

# Physical Chemistry

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The course will follow mostly the Engel and Reid book Physical Chemistry, which is available in the Pearson web page.

See instructions how to login to the book from the MyCourse course front pages

The course will cover chapters 1-9 and 36 (Elementary Chemical Kinetics)

This material and a video link (Zoom) are in the MyCourse page.

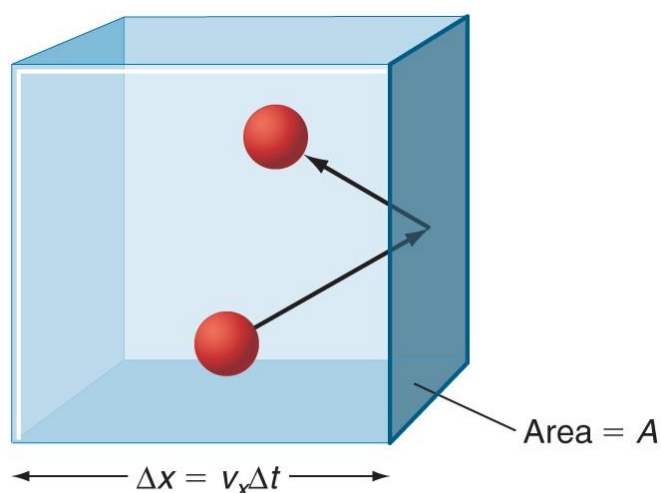
There will also be exercises in the course.

## Thermodynamics

### Ideal gas from molecular perspective    Engel & Reid chapter 1.2

We can derive the ideal gas law from very simple concepts of molecular collisions.

When a molecule with velocity  $v$  and with  $x$ -component with  $v_x$  collide to the container wall it will give a momentum,  $p$ , of  $2mv_x$  to the wall. This will also create a force to the wall.  $F=ma$



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$a = \frac{dv}{dt} = 2v_x/\Delta t$  for each collision so  $F = 2mv_x/\Delta t$  but how many collisions there are in a second. This depend on the density of the system. The molecules from  $\Delta x = v_x \Delta t$  from the wall can collide to the wall within  $\Delta t$  if the velocity is towards the wall. The area of the surface is A and the number

of molecules in the  $A\Delta x$  volume is  $A\Delta x\rho$ , where  $\rho_N = N/V$  is the gas number density (not the mass density or density). The molecules  $v_x$  velocity can be either towards or away from the surface so only half of the molecules will collide so

$$N_{coll} = \frac{1}{2}\rho_N A v_x\Delta t$$

and the force is

$$F = 2mv_xN_{coll} / \Delta t = m \rho_N A v_x^2$$

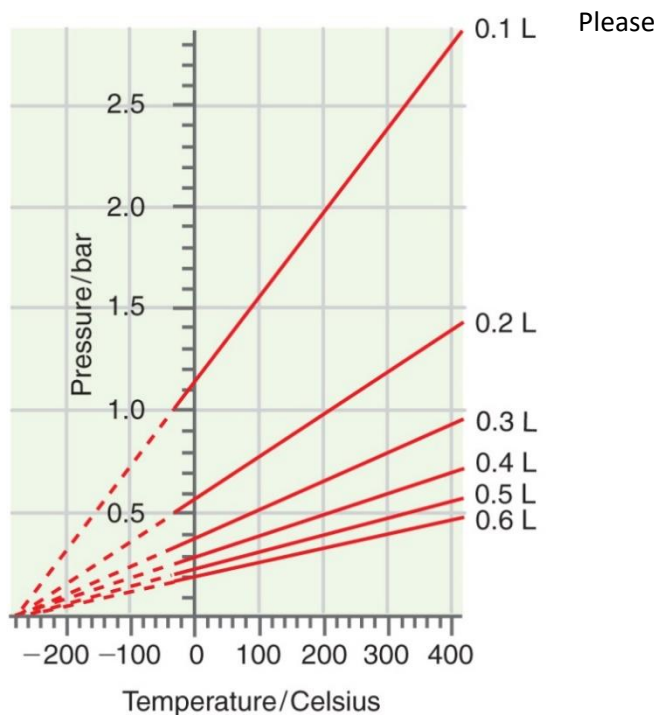
and the pressure

$$P = \frac{F}{A} = \rho_N m v_x^2 = \rho_N 2 * E_{kin}$$

The molecules kinetic energy is related to temperature. We do not proof it here but  $E_{kin} = k_b T$  where  $k_b$  is the Boltzman constant. So

$$P = \rho_N k_b T = \frac{Nk_b T}{V} = \frac{nN_A k_b T}{V} = \frac{nRT}{V}$$

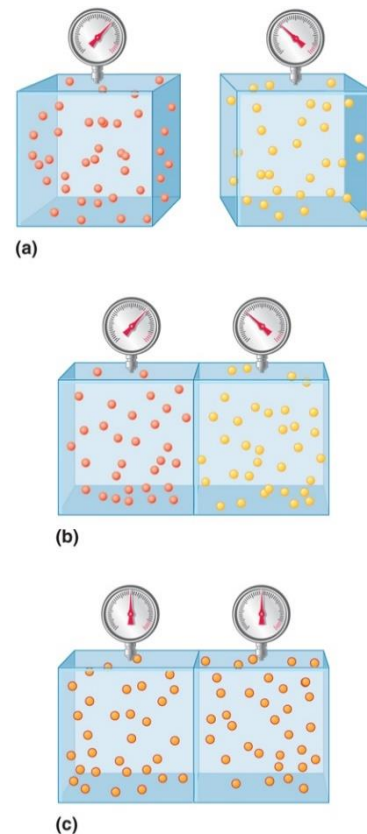
here the  $R$  is ideal gas constant. The temperature here is in Kelvins. The ideal gas equation can be used to estimate the absolute zero temperature. Here the pressure of dilute gas is measured in fixed volume on different temperatures.



Some definitions of Thermodynamics Engel & Reid chapter 1.3

The key concept in thermodynamics is that systems need to be in equilibrium with respect of some variable like **pressure P**, **temperature T**, **volume V** and **particle number N** (or concentration). Some of them (P,T,V,N) or total energy E can/should be constant.

Two different systems can be in thermal equilibrium if they can change energy, case (c). If the systems have insulating walls, they can be in contact but the temperature is different, case (b). The case (b) is called **adiabatic**. Here we assume that the containers have the same volume and number of gas molecules. The meter can indicate the pressure or temperature of the system.



Zeroth law of thermodynamics:

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*If two systems are separately in thermal equilibrium with a third system they also are in equilibrium.*

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### Intensive and extensive variables Engle & Reid chapter 1.4

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All thermodynamical variables are either intensive – they do not depend on the **system size** – or extensive – they depend on the system size. Pressure P and temperature T are intensive whereas volume V and particle number N are extensive. If in a thermodynamical equation, have extensive variable on the left side also on the right side need to be an extensive variable.

$$P = \rho_N k_b T = \frac{k_b N T}{V} = \frac{n R T}{V}, \quad P V = k_b N T = n R T$$

### Partial pressures

Almost always the systems contain several different molecules, so does the ideal gas pressure depend on the different molecules? Answer: No. The total pressure is the sum of the pressure of each molecule type.

$$P = \sum_i P_i ; P_i = n_i R T$$

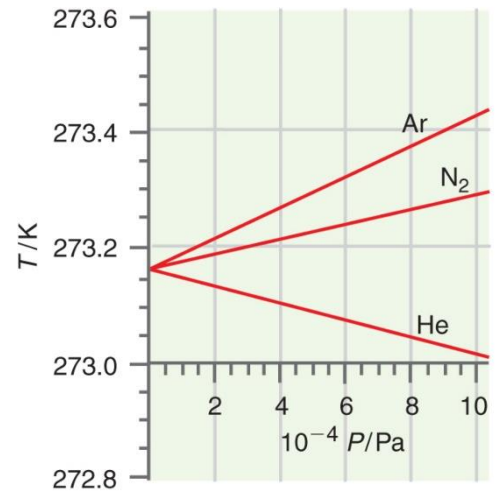
here the  $P_i$  are the partial pressures of each gas and  $n_i$  are the molecular density of each type of gas. One can also define the mole fraction as  $x_i = n_i/n$ .

Examine the Problem 1.2

## Real gases

## Engel & Reid chapter 1.5

The ideal gas is an idealization since all molecules will interact and they have some size. This can be seen in several experiments. E.g. in the estimation of the absolute zero temperature. At finite pressures the estimation differ from one gas to another. Note these are very weakly interacting gases with low boiling points.



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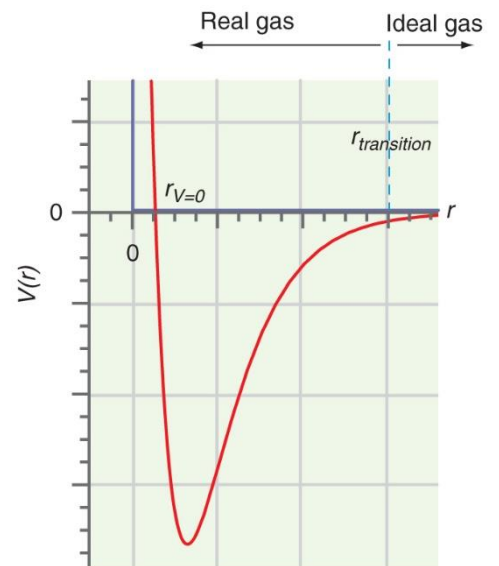
One can draw a qualitative molecule-molecule interaction curve. When the molecules are far away ( $r_{transition}$ ) they do not interact and this is the case in dilute gases. When they get closer there is an attractive part up to distance  $r(V=0)$  and then the interaction becomes repulsive. This interaction model is schematic and the details depend from molecule to molecule.

**Question:** which is more ideal gas – water vapor or Argon. Why?

The molecular interactions will modify the ideal gas law and there are several different real gas laws. One of the often used is the van der Waals equation

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

where  $a$  and  $b$  are gas dependent parameters. There are quite many of them listed in Table 7.4. The parameter  $b$  is related to molecules volume and it will increase the pressure. The  $a$  is related to the attractive interaction. (The second term is negative and thus it reduces the pressure.)



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Examine the Problem 1.4

# Internal Energy and First Law of thermodynamic chapter 2.1

Engel & Reid

Energy is a fundamental quantity in many chemical systems. In thermodynamics, there are several energies. We start with the Internal Energy  $U$ .  $U$  contain all possible energy form of the molecules. These include the kinetic energy, molecular interactions, possible bond energy, rotation and vibration energy. The distribution of the  $U$  can vary between these but in a closed system  $U$  cannot change.

This is the first law of thermodynamics

*In isolated system, the internal energy  $U$  is constant*

The internal energy can be divided to  $U_{\text{system}}$  and  $U_{\text{environment}}$ . For an isolated system  $\Delta U_{\text{system}} = -\Delta U_{\text{environment}}$ . We are mostly interested of the system and subindex is usually leaved out.

If some work  $w$  is introduced to a system, it will heat  $q$ . The internal energy is a sum of these

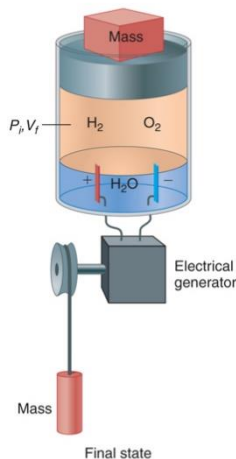
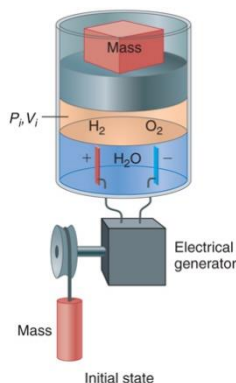
$$\Delta U = q + w$$

If we compress an isolated container with weight  $M$  with distance  $x$  the work is

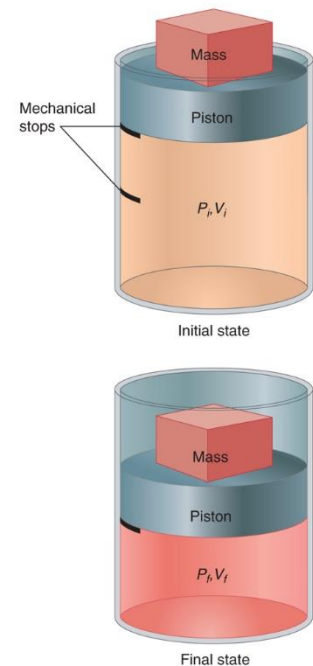
$$w = \int_{x_1}^{x_2} F \cdot dx = Mgx$$

for isolated system  $\Delta U = 0$  so the heat is  $w = -q$

$$q = - \int_{V_1}^{V_2} P dV$$



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A similar example with electrochemical water splitting reaction. This is more complex since the reaction will produce gases,  $H_2$  and  $O_2$  but all the work put in to the system will go to heat and work. Note that the mass will increase.

## Heat

## Engel & Reid chapter 2.3

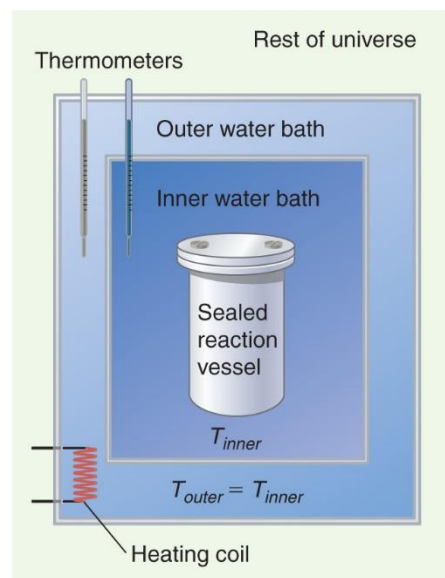
The heat is rather mysterious object

- The only appears during the change of state
- The net effect of heat is to change the internal energy of the system.
- The heat flow from hot to cool. If the system is heating the  $q$  is positive and vice versa.

Warning the paragraph 2.3. is difficult. Read it carefully.

Examine the Problem 2.2

Where the extra energy will go?



## Heat Capacity

## Engel & Reid chapter 2.5

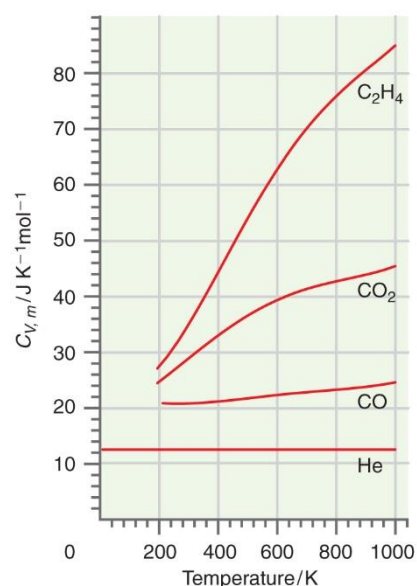
The heat capacity is the ability of the system to store heat (or energy). When energy is added to the system its temperature increases

$$C = \lim_{T \rightarrow 0} \frac{q}{T_f - T_i} = \frac{dq}{dT}$$

The heat capacity depend on the systems. For example water have high heat capacity whereas gases have very low one. The  $C$  also depend on the experimental conditions. If the pressure  $P$  or volume  $V$  is kept constant where have two different heat capacities,  $C_V$  and  $C_P$ . Often the molar  $C$  is used, so the  $C$  is divided by the amount of material, it symbol is  $C_m$  (and also  $C_{P,m}$  and  $C_{V,m}$ ). Some values of  $C_{P,m}$  are given in Appendix A Tables 2.3 and 2.3.

