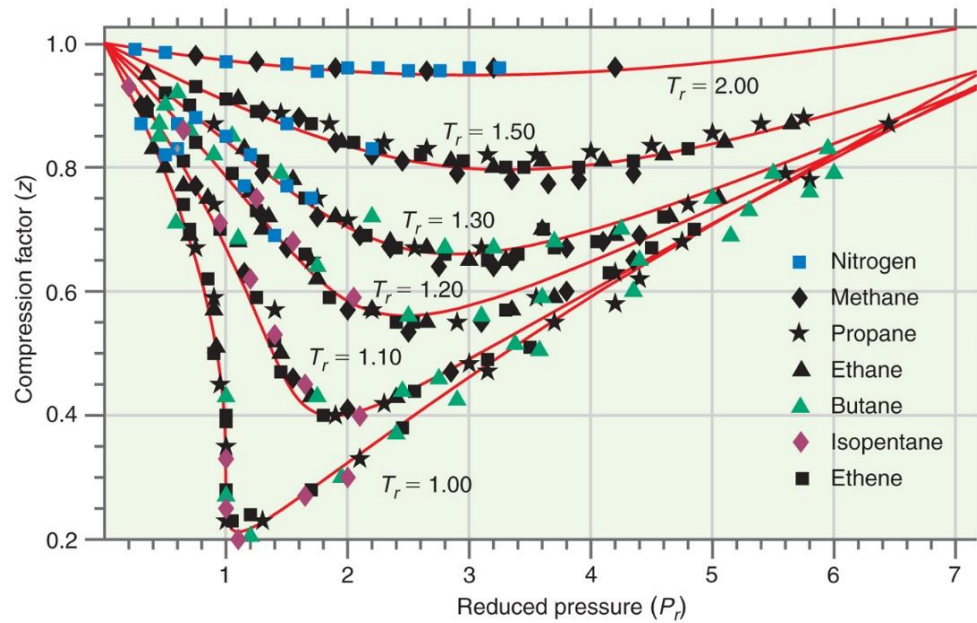
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| Fugacity | Engel & Reid chapter 7.5 |

In the previous chapters we have always assume that the gases are ideal. As we have seen above that is not true. We can replace the pressure with quantity fugacity, f for example the chemical potentials

$$\mu(T,P) = \mu^o(T) + RT \ln \frac{P}{P^o}$$

now we replace pressure with fugacity

$$\mu(T,P) = \mu^o(T) + RT \ln \frac{f}{f^o}$$

how can be compute the fugacity. The ideal and real chemical potential different is

$$\mu^{real}(T,P) - \mu^{ideal}(T,P) = \int_0^P (V_m{}^{real} - V_m^{ideal})dP'$$

we can define the fugacity as

$$\ln f = \ln P + \frac{1}{RT}\int_0^P (V_m{}^{real} - V_m^{ideal})dP'$$

of using fugacity coefficient γ, $f = \gamma(T,P)P$.

in small pressures the $f \approx P$ but at high pressures the difference can be quite large. The fugacity coefficient is an easy way to deal with the non-ideal gases. In general it is quite linear to pressures up to 200 bar.

As far as I know there is no simple general model for fugacity. We can used vdW or Redlich-Kwong parameters. There are several more complex model and there are programs that can compute fugacities for several componds.
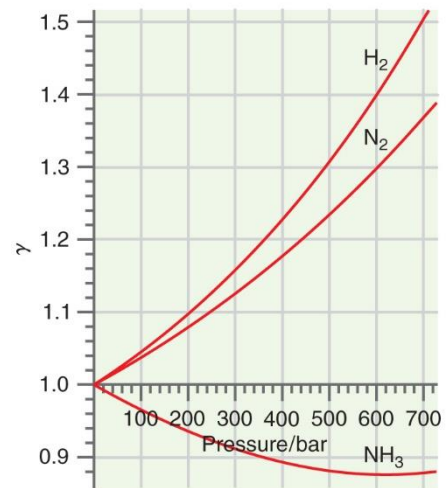
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An interesting fugacity calculator for water. It will show the fugacity and fugacity coefficient on different pressures and volume.