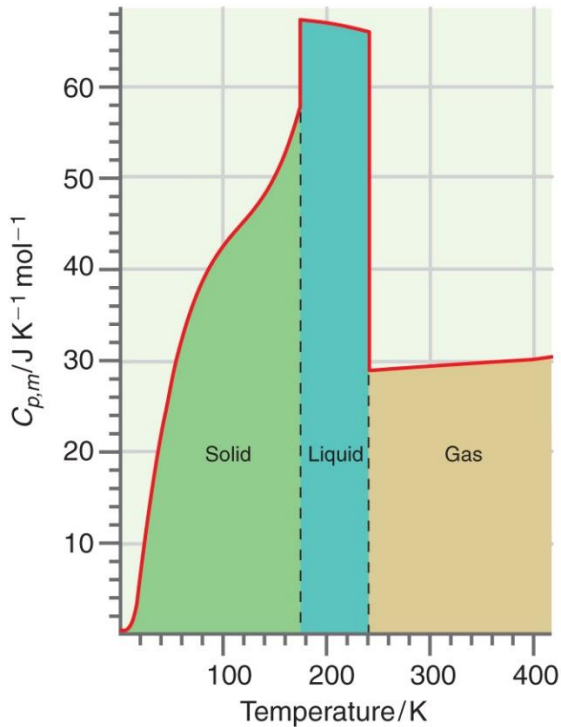
On the left, there is heat capacities of some gases at different temperatures. Note that the values changes quite a lot (except for He). Read the explanation form the text book.

The heat capacity depend on the degrees of freedom (dof) of the molecules. He has only translation dof and each atom have (kinetic) energy of  $3k_bT/2$  then the molar heat capacity of He is



$3R/2 = 12.741 \text{ J/(K mol)}$ . CO molecule can also rotate but at low temperatures the vibrations are not active so CO have  $C_{V,m} = 5R/2 = 20.785 \text{ J/(K mol)}$

The heat capacity can be measured to any system. Below is the  $C_{p,m}$  for  $\text{Cl}_2$ . The higher  $C_{p,m}$  for solid and liquid is due to molecular interactions. Note also the sharp changes in the phase transitions.



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The  $C_{p,m}$  and  $C_{v,m}$  are related

## State and Path Functions chapter 2.6

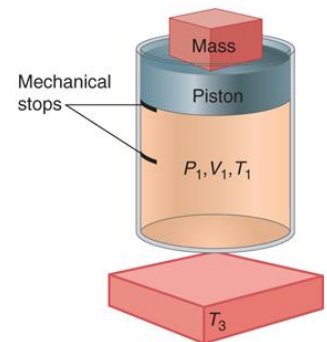
Engel & Reid

So called state functions are very useful in thermodynamics. They depend only on the initial and final values of the system not how we get there. Importantly the internal energy  $U$  is a state functions.

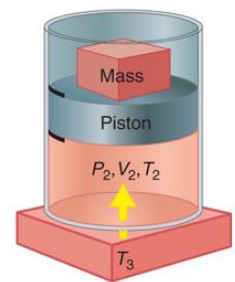
$$\Delta U = \int_i^f dU = U_f - U_i$$

That is simple but the work,  $w$ , and heat,  $q$ , are not state functions. They depend how the system has been changed.

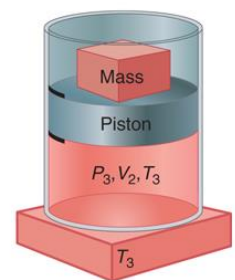
Let's look the example in chapter 2.6. We start with container that has gas at pressure  $P_1$ , volume  $V_1$  and temperature  $T_1$ . When this is compressed to  $P_2, V_2$  and  $T_2$  the work done is



Initial state



Intermediate state



Final state

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$$w = - \int_{V_i}^{V_f} P_{ext} dV = P_{ext} \Delta V$$

by varying the mass on top of the piston we can modify the  $P_{ext}$  so the work depend on the mass or the procedure we choose. Work (and heat) are not state functions, they are called path functions. If we know  $w$  in the process we can compute the heat as

$$q = \Delta U - w = \Delta U + P_{ext} \Delta V$$

## Reversible and Irreversible process

## Engel & Reid chapter 2.8

This is an important example of the thermodynamical processes. We look a constant temperature compression cycle. This is assumed to be part of large temperature reservoir and its temperature is always constant.

Let us look first the irreversible cycle. We start at  $T_1, P_1,$  and  $V_1,$  then the pressure is rapidly reduced to  $P_2,$  and then the volume will expand to  $V_2.$  (The temperature is constant,  $T_1 = T_2 = T$ ).

Then at  $P_2, V_2$  the pressure is rapidly changed to  $P_1,$  and the volume will compress back to  $V_1.$

The work done in expansion is  $-P_2 \Delta V = -P_2(V_2 - V_1)$  and in the compression  $-P_1 \Delta V = -P_1(V_1 - V_2)$  and the total work is

$$w_{tot} = w_{exp} + w_{comp} = -(P_2 - P_1)(V_2 - V_1) > 0$$

because the process is cyclic (the initial and final states are same)  $\Delta U = 0$  and the total heat is  $q_{tot} = -w_{tot}.$

In the reversible process the pressure change is slow and  $P = P_{ext}.$  For ideal gas we can compute the expansion work

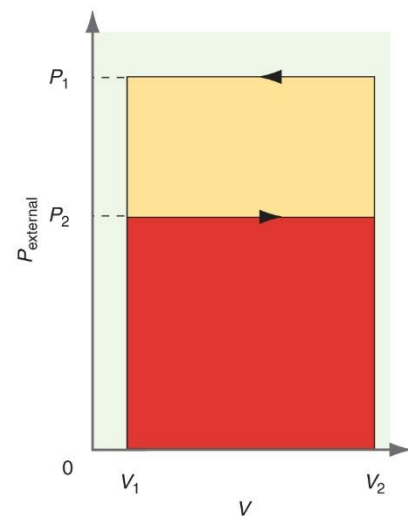
$$w_{exp} = - \int_{V_1}^{V_2} P_{ext} dV = - nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1}$$

and similarly the compression work

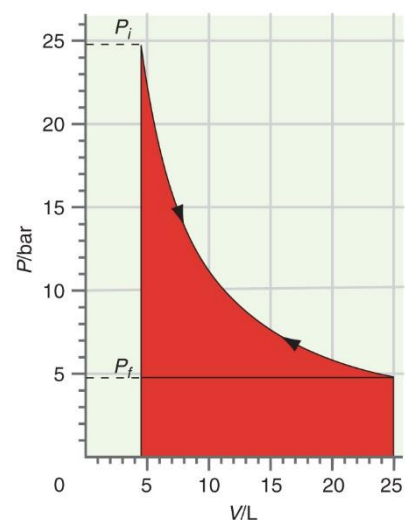
$$w_{comp} = -nRT \ln \frac{V_1}{V_2}$$

Now the  $w_{comp} = -w_{exp}$  and  $w_{tot} = 0.$

The example problem 2.4. illustrates the differences of the reversible and irreversible processes.



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## Enthalpy

## Engel & Reid chapter 2.9

Often in chemical systems (reactions) the change in energy is important. How we can measure the energy. If the process is in constant volume the work = 0,  $w = - \int P_{ext} dV = 0$  and then the

$$\Delta U = q_v$$

The q can be measured from the heat flow of the system. The problem is that usually it is difficult to keep the system in constant volume. The more natural control variable is the pressure. (Like in normal lab conditions.)

Now the change in internal energy is

$$\Delta U = \int_i^f dU = U_f - U_i = \int_i^f dq_P - P \int_i^f dV = q_P - P(V_f - V_i)$$

we can rearrange them a bit

$$U_f + PV_f - (U_i + PV_i) = q_P$$

now we can define a new "energy" the **enthalpy**  $H = U + PV$ . The enthalpy is the relevant "energy" in the constant pressure case and that is usually reported in chemical reactions. When we define a reaction endo- or exothermic we refer to its enthalpy.

## Internal energy, Enthalpy and Heat capacity 2.10

## Engel & Reid chapter

For ideal gas the internal energy and enthalpy can easily be formulated with the heat capacity:

In constant volume system:

$$\Delta U = q_v = C_V(T_f - T_i)$$

For ideal gas this holds also for non constant volume systems.

In constant pressure systems.

$$\Delta H = q_P = C_P(T_f - T_i)$$

also for ideal gas the two heat capacities have simple relation

$$C_P - C_V = nR$$

**Go through example 2.5**

This is a long one but important to go through.

## Reversible adiabatic expansion of ideal gas 2.11

Engel & Reid chapter

In atmospheric conditions, the reversible adiabatic  $q=0$  processes are important. The air masses moves quite slowly and  $P = P_{external} = \frac{nRT}{V}$ .

We can compute the work as

$$w = - \int_{V_i}^{V_f} P_{ext} dV = -nR \int_{V_i}^{V_f} T \frac{dV}{V} = \int_{T_i}^{T_f} C_V dT$$

but this is not very convenient we can start for the difference form

$C_V dT = -P_{ext} dV = \frac{nRT}{V} dV \Rightarrow \frac{C_V dT}{T} = nR \frac{dV}{V}$  and this can be integrated

$$-nR \int_{V_i}^{V_f} \frac{dV}{V} = \int_{T_i}^{T_f} C_V \frac{dT}{T}$$

if the  $C_V$  is quite constant

$$-nR \ln \frac{V_f}{V_i} = C_V \ln \frac{T_f}{T_i} \Rightarrow (C_V - C_P) \ln \frac{V_f}{V_i} = C_V \ln \frac{T_f}{T_i} \Rightarrow \left(1 - \frac{C_P}{C_V}\right) \ln \frac{V_f}{V_i} = \ln \frac{T_f}{T_i}$$

we have used the relation  $C_P - C_V = nR$  (which is valid for ideal gas). We can define  $\gamma = C_P/C_V$

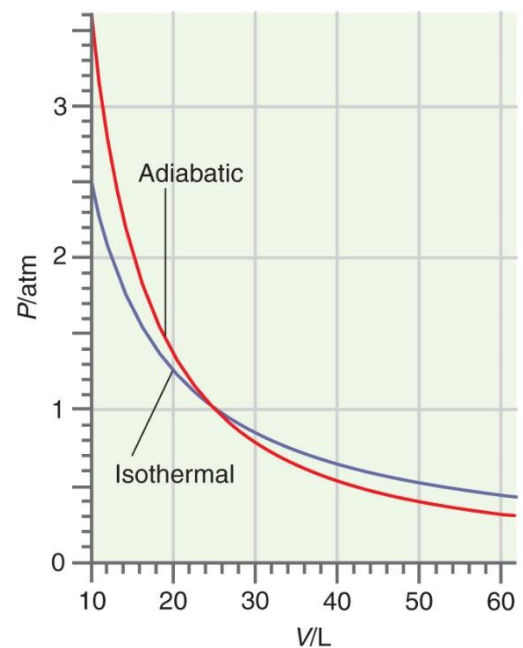
$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma}, \quad \frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} \Rightarrow P_i V_i^\gamma = P_f V_f^\gamma$$

The equations provides convenient tool to estimate the P-V-T behavior in the adiabatic process.

### Go through example 2.7

The initial temperature of the air at 2000 m is 288 K and pressure is 0.802 atm. if will rise adiabatically to 3500 m and pressure 0.602 atm. The  $C_{P,m}$  of air is 28.86 J/(K mol). What is the temperature at 3500 m.

Answer: 265 K (below freezing)



## Mathematic of state functions

## Engel & Reid chapter 3.1

The state functions are basically normal functions which depend on the variables P, T, and V. A simple example is the ideal gas law. ONLY two of the variables can be used simultaneously. Like P is defined by T and V.

$$P = \frac{nRT}{V}$$

we can take derivatives of P with respect of T or V while keeping the other constant

$$\left(\frac{\partial P}{\partial T}\right)_V, \left(\frac{\partial P}{\partial V}\right)_T$$

An important quantity is the change of P with respect of dT and dV.

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

We can define isothermal compressibility  $\kappa$  and isobaric volumetric thermal expansion coefficients  $\beta$  as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P, \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

These can be measured experimentally and some values are listed in Tables 3.1 and 3.2.

With the equation in the book the derivatives in dP can be written as

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}, \quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{\kappa V}$$

and

$$dP = \frac{\beta}{\kappa} dT - \frac{1}{\kappa V} dV$$

Go through example 3.1

## Dependence of U on V and T

## Engel & Reid chapter 3.2

The change of U with respect of V and T is

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

The first derivative is the (constant volume) heat capacity

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

the second derivative is bit more complicated. It can be written as

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

and for ideal gas this term is = 0 (use  $P=nRT/V$ ). Clearly for gases the dT term is larger.

integral of dU

$$\Delta U = \int_{T_1}^{T_2} C_V(T) dT + \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV$$

Go through example 3.5

For van der Waals gas

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = \frac{n^2 a}{V^2}$$

and

$$\Delta U_T = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV = n^2 a \int_{V_1}^{V_2} \frac{dV}{V^2} = n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

For the size of the two terms for internal energy of  $N_2$  go through example 3.6

## Dependence of Enthalpy on T at constant P chapter 3.4

Engel & Reid

The enthalpy can be treated in similar way as U. Here we use the variables T and P

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

As discussed before

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

and in this system the P is constant so  $dP = 0$ .

$$\Delta H = \int_{T_1}^{T_2} C_P(T) dT$$

Go through example 3.7

Note that the  $C_p$  model of graphite is quite complex but it is needed because the  $C_p$  is not constant in the range of 300 to 600 K.

## Relation of $C_p$ and $C_v$

Engel & Reid chapter 3.5

We note earlier that for ideal gas the  $C_p - C_v = nR$  but the more general relations if more complex.

$$C_p = C_v + T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P = C_v + TV \frac{\beta^2}{\kappa}$$

## Joule-Thomson experiment

Engel & Reid chapter 3.7

The Joule-Thomson experiment is a convenient way to measure the non-ideality of gases. In this experiment gas, originally at  $P_1, V_1, T_1$  will be pressed through a porous membrane and at the end the  $P, T$  and  $V$  are  $P_2, V_2, T_2$ . The cylinder is isolated.

The work done is

$$\begin{aligned} w &= w_{left} + w_{right} \\ &= - \int_{V_1}^0 P_1 dV - \int_0^{V_2} P_2 dV \\ &= P_1 V_1 - P_2 V_2 \end{aligned}$$

The system is insulated so  $q=0$  and  $\Delta U = U_2 - U_1 = w = P_1 V_1 - P_2 V_2$  this can be rearranges as  $U_1 + P_1 V_1 = U_2 + P_2 V_2 \Rightarrow H_1 = H_2$  so the enthalpy do not change. We are interested of the  $\Delta T / \Delta P$ . For real gases this is not zero. We can define the Joule-Thomson coefficient as

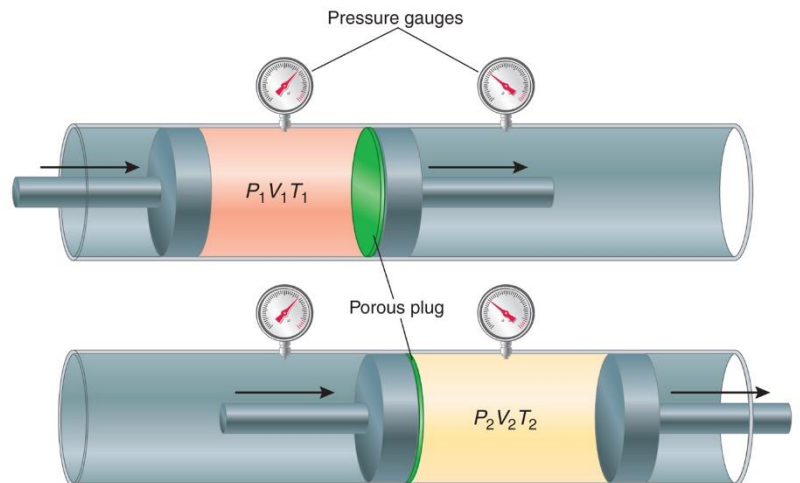
$$\mu_{J-T} = \left( \frac{\partial T}{\partial P} \right)_H$$

the coefficient can be positive of negative. See table 3.3. We can also get the enthalpy pressure relation using the J-T coefficient. For isenthalpic process

$$dH = C_p dT + \left( \frac{\partial H}{\partial P} \right)_T dP = 0$$

and

$$C_p \left( \frac{\partial T}{\partial P} \right)_H + \left( \frac{\partial H}{\partial P} \right)_T = 0 \Rightarrow \left( \frac{\partial H}{\partial P} \right)_T = -C_p \mu_{J-T}$$



**TABLE 3.3** Joule-Thomson Coefficients for Selected Substances at 273 K and 1 atm

Gas	$\mu_{J-T}$ (K/MPa)
Ar	3.66
$C_6H_{14}$	-0.39
$CH_4$	4.38
$CO_2$	10.9
$H_2$	-0.34
He	-0.62
$N_2$	2.15
Ne	-0.30
$NH_3$	28.2
$O_2$	2.69

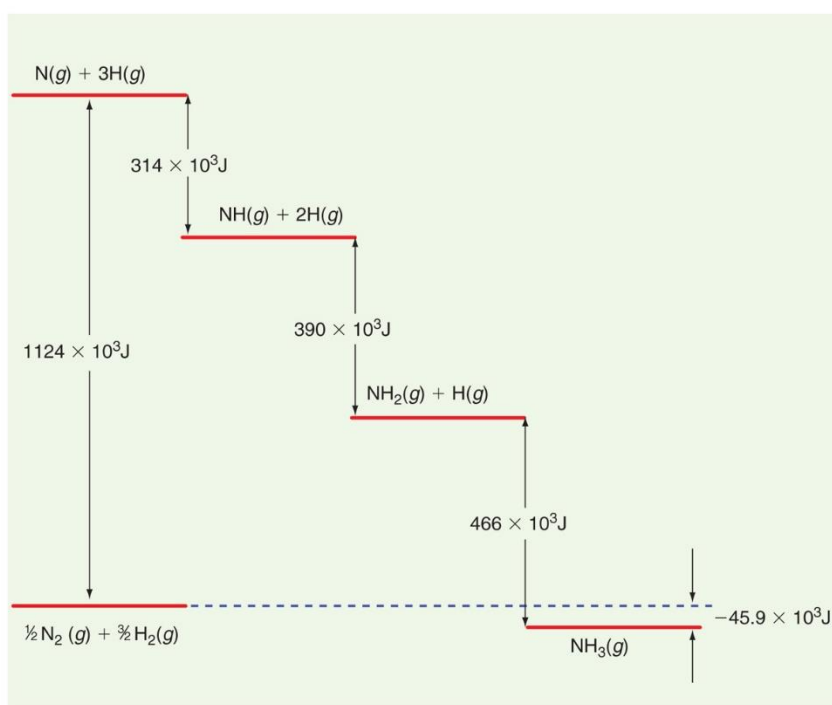
Source: Linstrom, P. J., and Mallard, W. G., eds. *NIST Chemistry Webbook: NIST Standard Reference Database Number 69*. Gaithersburg, MD: National Institute of Standards and Technology. Retrieved from <http://webbook.nist.gov>.

## Thermochemistry

## Engel & Reid chapter 4

The thermochemistry is an interesting part of chemistry. It connects the thermodynamics to chemical reactions. Thermochemistry and reaction kinetics are essential tools for understanding the chemical reactions. We will discuss the kinetics later. In any chemical reaction, each compound have well defined enthalpy if the reaction is in constant pressure.

Example: ammonia forming in gas phase  $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$



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The total reaction enthalpy change is quite small,  $-46 \text{ kJ/mol}$  but it is very difficult to break the  $\text{N}_2$  molecule. In reality, this reaction do not happen in gas phase. It need some catalyst. The thermochemistry is not restricted to gas phase. The reaction can happen in solution, in solid material or on surface.

When tabulating the reaction enthalpy values the pressure is set to 1 atm, the temperature to 298.15 K (25 C) and amount of material is 1 mol. This is called the standard enthalpy of reaction,  $\Delta H_R^\circ$ . The reaction enthalpy is the difference of product and reactant enthalpies

$$\Delta H_R^\circ = H_{\text{prod}}^\circ - H_{\text{react}}^\circ$$

The reaction enthalpies are very useful quantities but there are so many reactions that they are not convenient to list. We can define standard enthalpy of formation  $\Delta H_f^\circ$ . It is the reaction enthalpy of 1 mol of pure material to its most stable form.

This need an example: reaction  $\text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow 3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{l})$

here  $\text{H}_2$  is in it most stable form, so  $\Delta H_f^\circ(\text{H}_2) = 0$ , the formation enthalpy of liquid water is

$$\Delta H_f^\circ(H_2O, l) = H_m^\circ(H_2O, l) - H_m^\circ(H_2, g) - \frac{1}{2}H_m^\circ(O_2, g)$$

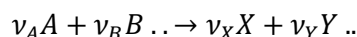
and the formation enthalpy of Fe<sub>3</sub>O<sub>4</sub> is

$$\Delta H_f^\circ(Fe_3O_4, s) = H_m^\circ(Fe_3O_4, s) - H_m^\circ(Fe, s) - 2H_m^\circ(O_2, g)$$

the reaction enthalpy is

$$\Delta H_R^\circ = 4\Delta H_f^\circ(H_2O, l) - \Delta H_f^\circ(Fe_3O_4, s)$$

In more general reaction



the reaction enthalpy is

$$\Delta H_R^\circ = \sum_i \nu_i H_f^\circ(i), \text{ where } \sum_i \nu_i = 0$$

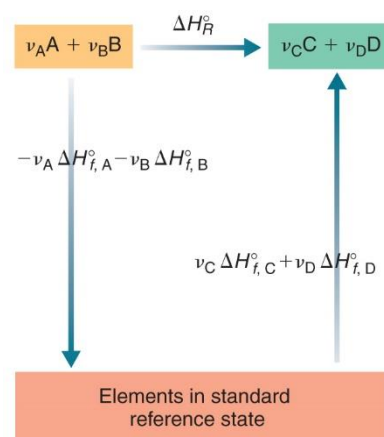
we still have quite many enthalpies in the equations above. It is very convenient to choose the molar enthalpies of pure substances in its most stable form to 0.

$$\Delta H_f^\circ(Fe_3O_4, s) = H_m^\circ(Fe_3O_4, s) - H_m^\circ(Fe, s) - 2H_m^\circ(O_2, g)$$

$H_m^\circ(Fe, s) = 0$  and  $H_m^\circ(O_2, g) = 0$  then  $\Delta H_f^\circ(Fe_3O_4, s) = H_m^\circ(Fe_3O_4, s)$   
this do not change the final reaction enthalpies.

See Table 4.1 and 4.2

What is the formation enthalpy of diamond?

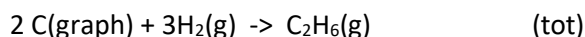


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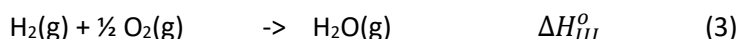
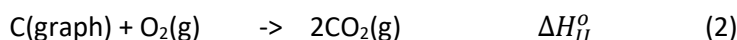
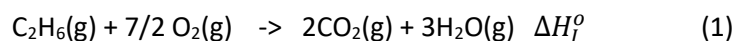
## Hess's law

## Engel & Reid chapter 4.3

Even most of the pure substances enthalpies are known sometimes it is convenient to use other reaction and their enthalpies



one can also use the following oxidation reactions



the reaction (tot) can also be written as  $2*(2) - (1) + 3*(3)$

Excercise: From table 4.1 and 4.2 what are the enthalpies  $\Delta H_I^\circ$ ,  $\Delta H_{II}^\circ$  and  $\Delta H_{III}^\circ$

Go through example 4.1

## Temperature dependence of reaction enthalpy

### Engel & Reid chapter 4.4

The standard conditions are 1 atm pressure and room temperature but how to compute the reaction enthalpies at other temperatures. We can use the heat capacity.

$$\Delta H_R^{\circ}(T) = \Delta H_R^{\circ}(T = 298.15K) + \int_{T_1}^T C_P(T') dT'$$

Go through example 4.2

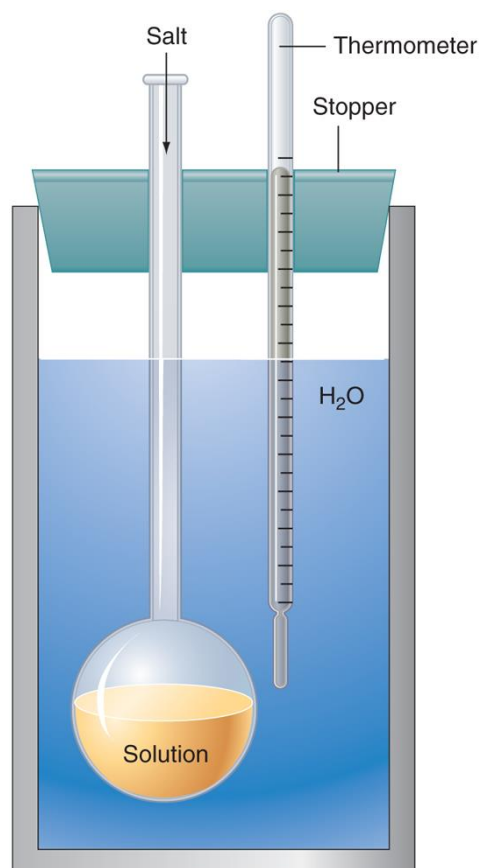
Note that in this example the temperature dependence of heat capacity is taken into account. If this is not known we can assume that the  $C_P$  is constant (and it is listed in table 4.1 and 4.2).

## Calorimeter

### Engel & Reid chapter 4.5

Calorimeter is a device that can be used to determine the enthalpies. A simple example is the measurement of dissociation enthalpies of salts. We can add known amount of salt to water and measure the temperature change of the surrounding water. The whole system needs to be insulated from the environment. The top cap of the container is not tight so the system is in constant pressure (so we measure the enthalpy).

Go through example 4.4





# Entropy and all that

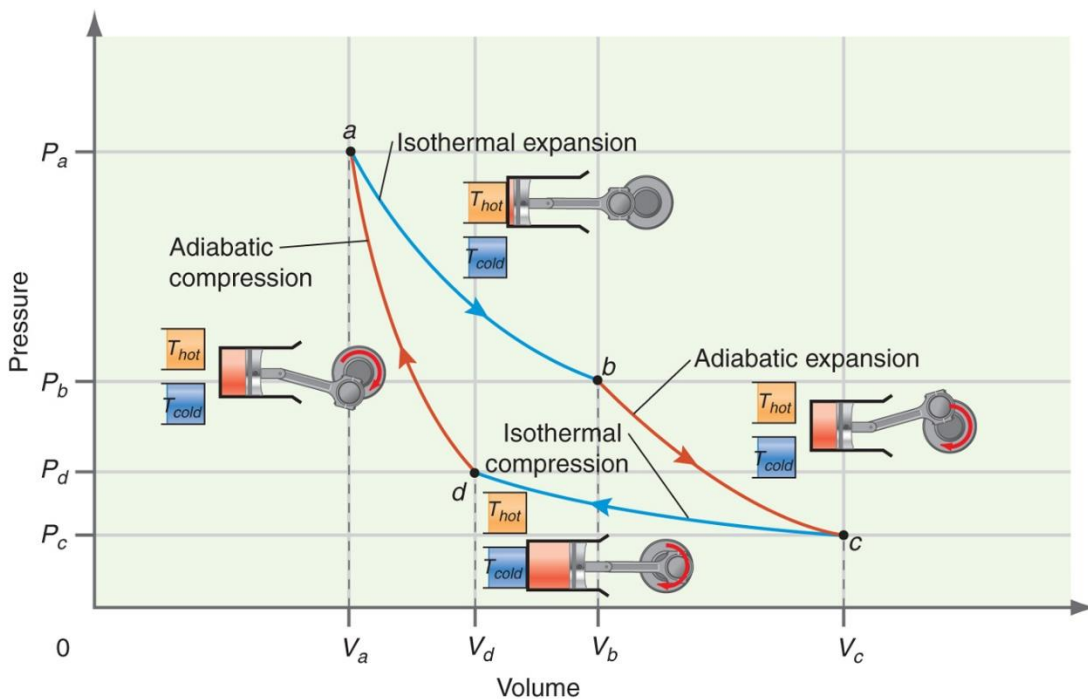
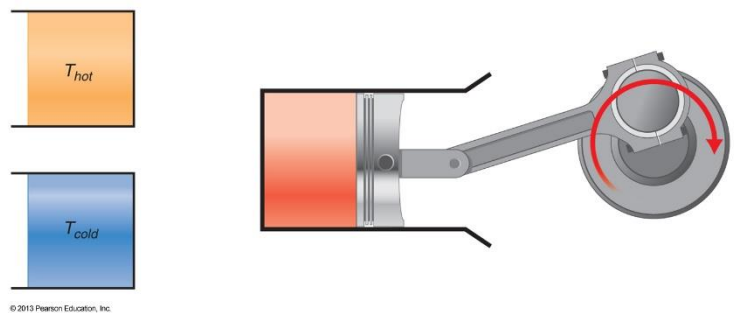
# Engel & Reid chapter 5

So far we have concentrated to energy and enthalpy but there is also a very important quantity, entropy. It can be connect to the order in the system. As an example when water evaporates the entropy increases. The water molecules in gas have a lot of space and they are not well defined spaces. In liquid the molecules have much closer to each other. They can still move but not so rapidly. The entropy increases also when ice melt. In ice the molecules are in fixed positions.