https://demonstrations.wolfram.com/FugacityFromEquationOfStateForWater/

The phase diagrams describe the behavior of materials with respect of temperature and pressure. As we all know the material can be solid, liquid or gas phase. There can be several solid phases. Thermodynamically it is convenient to use the chemical potential (or molar Gibbs energy) to describe the phases. The difference of chemical potential can be written as (T and P as variables)
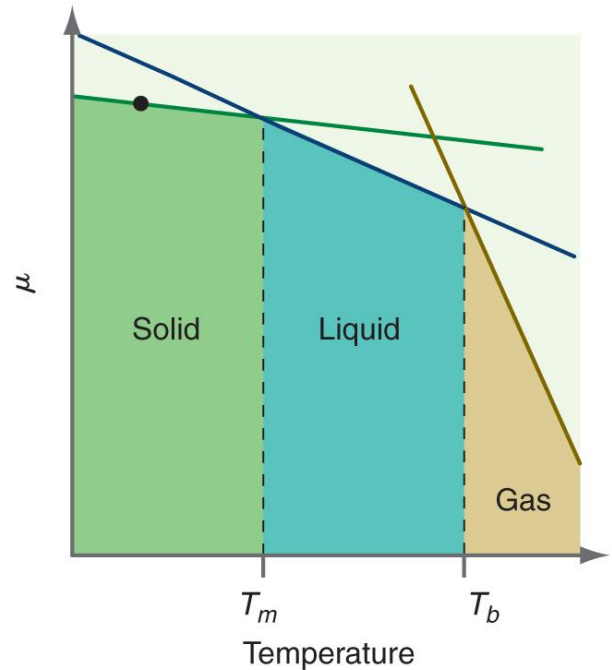
$$d\mu = -S_m dT + V_m dP$$

and

$$\left(\frac{\partial \mu}{\partial T}\right)_P = S_m \quad \text{and} \quad \left(\frac{\partial \mu}{\partial P}\right)_T = V_m$$

The entropy and volume are always positive. If the pressure changes are small the μ decrease with T. The entropy of different phases increases

$$S_m^{gas} > S_m^{liq} > S_m^{solid}$$

(The slopes in figure 8.1)

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Fig 8.1. T_m is the melting temperature and T_b boiling temp.

The pressure effect can be described easily. Typically the $V_m^{gas} \gg V_m^{liq} \approx V_m^{solid}$, so the gas chemical potential is sensitive to the pressure change but liquid and solid less. In all cases the μ will increase with the pressure. Below the left figure correspond a case where $V_m^{liq} > V_m^{solid}$ and the left on the opposite case, $V_m^{liq} < V_m^{solid}$.
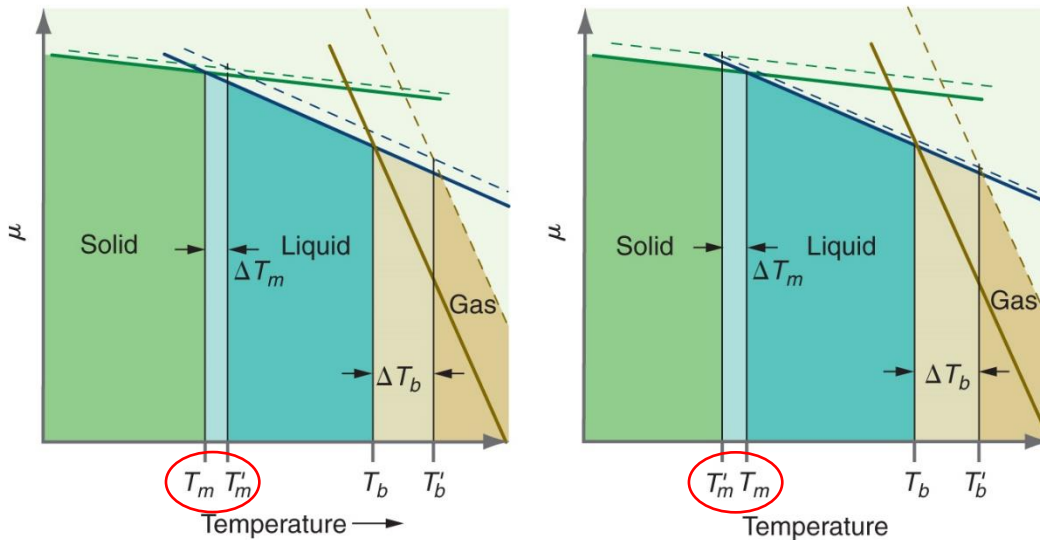
Fig 8.2. the solid lines correspond to pressure P_1 and dashed to higher pressure P_2. In left figure $V_m^{liq} > V_m^{solid}$ and right $V_m^{liq} < V_m^{solid}$