# Heat engine

# Engel & Reid chapter 5.2

The simplest model engine is the heat engine. In consist of two very large temperature reservoirs, a cold and hot one, and an ideal and thermally isolated piston. The piston can be in contact to the hot or cold reservoir. The system can do work in the Carnot cycle. The cycle have four steps.



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Now the work, heat and internal energy in the cycle can be computed.

**TABLE 5.1 Heat, Work, and  $\Delta U$  for the Reversible Carnot Cycle**

Segment	Initial State	Final State	$q$	$w$	$\Delta U$
$a \rightarrow b$	$P_a, V_a, T_{hot}$	$P_b, V_b, T_{hot}$	$q_{ab} (+)$	$w_{ab} (-)$	$\Delta U_{ab} = 0$
$b \rightarrow c$	$P_b, V_b, T_{hot}$	$P_c, V_c, T_{cold}$	0	$w_{bc} (-)$	$\Delta U_{bc} = w_{bc}(-)$
$c \rightarrow d$	$P_c, V_c, T_{cold}$	$P_d, V_d, T_{cold}$	$q_{cd} (-)$	$w_{cd} (+)$	$\Delta U_{cd} = 0$
$d \rightarrow a$	$P_d, V_d, T_{cold}$	$P_a, V_a, T_{hot}$	0	$w_{da} (+)$	$\Delta U_{da} = w_{da}(+)$
Cycle	$P_a, V_a, T_{hot}$	$P_a, V_a, T_{hot}$	$q_{ab} + q_{cd} (+)$	$w_{ab} + w_{bc} + w_{cd} + w_{da} (-)$	$\Delta U_{cycle} = 0$

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The heat in the cycle is  $q_{ab} + q_{cd}$  but because the cycle  $U=0$  the total work is  $-(q_{ab} + q_{cd})$ . We can always get less work out of the system than the thermal processes provide. So the  $w_{cycle} < 0$  or  $|q_{ab}| > |q_{cd}|$ .

The efficiency of the Carnot engine is

$$\epsilon = \frac{w_{cycle}}{q_{ab}} = 1 - \frac{|q_{cd}|}{|q_{ab}|}$$

The second law of thermodynamics

---

*It is impossible to take more energy out from a heat engine than will flow in from the temperature reservoirs*

---

We can also rewrite the efficiency in a more useful form in the case of ideal gas. See the equations 5.5 and 5.6 in the book.

$$\epsilon = 1 - \frac{T_{cold}}{T_{hot}}$$

this is a very simple equation and it tells that the higher the temperature difference is the more efficient the engine can be. This is for an ideal engine but all real engines have temperature leaks, friction and the gases are not ideal so the real efficiency is always lower than this theoretical value. The key information is that the higher the temperature difference is the higher the efficiency. Thus the diesel engine is more efficient than gasoline engine.

## Entropy

## Engel & Reid chapter 5.3

The entropy is a bit difficult concept in thermodynamics but it is very important. We can use the efficiency equations to define entropy.

$$\epsilon = 1 - \frac{T_{cold}}{T_{hot}} = \frac{q_{ab} + q_{cd}}{q_{ab}} \Rightarrow \frac{q_{ab}}{T_{hot}} + \frac{q_{cd}}{T_{cold}} = 0$$

the later part can be generalize to the reversible heat and for heat cycle we can write

$$\oint \frac{dq_{reverser}}{T} = 0$$

where the integral is over the whole cycle. We will define entropy, S, as

$$dS = \frac{dq_{reverser}}{T}$$

and

$$\Delta S = \int \frac{dq_{reverser}}{T}$$

Entropy is a state function.

Some examples:

Reversible isothermal compression of ideal gas,  $V_i \rightarrow V_f$

$$q_{reverser} = nRT \ln \frac{V_f}{V_i}, \quad \Delta S = \int \frac{dq_{reverser}}{T} = nR \ln \frac{V_f}{V_i}$$

in constant pressure and temperature change,  $T_i \rightarrow T_f$ ,

$$q_{reverser} = C_p dT, \quad \Delta S = \int \frac{nC_{p,m} dT}{T} \approx nC_{p,m} \ln \frac{T_f}{T_i}$$

here we assume that the  $C_p$  is constant in the temperature interval. In the case of constant volume we can change the P to V.

Because the entropy is a state function it can be computed easily for  $V_i T_i \rightarrow V_f T_f$  process

$$\Delta S \approx nR \ln \frac{V_f}{V_i} + nC_{v,m} \ln \frac{T_f}{T_i}$$

and  $P_i T_i \rightarrow P_f T_f$  process

$$\Delta S \approx nR \ln \frac{P_f}{P_i} + nC_{p,m} \ln \frac{T_f}{T_i}$$

Go through example 5.4

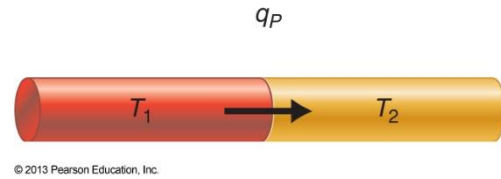
What are the contribution of the  $\int \frac{nC_{v,m} dT}{T}$  and  $nR \ln \frac{V_f}{V_i}$  terms?

Go through example 5.5 and 5.6

In isolated system the entropy will always increase  
Reid chapter 5.5

Engel &

If we study entropy change in isolated system we will find that in realistic processes the entropy will always increase. We can first look an isolated (metal) rod, which left half have initial temperature  $T_1$  and the right one  $T_2$ . The metal will conduct heat and there will be a change of heat of  $q_p$ . The heat will flow from hot to cool part of the rod. Assume the  $T_1$  part will give  $q_p$  amount of heat.



The initial entropy change is (we do not consider the temperature change or equilibration)

$$\Delta S = \int \frac{dq_{revers}}{T} = \frac{q_p}{T_1} - \frac{q_p}{T_2} = q_p \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

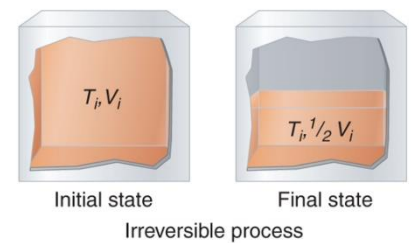
the  $q_p$  is negative because the hot part will lose heat. If  $T_1 > T_2$  the entropy increases.

Another example: we can study a gas system with initial state of  $T_i V_i$  which will spontaneously (irreversibly) and isothermally located to half of the volume. The entropy change of this process is

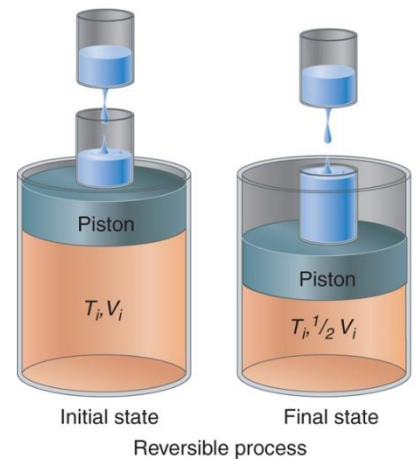
$$\Delta S = nR \ln \frac{V_f}{V_i} = nR \ln \frac{1/2 V_i}{V_i} = nR \ln \frac{1}{2} = -nR \ln 2$$

the entropy change is negative but the process is absurd. The reverse process is realistic and its entropy change is  $nR \ln 2$  which is positive.

Note that the entropy change can be negative if some external work is done, like in example (b).



(a)



(b)

## Clausius Inequality Engel & Reid chapter 5.6

For irreversible process

$$\Delta S > \frac{dq}{T}$$

for isolated system  $dq = 0$  but if the process is irreversible the  $\Delta S > 0$ .

## Entropy of system and surrounding Engel & Reid chapter 5.7

Go through example 5.7

In the piston example above (b) the entropy change of the system is negative ( $V_f < V_i$ )

$$\Delta S_{system} = nR \ln \frac{V_f}{V_i}$$

there is heat transfer from the piston to the surrounding  $q_{surroun} = -q_{system}$  and then the entropy of the surrounding is

$$\Delta S_{surroun} = -\Delta S_{system}$$

and total entropy = 0. Note the compression is done reversibly.

Go carefully through example 5.8

What is the difference between 5.7 and 5.8.

The process 5.8 is irreversible and thus the total entropy is positive.

In any real process

$$\Delta S_{tot} > 0$$

## Absolute entropy

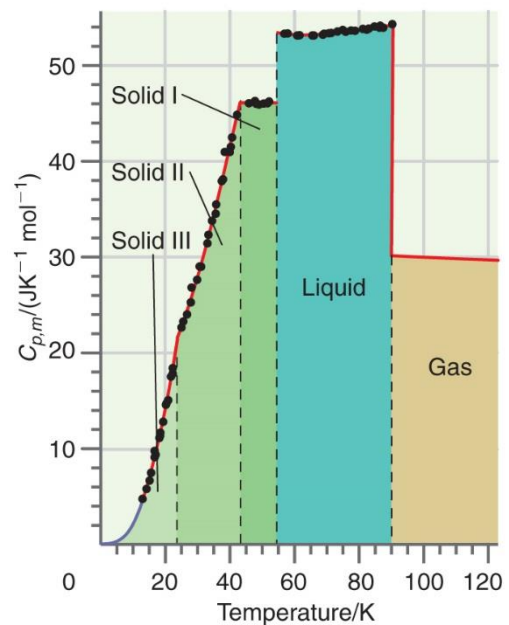
## Engel & Reid chapter 5.8

We can also compute the absolute entropy by integrating the heat capacity. At constant pressure the entropy is

$$S_m(T) = S_m(0K) + \int_0^{T_f} \frac{C_{P,m,sol}(T')dT'}{T'} + \frac{\Delta H_{fusion}}{T_f} + \int_{T_f}^{T_b} \frac{C_{P,m,liq}(T')dT'}{T'} + \frac{\Delta H_{vapor}}{T_b} + \int_{T_b}^T \frac{C_{P,m,gas}(T')dT'}{T'}$$

where the  $C_{P,m,sol}(T)$  solid heat capacity, liq note the liquid and gas the gas. The  $H_{fusion}$  is the enthalpy related to melting and  $H_{vapor}$  the enthalpy of vaporization.  $T_f$  is the freezing temperature,  $T_b$  boiling temp. If there are phase transitions of the solid the enthalpies of them need to be taken into account.

At low temperatures the solid heat capacity is close to 0 also at 0K the entropy is =0. This is the third law of thermodynamics



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*Entropy at 0 K of a pure and perfect crystalline material is 0.*

---

Go through example 5.9

Standard state entropy. As for the enthalpy we can tabulate the molar entropy at 1 atm pressure and 298.15 K.

$$S_m(P) = S_m^0 - T \ln \frac{P}{1 \text{ atm}}$$

note that at very low pressures the entropy become very large.

## Reaction entropy

## Engel & Reid chapter 5.10

As we know the absolute entropies of compounds we can define the reaction  $\nu_A A + \nu_B B \dots \rightarrow \nu_X X + \nu_Y Y \dots$  entropy simply as

$$\Delta S_R^0 = \sum_i \nu_i S_i^0$$

the reaction  $\text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow 3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{l})$  entropy is  $-308.9 \text{ J}/(\text{K mol})$  (see the details in chapter 5.10). This is strongly negative since the hydrogen gas have high entropy and it is consumed in the reaction.

The entropy at different temperatures can be using equation

$$S_m(T) = S_m^0 + \int_{298.15}^{T_f} \frac{\Delta C_{p,m}(T') dT'}{T'}$$

Go through example 5.10

## Heat pumps, car engines etc.

## Engel & Reid chapter 5.11

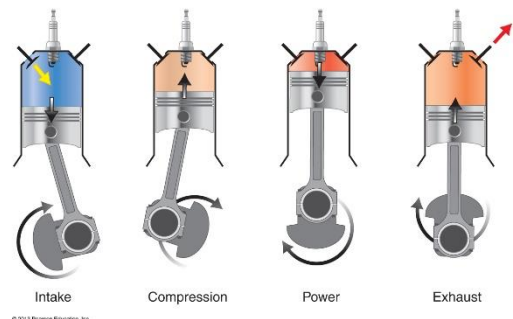
There are several interesting examples of real application in this chapter. Read it.

The refrigerator is a good example of a heat engine. It uses electricity to keep its interior cool. Its performance can be computed as

$$\eta = \frac{T_{cold}}{T_{hot} - T_{cold}}$$

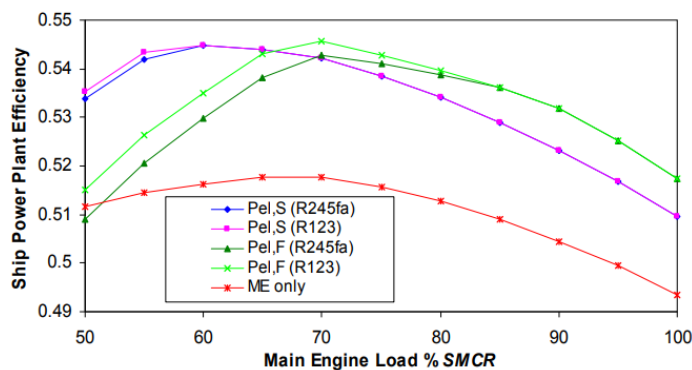
the typical temperature are  $T_{cold} = 277 \text{ K}$  and  $T_{hot} = 294 \text{ K}$  then the theoretical efficiency is 6.5. This is far from real refrigerators. The book quote factor 1.5 but the European refrigerators are better.

The heat engine principles can be used for combustion engines. The gasoline engine will not have very high combustion temperature since the gasoline will ignite itself at temperature above ca. 600 K. The cold part of the engine is around  $100^\circ\text{C}$  or 370 K (the temperature of the cooling system) then the ideal efficiency is  $1 - 370/600 = 38\%$ . The friction and use in non-ideal range; the real efficiency is around 20 – 30 %.



The diesel engine will operate at much higher temperatures. The diesel fuel will be injected to the hot cylinder at the end of compression. The maximum temperature is cs. 950 K. The efficiency is  $1 - 370/950 = 61\%$ . The book has more complex analysis and with that the efficiency of 64 %. These again are unrealistic values and the real car diesel engines have efficiency around 30 to 35 %.

The large marine engines can have efficiency above 50 %. (from Energies 2015, 8, page 4292)



**Figure 19.** Ship Power Plant Efficiency with organic fluids— $\eta_{p,ship}$  (power only).

Wärtsilä make the most efficient marine engines.

<https://www.wartsila.com/marine/build/engines-and-generating-sets/diesel-engines/wartsila-31>

Note that the electric cars engine efficiency is close to 100 %. It is not a heat engine.

## Chemical equilibrium

## Engel & Reid chapter 6

The entropy can be combined to thermodynamical energy. We know from the Clausius inequality that  $TdS > dq$ . In a constant temperature process we can write

$$d(U - TS) \leq dw_{tot} = dw_{expansion} + dw_{nonexpan}$$

the  $w_{expansion}$  is the expansion work done to the system (and  $w_{nonexpan}$  nonexpansion work). The left hand of the equation is interesting. We can define the **Helmholtz energy** as  $A=U-TS$ . The Helmholtz energy describe the maximum amount of work that can be done by a chemical reaction. The entropy part is important since the disorder in the reaction often increases and not all the energy can be used.