Note that the boiling temperature always increase with the pressure but the direction of the melting temperature depends on the liquid and solid molar volumes.

> Pressure-Temperature phase diagrams   Engel & Reid chapter 8.2

The most convenient way to look the phase changes is to use the P-T phase diagram. It contains a lot of information. Typically, the phase changes with increasing temperature goes from solid to liquid and then to gas, **line a**, but also solid to gas transition is possible, **line b**. A good example of the later is CO_2 at normal pressure. When increasing pressure, we can also see gas-liquid-solid transition, **line c**. The case near the critical point is interesting. Cooling the gas below the critical point is will liquefy normally, **line d** but we can go around the critical point along the blue line. We end up to a liquid but without any clear phase transition.
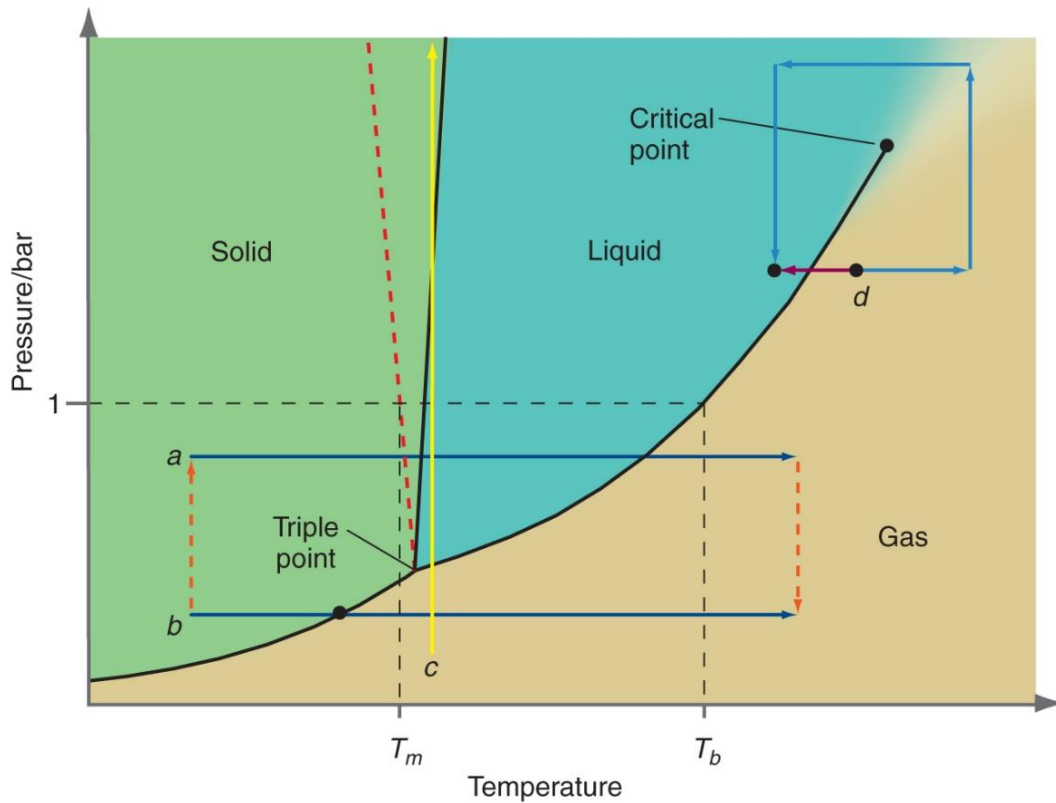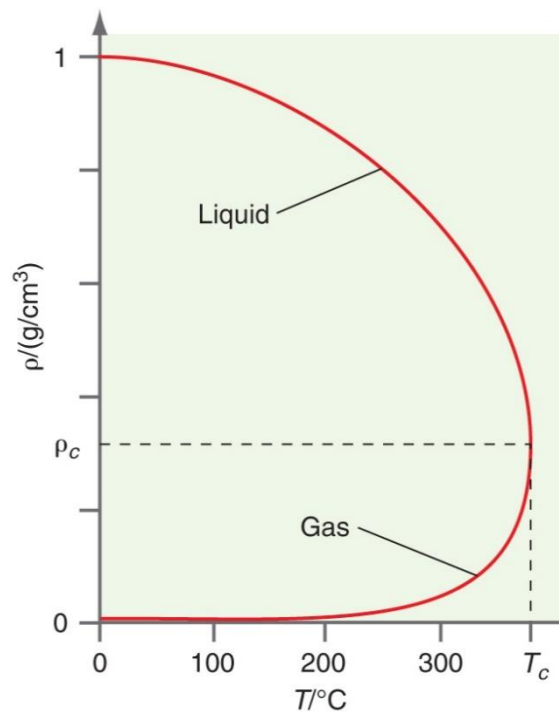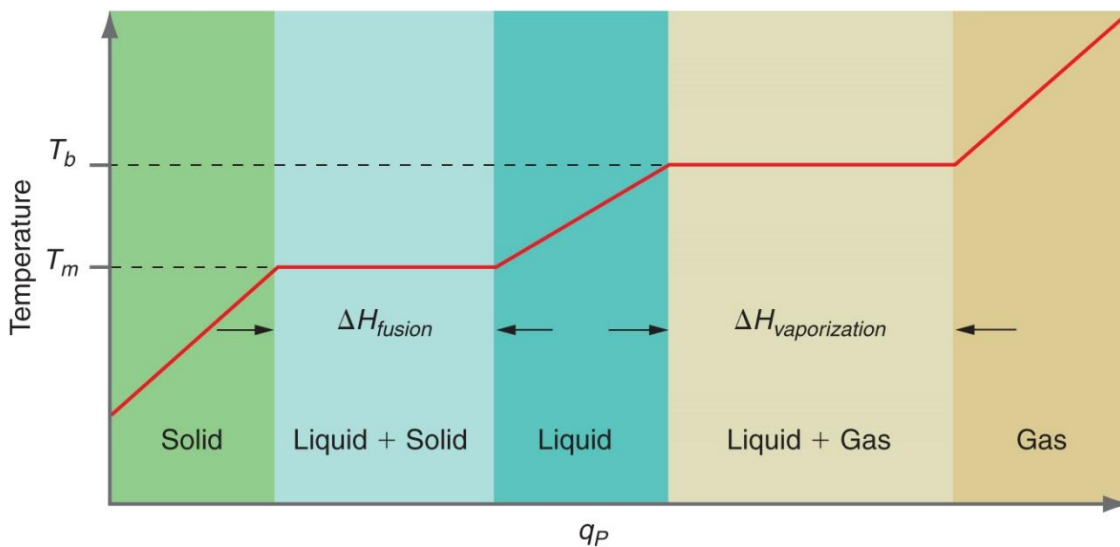
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evaporation temperature dependence of pressure is rather large but the melting temperature do not change much (very steep slope). The slope can be positive or negative. For water it is negative so with increasing pressure the melting temperature decrease. (That's why we can skate and ski.) The triple point is a unique P-T point where the gas, liquid and solid coexist. In Table 8.2 here are several parameters of different substances

One need to note that the liquid and gas coexist. At low temperatures, the gas density is very low but near the critical point the gas and liquid densities approach each other.