Go through example 6.1

Above the temperature was assumed to be constant.  $dT=0$ , if we choose also the constant volume,  $dV=0$  then the  $dw_{expansion} = 0$  and if the  $dw_{nonexpan} = 0$  the in this process the  $dA \leq 0$ .

As discussed before the constant volume systems are not common in chemistry, whereas the constant pressure is the normal case. In constant pressure, the proper energy is the enthalpy and here we can define **Gibbs energy** as  $G=H-TS$ .

$$dG - dw_{nonexpan} \leq 0$$

The Gibbs energy is the maximum nonexpansion work the system can do

Go through example 6.2

Look the differences of the results in 6.1 and 6.2. Comments?

## Gibbs reaction energy

Engel & Reid chapter 6.1

Again we can define Gibbs reaction energy

$$\Delta G_R^0 = \Delta H_R^0 - T\Delta S_R^0 = \sum_i \nu_i G_i^0$$

usually in chemical reaction no nonexpansion work is done so for spontaneous reactions

$$\Delta G_R^0 \leq 0$$

- if  $\Delta H_R^0 < 0$  and  $\Delta S_R^0 > 0$ , an exothermic reactions where entropy increases, the reaction is always spontaneous.
- if  $\Delta H_R^0 > 0$  and  $\Delta S_R^0 < 0$ , an endothermic reactions where entropy decreases, the reaction is never spontaneous.
- if  $\Delta H_R^0 > 0$  and  $\Delta S_R^0 > 0$  or if  $\Delta H_R^0 < 0$  and  $\Delta S_R^0 < 0$  the temperature and the magnitude of the terms determine does the reaction happen.

Note that at low temperatures the enthalpy dominates and at high temperatures the TS term.

The  $\Delta G_R^0$  have connections to chemical equilibrium and kinetics.

## Go through Engel & Reid chapter 6.2

### Temperature dependence of G

Engel & Reid chapter 6.3

Again mostly read 6.2

$$\int_{P^0}^P dG = \int_{P^0}^P V dP'$$

for liquids V is mostly constant

$$G(T, P) = G(T, P^0) + V(P - P^0)$$

for ideal gas

$$G(T, P) = G(T, P^0) + nRT \ln \frac{P}{P^0}$$

from Gibbs-Helmholtz equation

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H(T_1) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

here we assume that the enthalpy do not change much.

Go through example 6.4

## G and concentration changes

Engel & Reid chapter 6.4



So far we have not consider the concentration changes but the do change in chemical reactions. Often the starting materials are nearly fully consumed, so their concentrations at the end of reaction is close to 0. How this is put to thermodynamics.

The Gibbs energy will depend also on the concentrations,  $G(T,P,n_1,n_2,..)$

The derivative with respect of the concentrations is called the **chemical potential**,  $\mu$

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j, j \neq i}$$

For a pure system the chemical potential and molar Gibbs energy are identical.  $G=nG_m$

$$\mu_A = \left( \frac{\partial G}{\partial n_A} \right)_{T,P} = \left( \frac{\partial n_A G_{m,A}}{\partial n_A} \right)_{T,P} = G_{m,A}$$

This is not true for mixtures.

The chemical potential have very intuitive property. Let us assume a specie to have chemical potential  $\mu^I$  in one part of the system and  $\mu^{II}$  in the other.  $\mu^I > \mu^{II}$ . If the molecules can flow (change of  $dn$ ) form one system to another the Gibbs energy change

$$\Delta G = -\mu^I dn + \mu^{II} dn = (\mu^{II} - \mu^I) dn < 0$$

The flow occur, as long the two chemical potentials are equal.

Example: The water gas-liquid equilibrium. At every temperature the water vapor have some partial pressure, and the gas and liquid chemical potentials are equal.

## G for gas mixtures

## Engel & Reid chapter 6.5

Let us look a system where a gas (here hydrogen) and penetrate through a membrane to the right to gas b (here argon). The argon cannot go to left. What is the Gibbs energy of this system and final pressure of  $H_2$ . At equilibrium

$$\mu_{pure.H_2} = \mu_{mixt.H_2}$$

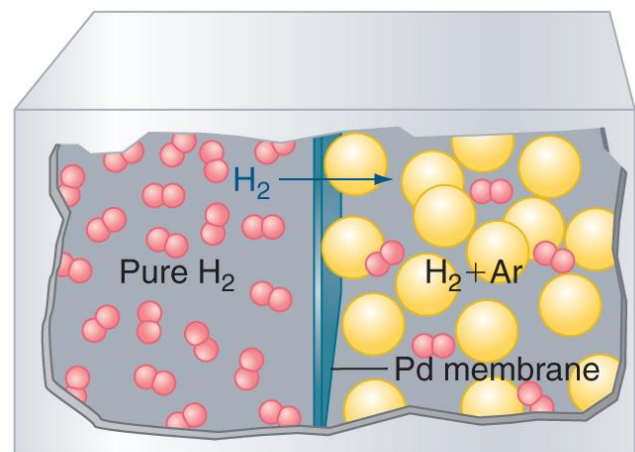
the chemical potential of the pure gas at pressure  $P_{H_2}$  is

$$\mu_{pure.H_2} = \mu_{H_2}^o + RT \ln \frac{P_{H_2}}{P^o}$$

in the mixture the  $H_2$  pressure is  $x_H P$  where  $x_H$  is the mole fraction of hydrogen and the chemical potential is

$$\mu_{mixt.H_2} = \mu_{H_2}^o + RT \ln \frac{x_H P}{P^o}$$

in equilibrium  $P_{H_2} = x_H P$  so the hydrogen pressure is the same on both sides.



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## G of gas mixing

## Engel & Reid chapter 6.6

Next we compute the Gibbs energy of gas mixing. If we have several gases, like He, Ne, Ar, Xe and we let them to mix what is the G. The system has total pressure P and the mole fractions:  $x_{He}$ ,  $x_{Ar}$ ,  $x_{Ne}$ , and  $x_{Xe}$ . (the amount of He is  $n_{He} = x_{He}n$ , where n is total amount of the gases.)

$$\begin{aligned} G_{tot} &= n_{He}(G_{m,He} + RT \ln x_{He}) + n_{Ne}(G_{m,Ne} + RT \ln x_{Ne}) + \dots + nRT \ln \frac{P}{P^o} \\ &= n_{He}G_{m,He} + \dots + nRT(x_{He} \ln x_{He} + \dots) + nRT \ln \frac{P}{P^o} \end{aligned}$$

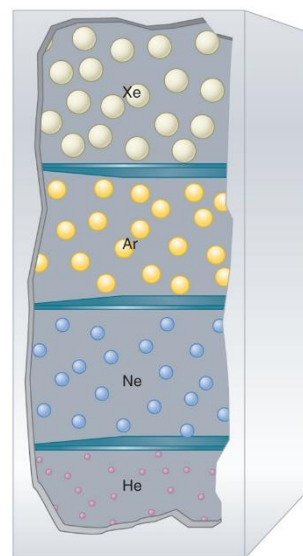
the  $x \ln x$  term is the Gibbs energy of mixing. This term would be missing if the gases were in separated containers (figure on right). In general the mixing Gibbs energy is

$$G_{mix} = nRT \sum_i x_i \ln x_i$$

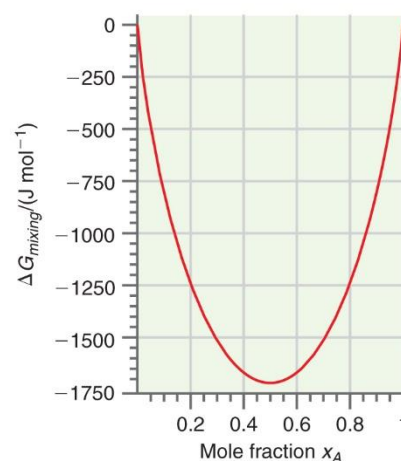
where the  $x_i$ 's are mole fractions. The  $x < 1$  thus the  $G_{mix}$  is negative and the process is spontaneous. The mixing entropy can be computed as

$$S_{mix} = -\left(\frac{\partial G}{\partial T}\right)_P = -nR \sum_i x_i \ln x_i$$

the mixing Gibbs energy is easy to plot for binary system. It has its minima at  $x=0.5$ .



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## Gibbs energy for chemical reaction Engel & Reid chapter 6.7

This is one of the most important equations in chemistry. It will tell will the reactions happen and its equilibrium constant. We have has the equation before:

$$\Delta G_R^o = \sum_i \nu_i G_i^o$$

Go through example 6.6

Go through example 6.7

Why the  $\Delta G_R^o$  is so sensitive to the temperature. (Answer: TS term)

## Chemical equilibrium

## Engel & Reid chapter 6.8

The equilibrium constant can be computed using the Gibbs energy. In principle this is simple since at equilibrium  $\Delta G_R = 0$

Let us look at a very simple reaction  $\alpha A(g) \leftrightarrow \beta B(g)$  (a more complex reaction is in the book). The gases have partial pressures of  $P_A$  and  $P_B$ .

$$\Delta G_R = \beta \mu_B + \beta RT \ln \frac{P_B}{P^o} - \alpha \mu_A - \alpha RT \ln \frac{P_A}{P^o} = \Delta G_R^o + RT \ln \frac{P_B^\beta P_A^{-\alpha}}{P^o^{\beta-\alpha}} = \Delta G_R^o + RT \ln Q_P$$

In equilibrium  $\Delta G_R = 0$  or  $\Delta G_R^o = -RT \ln Q_P$ . In this case the  $Q_P$  can be called the equilibrium constant  $K_P$

$$\Delta G_R^o = -RT \ln K_P \quad \text{or} \quad K_P = \exp(-\Delta G_R^o / RT)$$

the  $\Delta G_R^o$  depend only on temperature and thus the  $K_P$  also depend only in temperature. This is a bit confusing since  $Q$  have the pressures but the  $K$  is at equilibrium. ( $K$  do not have dimension.) For example is one of the gas pressure is changed the other equilibrium pressures will change such that  $K_P$  stays constant. On the other hand,  $K_P$  is very sensitive to the temperature.

Go through example 6.8 and 6.9

Note that all reactions will have some reactants and products, sometimes very little but something still.

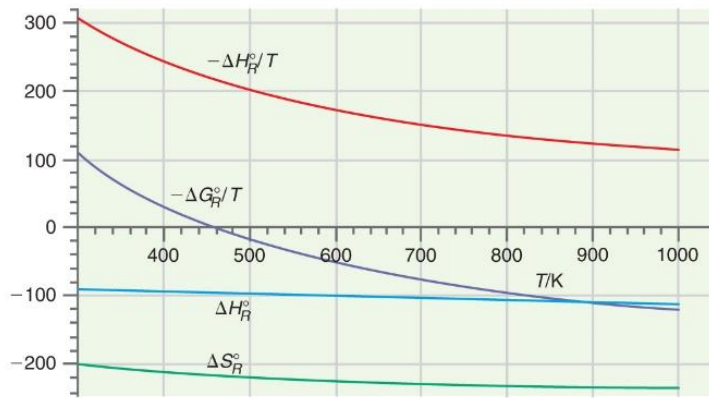
Go through example 6.10

why the mole fractions are  $(n_0 - \delta_{eq}) / (n_0 + \delta_{eq})$  and  $2\delta_{eq} / (n_0 + \delta_{eq})$

## Temperature dependence of $K_P$

## Engel & Reid chapter 6.10

The equilibrium constant has strong temperature dependence due to the exp function  $K_P = \exp(-\Delta G_R^o / RT)$ . How is the temperature dependence of Gibbs energy,  $\Delta G_R^o = \Delta H_R^o - T\Delta S_R^o$  or  $\Delta G_R^o / T = \Delta H_R^o / T - \Delta S_R^o$  here the main temperature dependence comes from the  $H/T$ , both  $H$  and  $S$  do not vary much over temperature.



(a)

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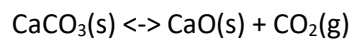
Go through example 6.11 (Reaction  $\text{Cl}_2 \leftrightarrow 2\text{Cl}$ )

Note the very large differences of  $K_p$ ,  $K_p(800\text{K}) = 4.22 \times 10^{-11}$ ,  $K_p(1500\text{K}) = 1.03 \times 10^{-3}$  and  $K_p(2000\text{K}) = 0.134$ . The Cl-Cl bond is quite strong.

## Liquid gas equilibrium

Engel & Reid chapter 6.11

The equilibrium coefficient is not limited to gas phase reactions. It is general and it can be used to any reaction. For example



the Gibbs energy is  $\Delta G_R = \mu_{eq}(\text{CaO}, s, P) + \mu_{eq}(\text{CO}_2, g, P) - \mu_{eq}(\text{CaCO}_3, s, P) = 0$  the chemical potential of solid materials have very small pressure dependence and we can replace them with 1 atm values

$$\mu^o(\text{CaO}, s) + \mu^o(\text{CO}_2, g) - \mu^o(\text{CaCO}_3, s) + RT \ln \frac{P_{\text{CO}_2}}{P^o} = 0 \quad \text{and} \quad \mu^o(\text{CaO}, s) + \mu^o(\text{CO}_2, g) - \mu^o(\text{CaCO}_3, s) = \Delta G_R^o$$

$$\ln K_p = \ln \frac{P_{\text{CO}_2}}{P^o} = -\frac{\Delta G_R^o}{RT}$$

so the gas pressure depend on the  $\Delta G_R^o$

Go through example 6.12

The problem 6.13 is interesting since it tells at which pressure diamond become more stable than graphite. In principle the diamonds are unstable at ambient conditions but luckily the transformation is very slow. ("Diamonds are NOT forever")

Go through example 6.13

## Ammonia synthesis

Engel & Reid chapter 6.14

This is an interesting example but we may go it through later if time allows.

## 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 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

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

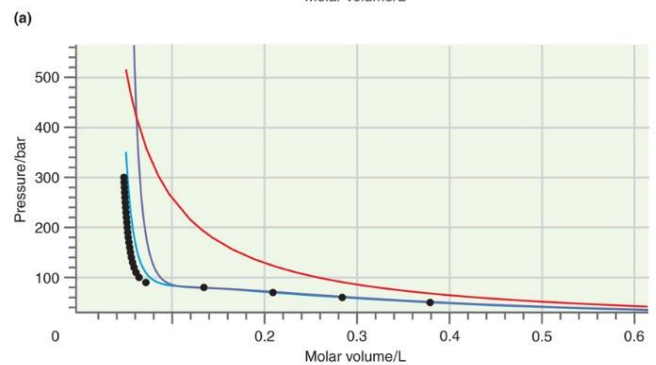
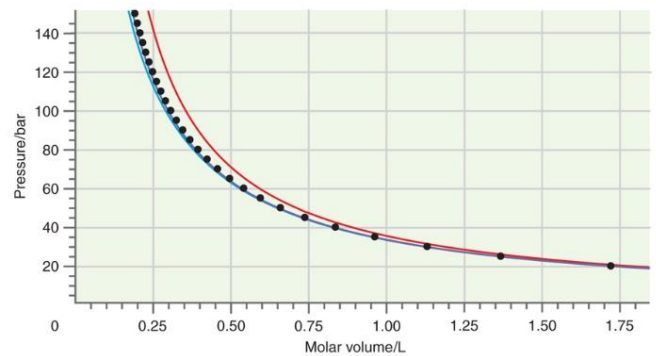
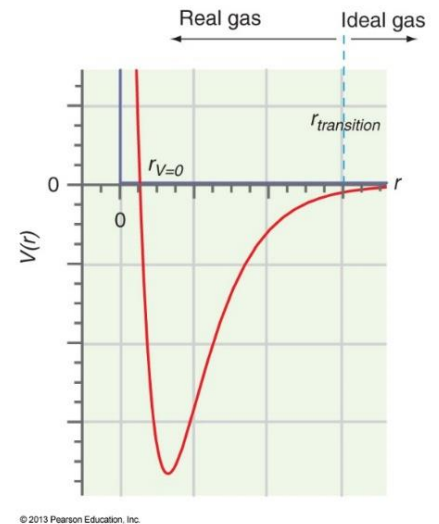
the  $a$  and  $b$  are empirical gas dependent parameters. See Table 7.4. (Appendix A). Note that parameter  $b$  is related to the molecules volume.

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

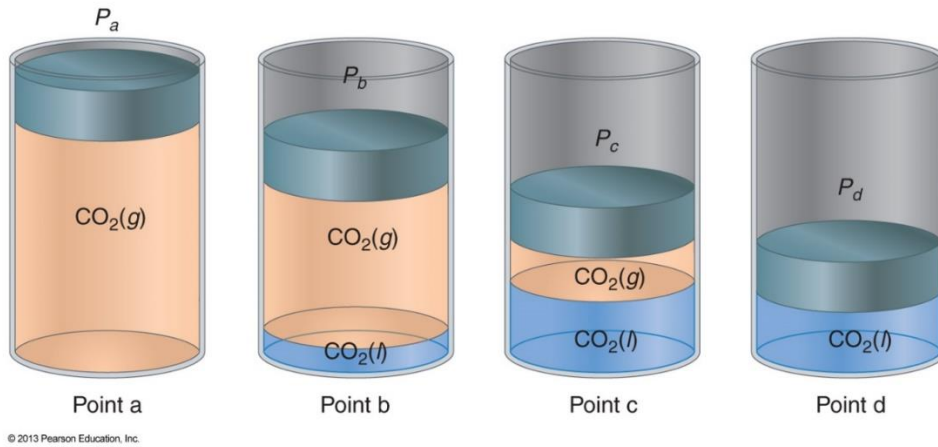
$$P = RT \left( \frac{1}{V_m} + \frac{B(T)}{V_m^2} + \frac{C(T)}{V_m^3} + \dots \right)$$

As one can expect the ideal gas equation does not work close to the boiling point. On the left is the P-V diagrams of CO<sub>2</sub>. The one above (a) is at 426 K and the lower at 310 K (the boiling point of CO<sub>2</sub> is 304 K at 76 bar.)

To understand better the liquid-gas behavior we need to look what happens in a pressure experiment. When the gas compresses 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<sub>2</sub> 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.

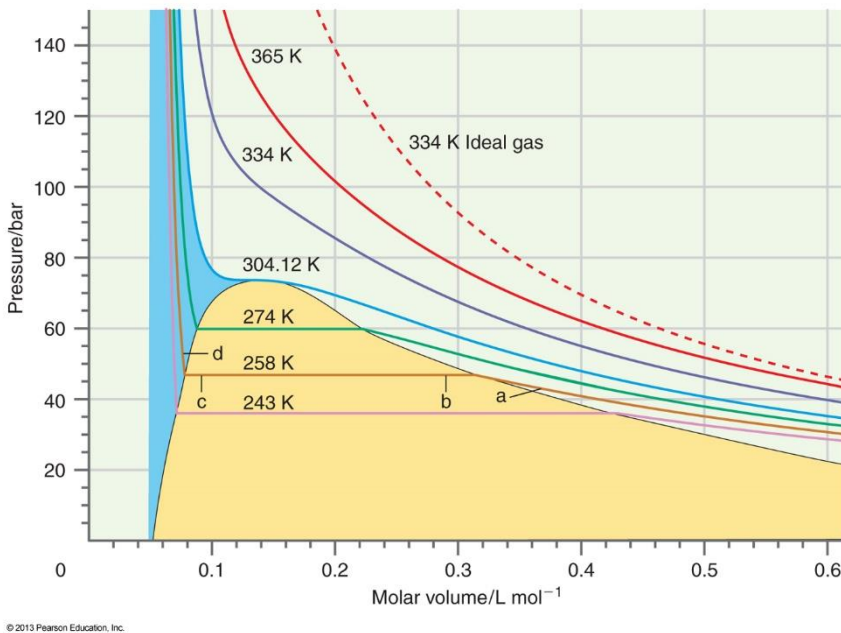


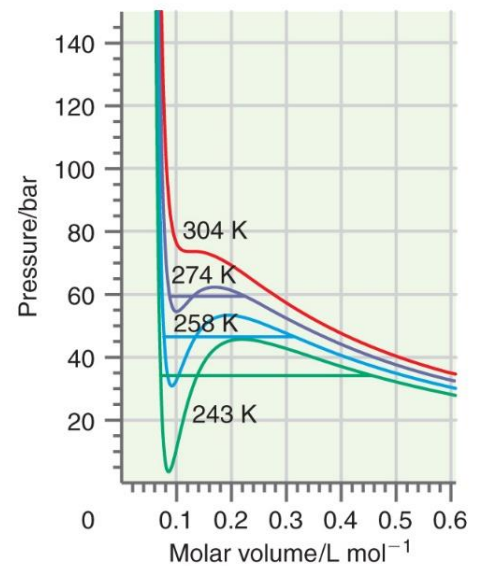
Figure 7.2 Isotherms of CO<sub>2</sub>

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 parameter 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.



## Compression factor Engel & Reid chapter 7.3

We see from the figure 7.2 that the ideal gas law give 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.

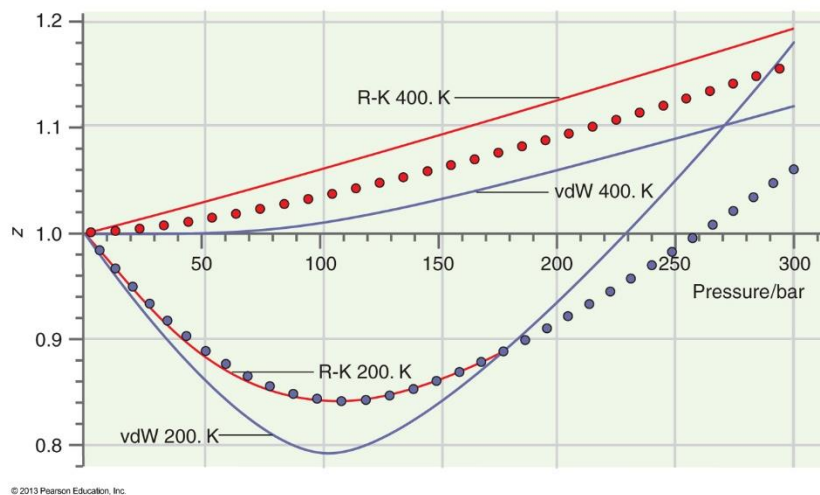
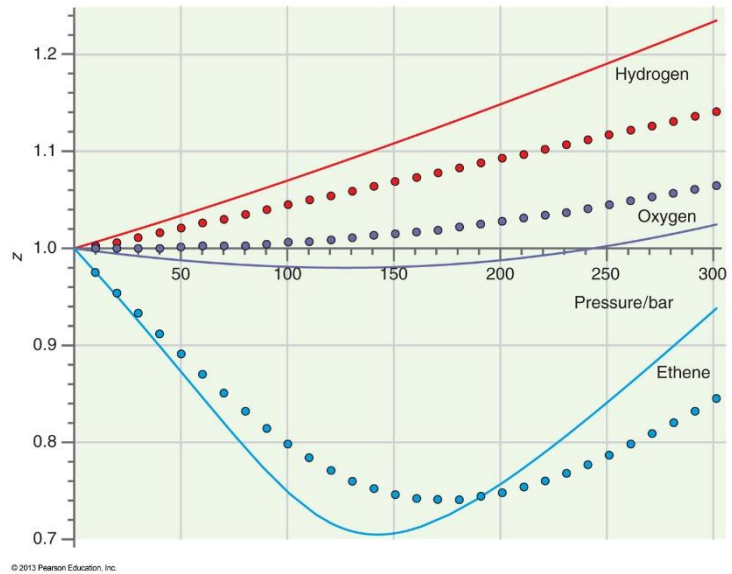


Figure 7.5: data for  $N_2$ .

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 depend from 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 the cancel each other and the ideal gas law is "better" than it should be.



## Corresponding states

## Engel & Reid chapter 7.4

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

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

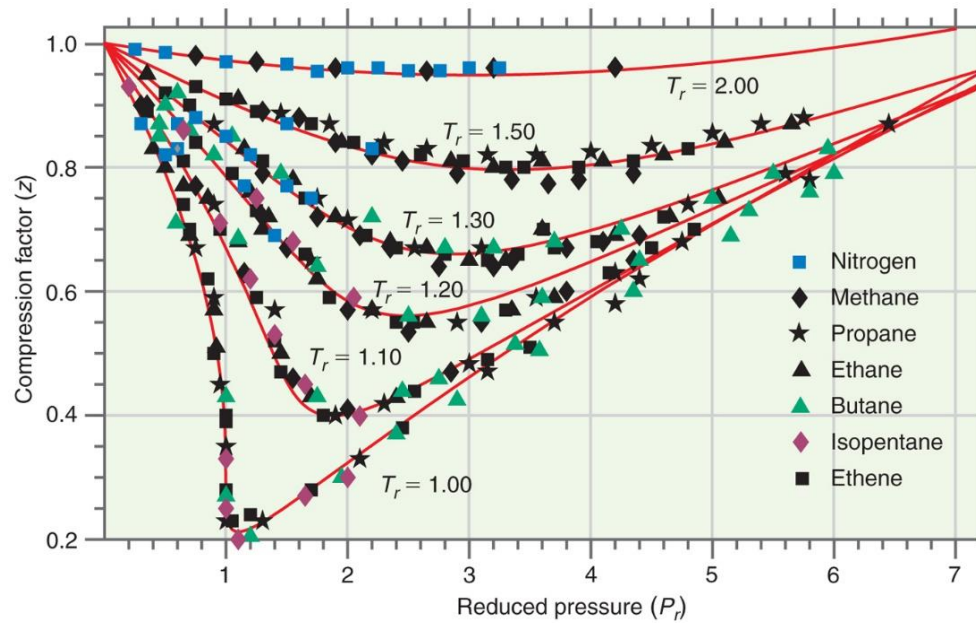
The reduced van der Waals equation is very convenient (the derivation is in the book)

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

this does not depend on the gas parameter  $a$  and  $b$ . It valid for ALL gases. This is rather surprising results and we need to see how this work with the 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 parameter 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

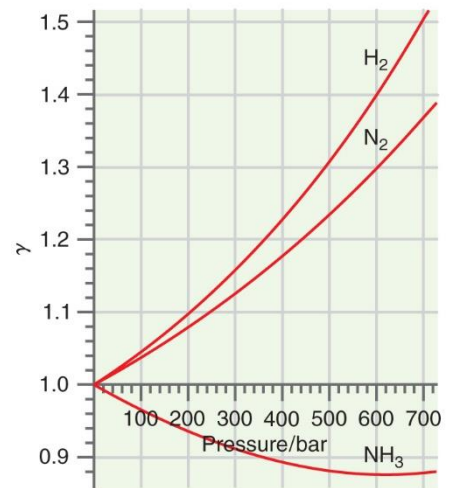
$$\mu^{real}(T, P) - \mu^{ideal}(T, P) = \int_0^P (V_m^{real} - V_m^{ideal}) dP'$$

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  $\gamma$ ,  $f = \gamma(T, P)P$ .

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.



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An interesting fugacity calculator for water.

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

# Phase diagrams

# Engel & Reid chapter 8

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. Often 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)

$$d\mu = -S_m dT + V_m dP$$

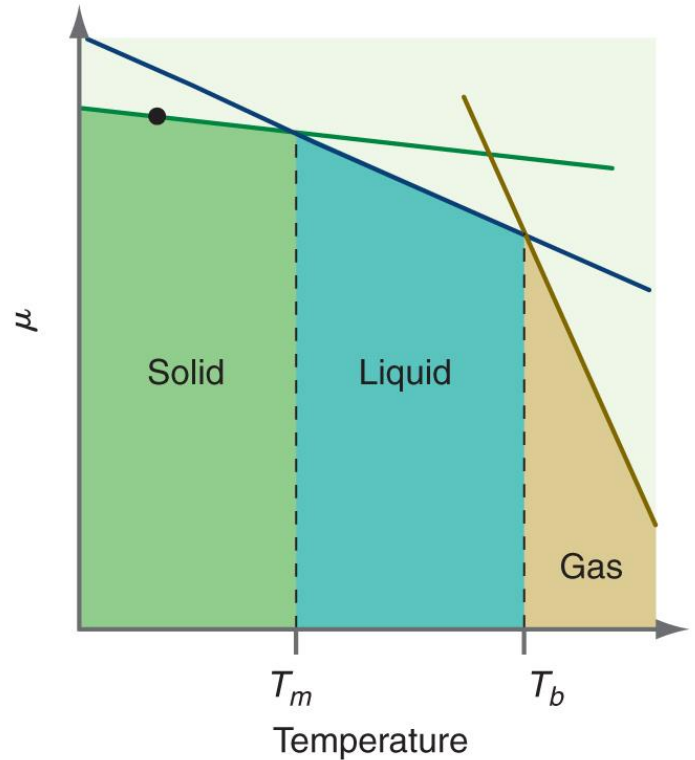
and

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

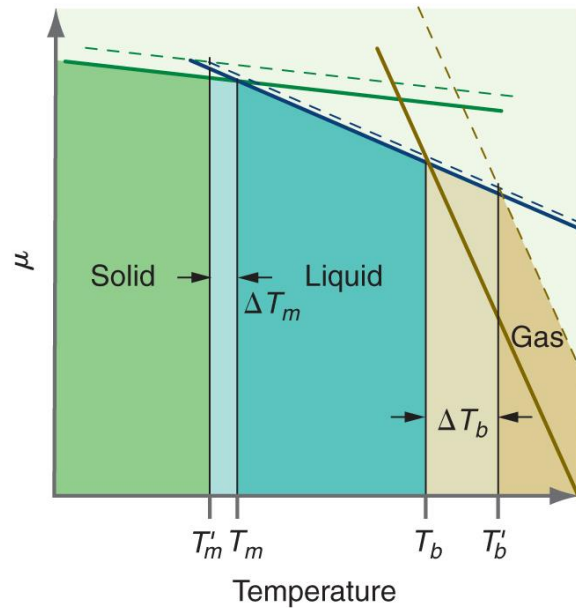
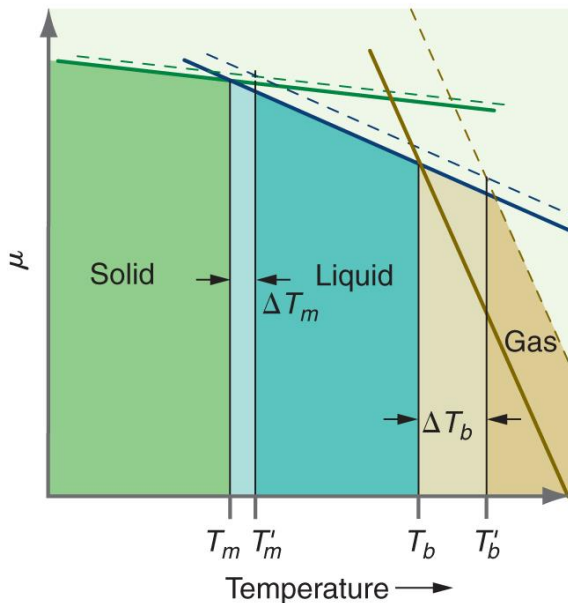
The entropy and volume are always positive. If the pressure changes are small the  $\mu$  decrease with T. The entropy of different phases increases

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

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 and liquid and solid less but in all cases the  $\mu$  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,  $V_m^{liq} < V_m^{solid}$ .