When a phase transition happen, some enthalpy is consumed. In evaporation this is called heat of evaporation ΔH_{vap} and in melting heat of fusion ΔH_{fus}. It is easy to have phase mixing at the melting and evaporation temperatures. Good example is water ice mixture.
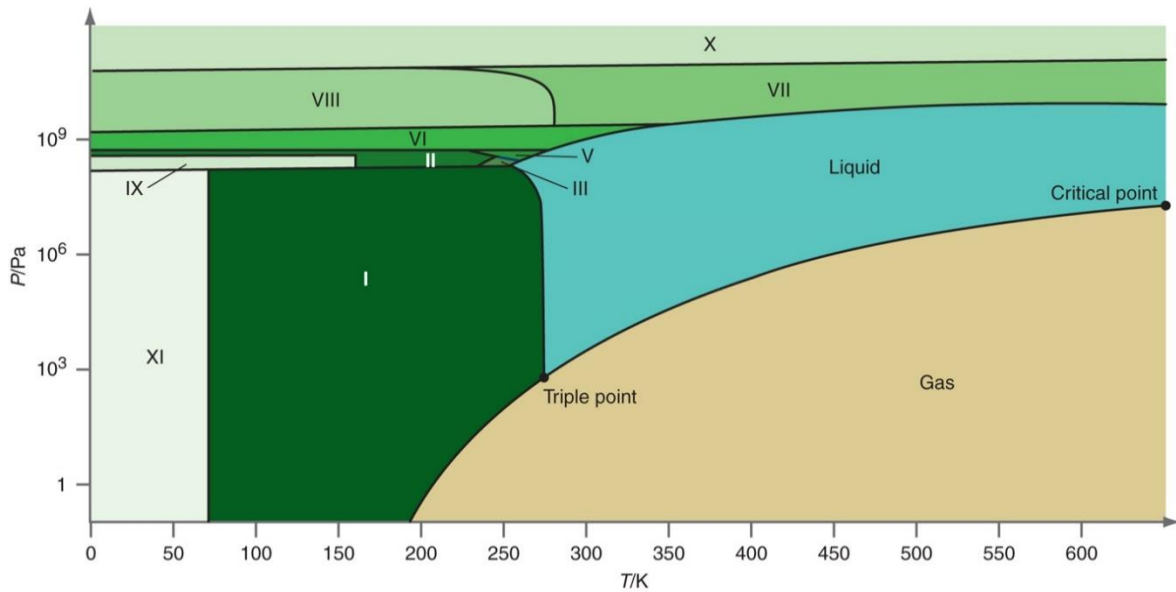
The phase diagrams can be very complex. Water is an excellent example. It has 11 know phases of ice. At extremely high pressures we can have ice(VII) at 600 K! See some other examples in the book.
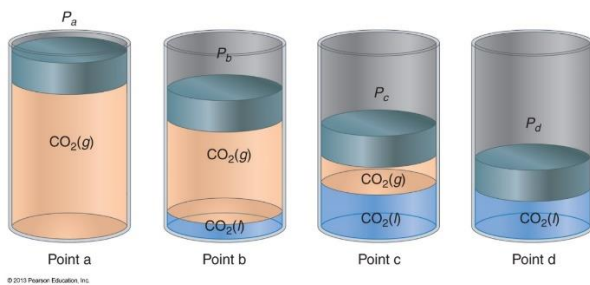
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Temperature-Volume phase diagram   Engel & Reid chapter 8.4

An alternative way to look the phase changes is to use the P-V phase diagram. The P-V diagram is particularly handy for phase coexistence. On the right there is a phase diagram of substance which $V_m^{liq} > V_m^{solid}$. If we follow the constant pressure line a, there is first solid, then solid-liquid coexist up to volume V_m^{liq}, the starting volume for the coexist is V_m^{solid}. Then liquid, then liquid-gas and finally just gas.