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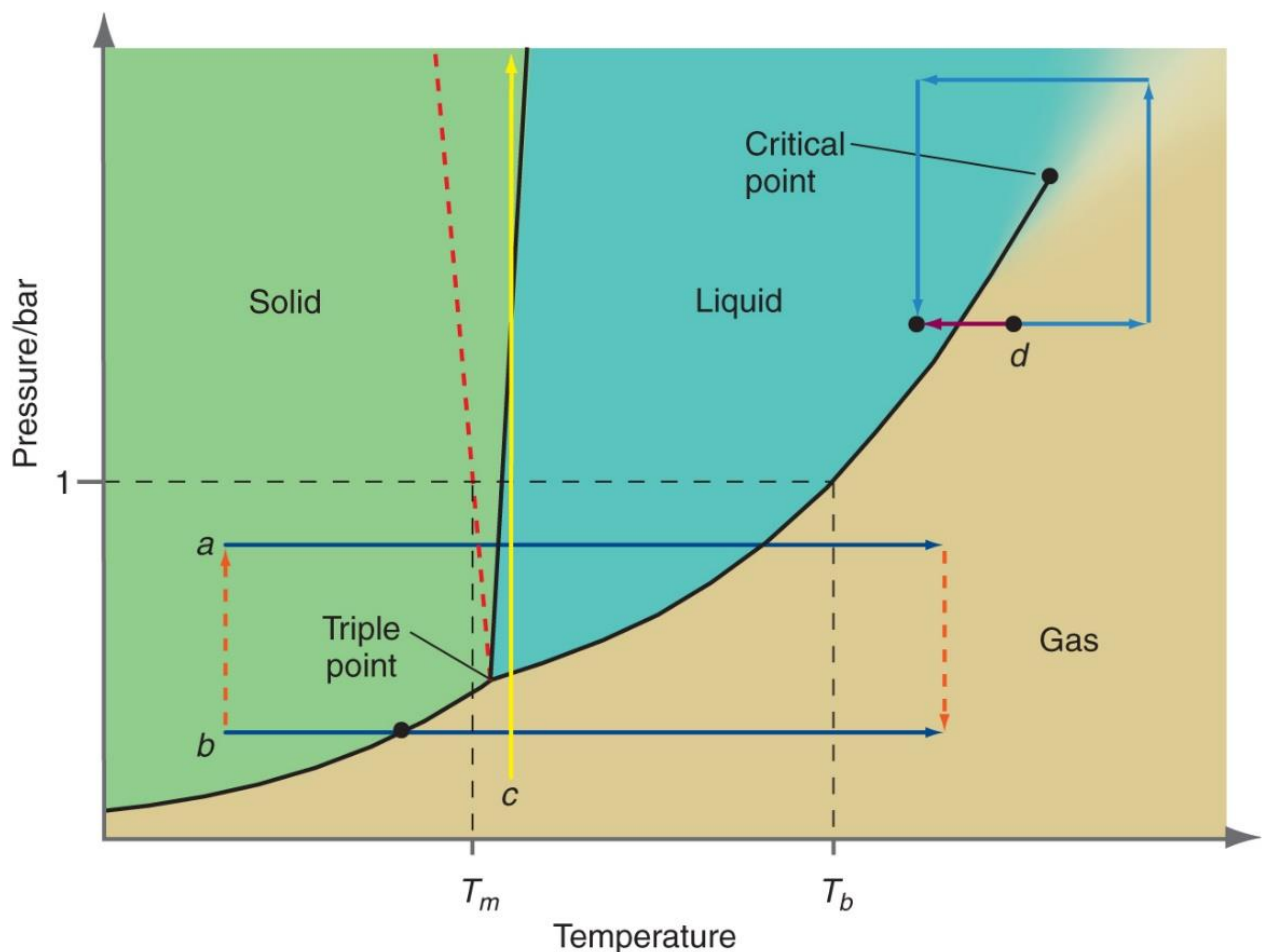


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Note that the boiling temperature always increase with the pressure but the direction of the melting temperature depend on the liquid and solid molar volumes.

## 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. They contain 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<sub>2</sub> 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.

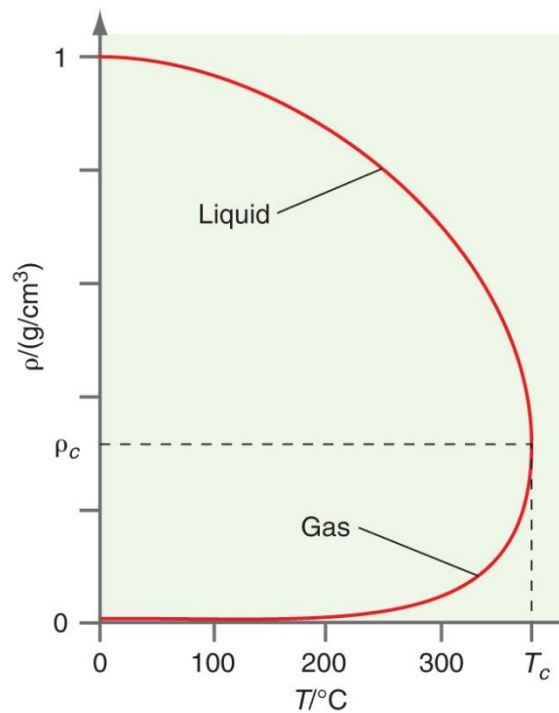


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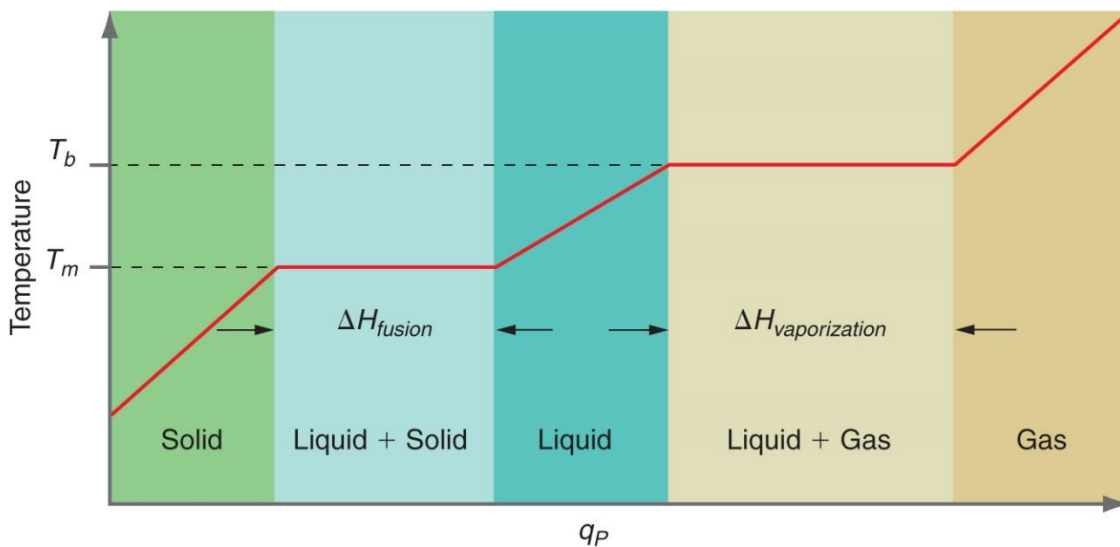
The evaporation temperature dependence of pressure is rather large but the melting temperature do not change much (very steep slope). The slope can be positive or negative. For water it is negative so with increasing pressure the melting temperature decrease. (That's why we can skate and ski.) The triple 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  $\Delta H_{vap}$  and in melting heat of fusion  $\Delta H_{fus}$ . It is easy to have phase mixing at the melting and evaporation temperatures. Good example is water ice mixture.

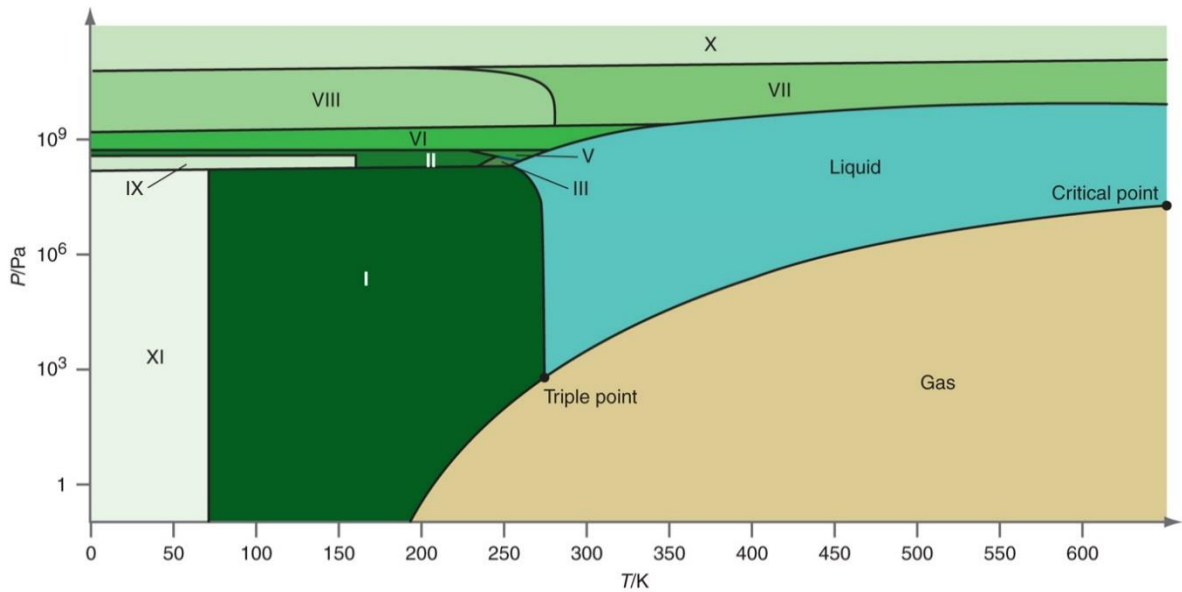


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The phase diagrams can be very complex. Water is an excellent example. It has 11 know phases of ice. At extremely high pressures we can have ice(VII) at 600 K! See some other examples in the book.



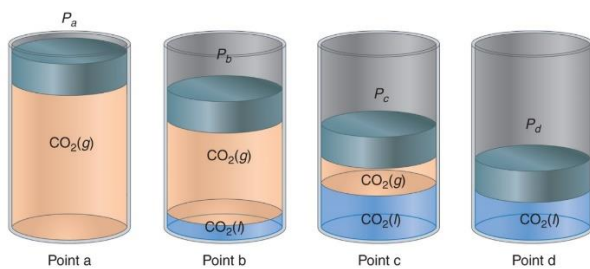
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## Temperature-Volume phase diagram

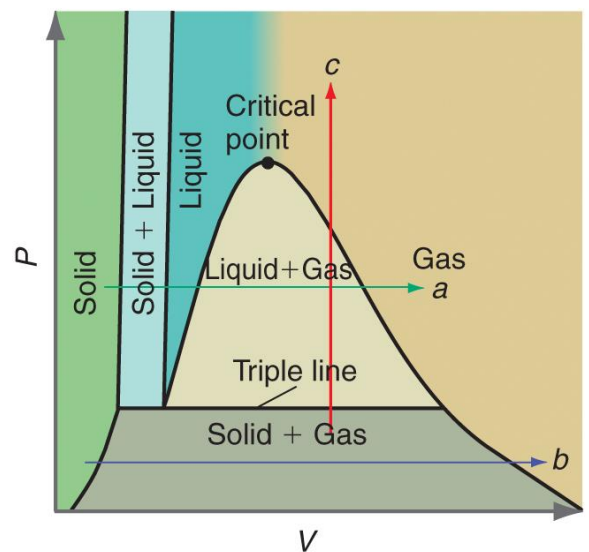
Engel & Reid chapter 8.4

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 left there is a phase diagram of substance which  $V_m^{liq} > V_m^{solid}$ . If we follow the line a, there is first solid, then solid-liquid coexist up to volume  $V_m^{liq}$ , then liquid, then liquid-gas and finally just gas.

Illustration of the liquid-gas coexist.



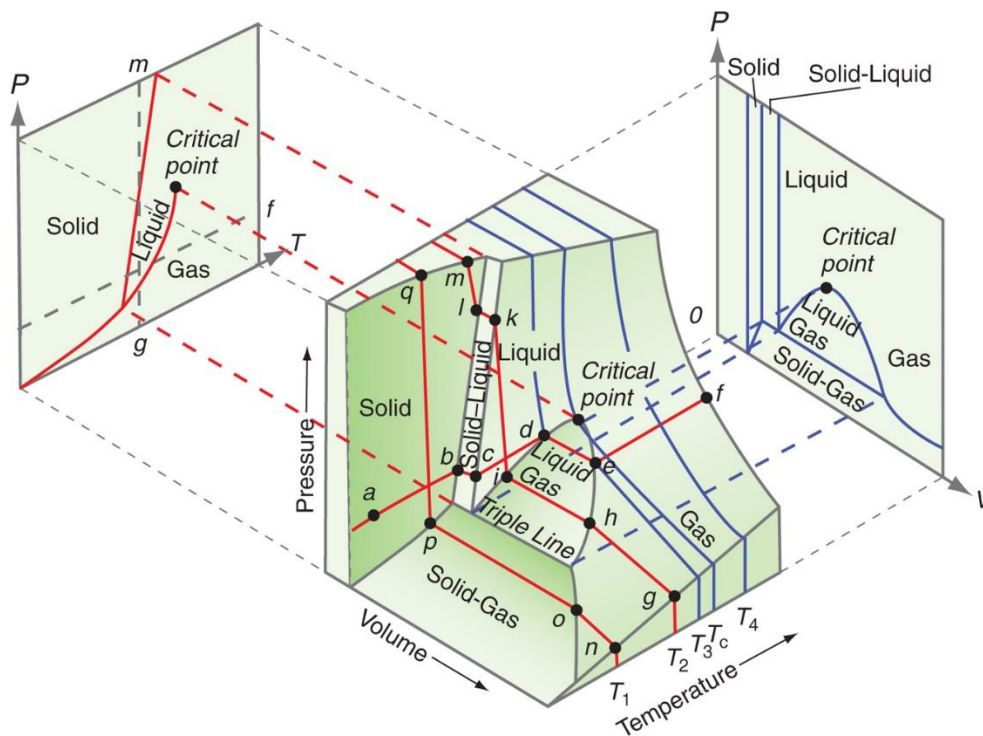
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In P-T diagram you do not see the phase coexist since the pressure do not change. Finally we can use P-V-T diagram. It is very complex but it is the most complete picture of the phases.