Illustration of the liquid-gas coexist.
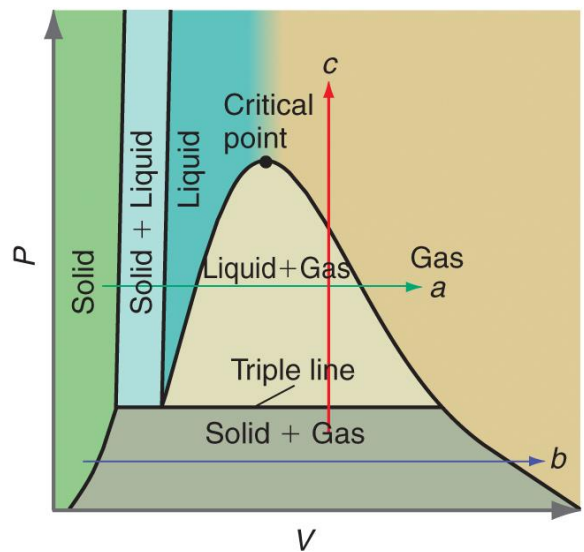
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The red line c is constant volume pressure line. At high pressure the system is in solid+gas phase then it reach to liquid+gas phase and finally to gas.

In P-T diagram you do not see the phase coexist since the pressure and temperature do not change. (Think of ice in water glass.) Finally, we can use the P-V-T diagram. It is very complex, but it is the most complete picture of the phases.

In the lecture I try to explain this a bit better.

Take a look of the a to f line. It corresponds to the f line in PT diagram and the a line we just discussed.
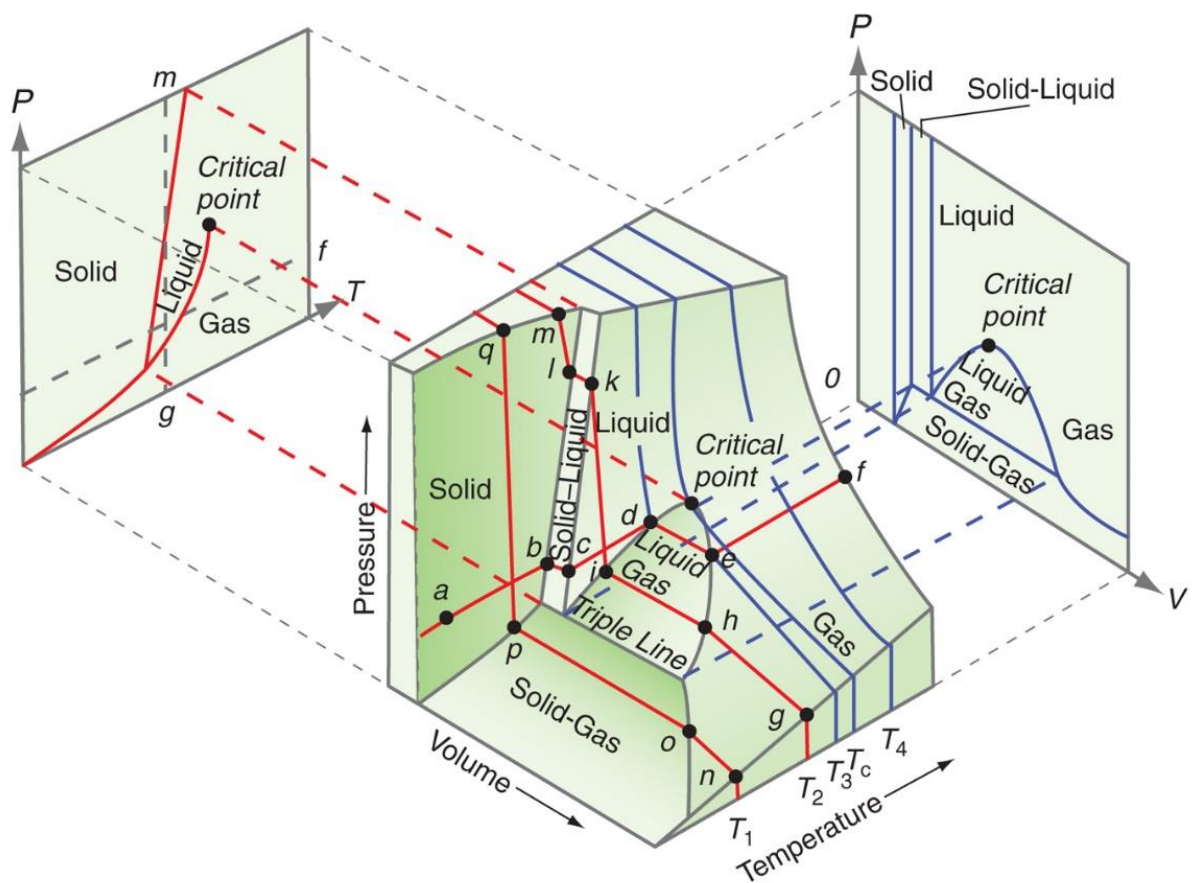
Clapeyron equation   Engel & Reid chapter 8.6

The Clapeyron equation is a useful way to estimate the slopes in the P-T diagrams. At phase transition the $\mu_\alpha(P,T) = \mu_\beta(P,T)$ and small variations in P and T have to keep the chemical potentials equal $\mu_\alpha(P,T) + d\mu_\alpha = \mu_\beta(P,T) + d\mu_\beta \quad => \quad d\mu_\alpha = d\mu_\beta$ and $d\mu_\alpha = -S_{\alpha,m}\, dT + V_{\alpha,m}dP$, $\mu_\alpha = -S_{\beta,m}\, dT + V_{\beta,m}dP \quad => \quad (S_{\beta,m} - S_{\alpha,m})dT = (V_{\beta,m} - V_{\alpha,m})dP$

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

Next, we need to find the ΔS_m and ΔV_m. The $\Delta G_{fusion} = \Delta H_{fusion} - T\Delta S_{fusion} = 0$ so the entropy can be computed form the enthalpy.

For **solid-liquid transition** a typical entropy change is 22 J/(K mol) , the volume change is very small, for material like Ag, K , AgCl the volume change is around $4*10^{-6}$ m³/mol. Water the volume change is negative and around $-2*10^{-6}$ m³/mol.

Now the dP/dT change is 55 bar/K for Ag etc. and -55 bar/K for water so if we increase the pressure by 1 bar the melting temperature increase (or for water decrease) by 1/55=0.02 K.

For **liquid-gas transition** the entropy change is around 90 J/(K mol) and the volume change is much larger. In gas the molar volume is 22.4 L/mol so the volume change is ca. $22*10^{-3}$ m³/mol. The dP/dT change is 0.041 bar/K. Now 1 bar change will change the boiling point ca. 24 K.

We can also use the Clapeyron equation to estimate the temperature change of the pressure change in solid-liquid transition

$$\int_{P_i}^{P_f} dP = \Delta P = \int_{T_i}^{T_f} \frac{\Delta S_m}{\Delta V_m} dT = \int_{T_i}^{T_f} \frac{\Delta H_m}{\Delta V_m} \frac{dT}{T} \approx \frac{\Delta H_m}{\Delta V_m} \ln \frac{T_f}{T_i}$$

for liquid-gas transition $\Delta V_m \approx V_{gas,m}$ ad we use the ideal gas law

$$dP = \frac{\Delta H_m}{\Delta V_m} \frac{dT}{T} = \frac{\Delta H_m}{V_{gas}} \frac{dT}{T} = \frac{P \Delta H_m}{R} \frac{dT}{T^2} \quad => \quad \frac{dP}{P} = \frac{\Delta H_m}{R} \frac{dT}{T^2}$$

$$\int_{P_i}^{P_f} \frac{dP}{P} = \frac{\Delta H_m}{R} \int_{T_i}^{T_f} \frac{dT}{T^2} \quad => \quad \ln \frac{P_f}{P_i} = -\frac{\Delta H_{vapor}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i}\right)$$

so the gas vapor pressure will increase exponentially with temperature.

Vapor pressure depend on applied pressure   Engel & Reid chapter 8.7

read the chapter

Surface tension   Engel & Reid chapter 8.8

So far, we have always assumed the surface to be flat. This is not always the case. Any system dislike the interphase and the interpahse cause energy cost. At contant V and T we can write

$$dA = \gamma d\sigma$$
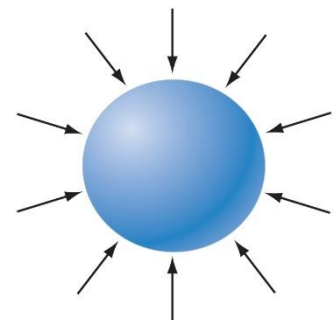
where A is Helmholtz energy and σ is the change of area (sorry of the notations, A is not surface). For a sphere $\sigma = 4\pi r^2$ and $d\sigma = 8\pi r dr$ the work done in the surface change is $\gamma d\sigma$ and we can get the force (dw=Fdr) $F = 8\pi r \gamma$ and now we can compute the pressure in- and outside the bubble.

$$P_{in} = P_{out} + \frac{F}{A} = P_{out} + \frac{2\gamma}{r}$$

so the pressure inside the bubble is larger. If the bubble is very large or the surface is flat the difference disappears. On the other hand, in very small bubbles the effect is big. For water the nm size droplet internal pressure is 2.7 times the external one. This makes the very small droplets unstable and also the droplet forming very difficult.
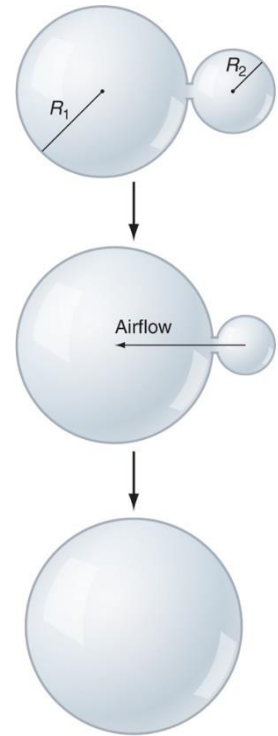
The pressure difference also makes foams unstable. There is higher pressure in small foam bubbles and if they can get contact to larger ones they will disappear. The real mechanisms in the foams are more complex than in bubbles since the foam bubbles are not spherical.

The surface tension also explains the capillarity effect. Water can rice quite high in a narrow (glass)tube. The curved surface will cause lower pressure on the top of the tube and that is compensated with the weight of the water pillar of height h. We assume that water surface is spherical. This assumes that water likes the tube material and it wets the glass. If the liquid do not like the tube the curvature can be negative and the capillary effect will push the liquid down. This is the case with mercury and glass. (and probably with Teflon and water).
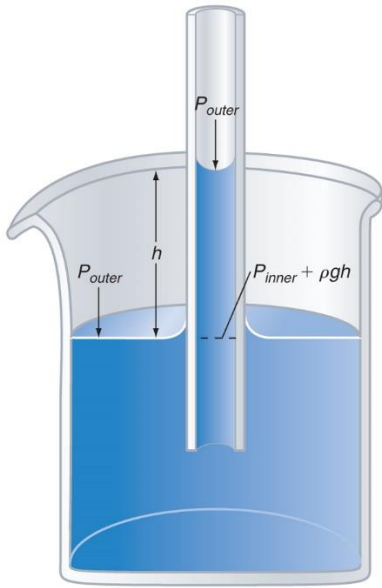
The height of the capillary rise is

$$h = \frac{2\gamma}{\rho g r}$$

where ρ is the density of the liquid, and g is the gravitational acceleration.

Go through problem 8.4

(a)