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



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## Clapeyron equation

## Engel & Reid chapter 8.5

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  $\mu_\alpha(P, T) + d\mu_\alpha = \mu_\beta(P, T) + d\mu_\beta \Rightarrow d\mu_\alpha = d\mu_\beta$  and  $d\mu_\alpha = -S_{\alpha,m} dT + V_{\alpha,m} dP$ ,  $\mu_\alpha = -S_{\beta,m} dT + V_{\beta,m} dP \Rightarrow (S_{\beta,m} - S_{\alpha,m}) dT = (V_{\beta,m} - V_{\alpha,m}) dP$

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

Next we need to find the  $\Delta S_m$  and  $\Delta V_m$ . The  $\Delta G_{fusion} = \Delta H_{fusion} - T\Delta S_{fusion} = 0$  so the entropy can be computed from 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  $4 \cdot 10^{-6} \text{ m}^3/\text{mol}$ . Water the volume change is negative and around  $-2 \cdot 10^{-6} \text{ m}^3/\text{mol}$ .

Now the  $dP/dT$  change is 55 bar/K for Ag etc. and -55 bar/K so if we increase the pressure by 1 bar the melting temperature increase (or for water decrease of 110K) by  $1/55 = 0.02 \text{ K}$ .

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.  $22 \cdot 10^{-3} \text{ m}^3/\text{mol}$ . 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  $\Delta V_m \approx V_{gas,m}$  and we use the ideal gas law

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

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

so the gas vapor pressure will increase exponentially with temperature.

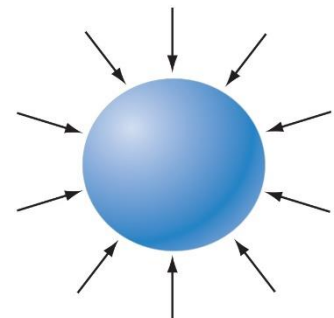
Vapor pressure depend on applied pressure      Engel & Reid  
chapter 8.7

[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 interphase cause energy cost. At constant V and T we can write

$$dA = \gamma d\sigma$$



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where  $A$  is Helmholtz energy and  $\sigma$  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 make 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 one they will disappear. Well the real mechanism in the foams are more complex than in bubbles since the foam bubbles are not spherical.

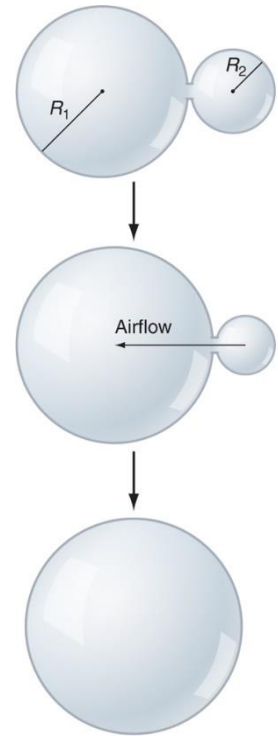
The surface tension also explains the capillarity effect. Water can rise quite high in a narrow (glass) tube. The curved surface will cause lower pressure on the top of the tube and that is compensated with the weight of the water pillar of height  $h$ . We assume that water surface is spherical. This 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

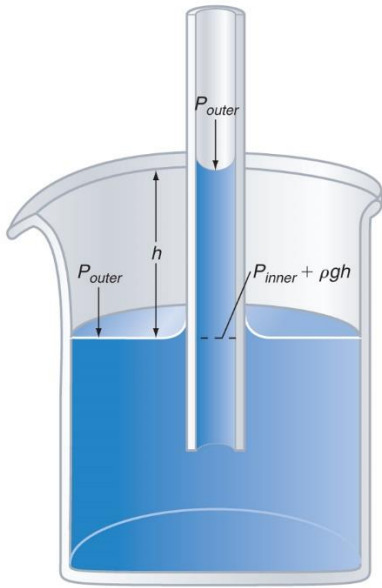
$$h = \frac{2\gamma}{\rho g r}$$

where  $\rho$  is the density of the liquid, and  $g$  is the gravitational acceleration.

Go through problem 8.4



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(a)

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## Real and ideal solutions

## Engel & Reid chapter 9

So far we have studied pure substances. These are not so relevant in chemistry. Almost always the solution(systems) is a mixtures of liquids. How we handle that. Let as first look the gas partial pressures next to mixed ideal solution. The partial pressure of mixture is, the **Raoult's law**

$$P_i = x_i P_i^*$$

where the  $P_i^*$  is the partial pressure of pure gas. There is no interaction effects here. This model is not very good since the two liquid components have different interactions.

We can now compute the solution chemical potential. The liquid and gas are in equilibrium.

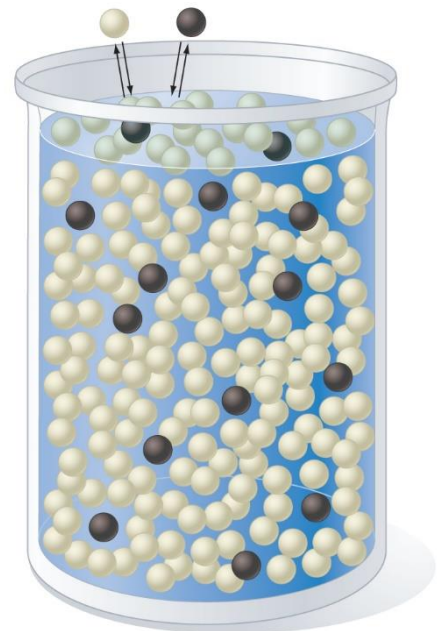
$$\mu_{solution,i} = \mu_{gas,i}$$

there are few lines in the book

$$\mu_{solution,i} = \mu^* + RT \ln \frac{P_i}{P_i^*} = \mu^* + RT \ln x_i$$

the \* always denote the pure system.

For an ideal solution  $\Delta H_{mix} = 0$ ,  $\Delta V_{mix} = 0$  and  $\Delta G_{mix} = nRT \sum_i x_i \ln x_i$ . Because  $x_i < 1$  the ideal system mixed Gibbs energy is always negative and the process is spontaneous.



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# Raoult's law for binary solution

# Engel & Reid chapter 9.3

The Raoult's law is very simple for binary solutions. The total pressure is

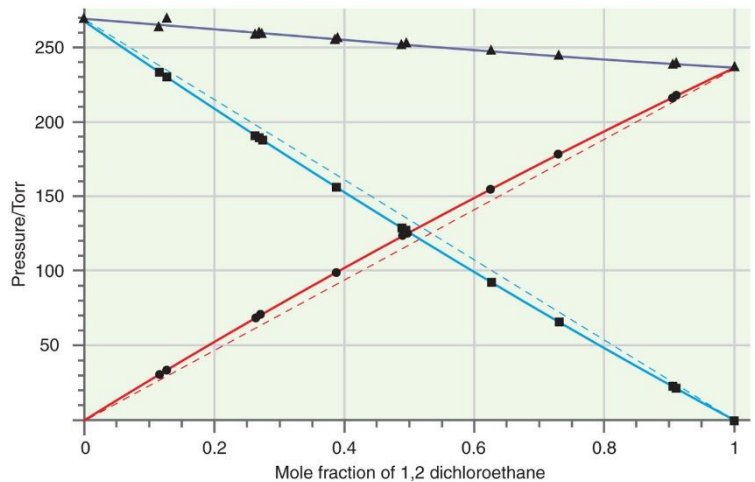
$$P_{tot} = P_1 + P_2 = x_1 P_1^* + (1 - x_1) P_2^* = P_2^* + (P_1^* - P_2^*) x_1$$

where  $x_1$  is the solution mole fraction of component 1. We can also define the gas mole fractions,  $y$ .

$$y_1 = \frac{P_1}{P_{tot}} = \frac{x_1 P_1^*}{P_2^* + (P_1^* - P_2^*) x_1}$$

Note that the  $x$  and  $y$  are NOT the same.

The figure 9.2. shows the gas pressures of mixture of benzene (blue) and dichloroethane (red). The dots are the experiments and dashed lines from the Raoult's law. The mole fraction refer to the solution. This system is close to ideal.



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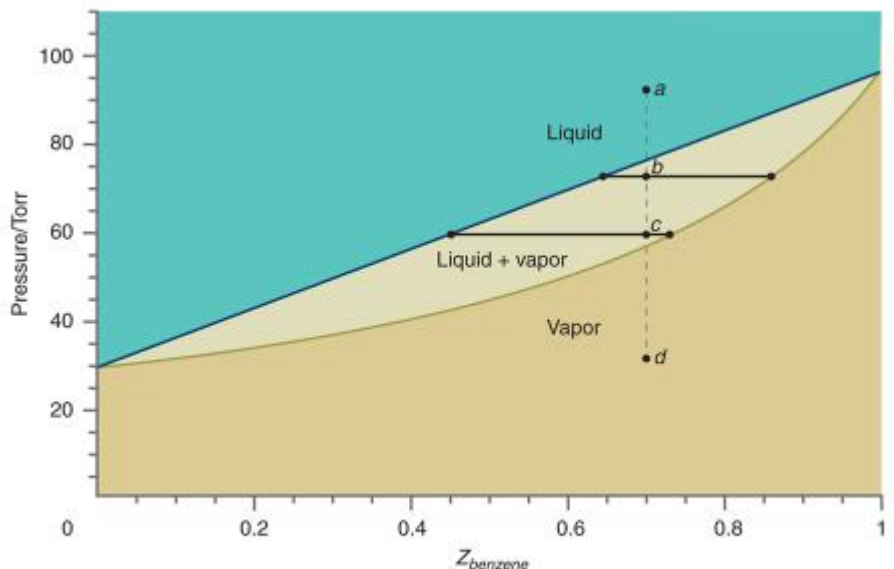
The vapor-liquid coexistence with respect the total pressure is bit complex. We will first define average composition of one component. We use benzene-toluene system as an example.

$$Z_{benz} = \frac{n_{benz,liq} + n_{benz,gas}}{n_{benz,liq} + n_{benz,gas} + n_{tolu,liq} + n_{tolu,gas}} = \frac{n_{benz}}{n_{tot}}$$

Now the P-Z diagram can be drawn. At high pressures the system is liquid (bluish are) and at low pressures gas (brown are). In between, the liquid vapor coexist.

Follow the example 9.3

Solution of 5 mol of benzene and 3.25 mol toluene is at 298 K. The pressure is reduced from 1 atm (760 Torr). The pure substance vapor pressures are 96.4 Torr (benzene) and 28.9 Torr (toluene).



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What is the pressure the vapor-liquid coexistence happen?

The total vapor pressure is  $(0.606 \cdot 96.4 + 0.394 \cdot 28.9)$  Torr = 69.8 Torr

What is the gas composition at this pressure?  $y_{\text{benz}} = 0.827$  Torr and  $y_{\text{tolu}} = 0.163$  Torr. These values are quite different than in solution. The gas is enriched with component that is more volatile (and have higher vapor pressure).

At the point b what is the gas liquid ratio. It can be compute with the lever rule. (read the book)

$$\frac{n_{\text{tot,liq}}}{n_{\text{tot,gas}}} = \frac{Z_B - x_B}{y_B - Z_B}$$

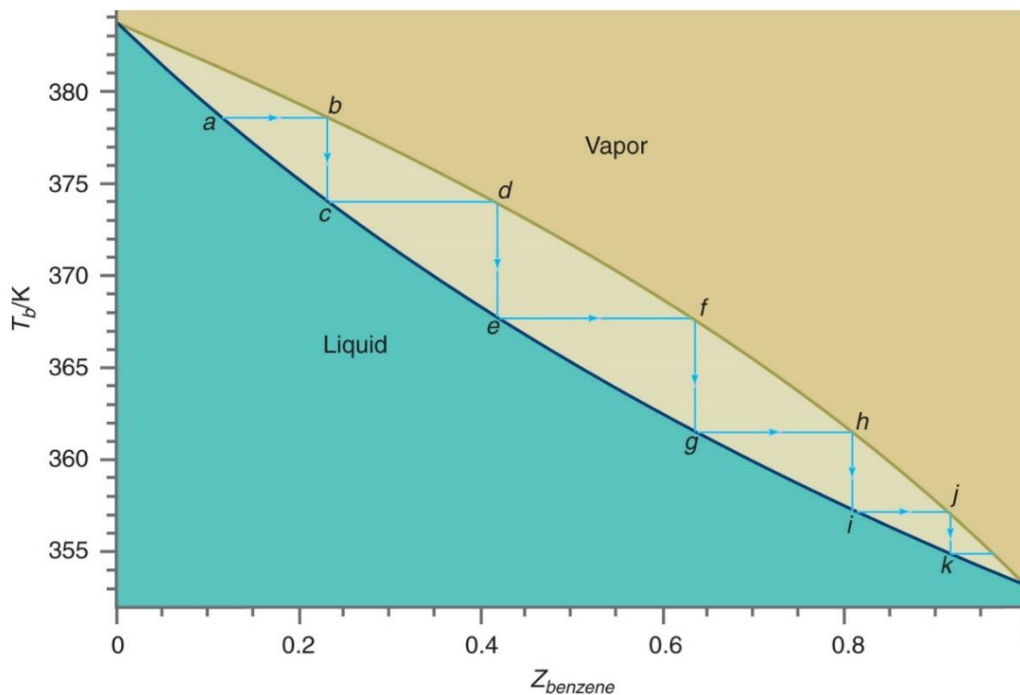
The parameters of the example was not given. I used values  $Z(\text{benz})=0.7$  and  $P(\text{tot})=72$  Torr, then I got  $x(\text{ben})=0.63852$  and  $y(\text{ben})=0.8549$  and  $n(\text{liq})/n(\text{gas})=2.52$ . The total amount of liquid is 71.6 % and gas 28.4 %.

Repeat the calculations at  $Z=0.7$  and  $P=60$  Torr (point c) (Answer:  $x(\text{ben})=0.46074$  and  $y(\text{ben})=0.74026$  and  $n(\text{liq})/n(\text{gas})=0.1683$ . The total liquid is 14.4 % and gas 85.6 %.)

## Fractional distillation

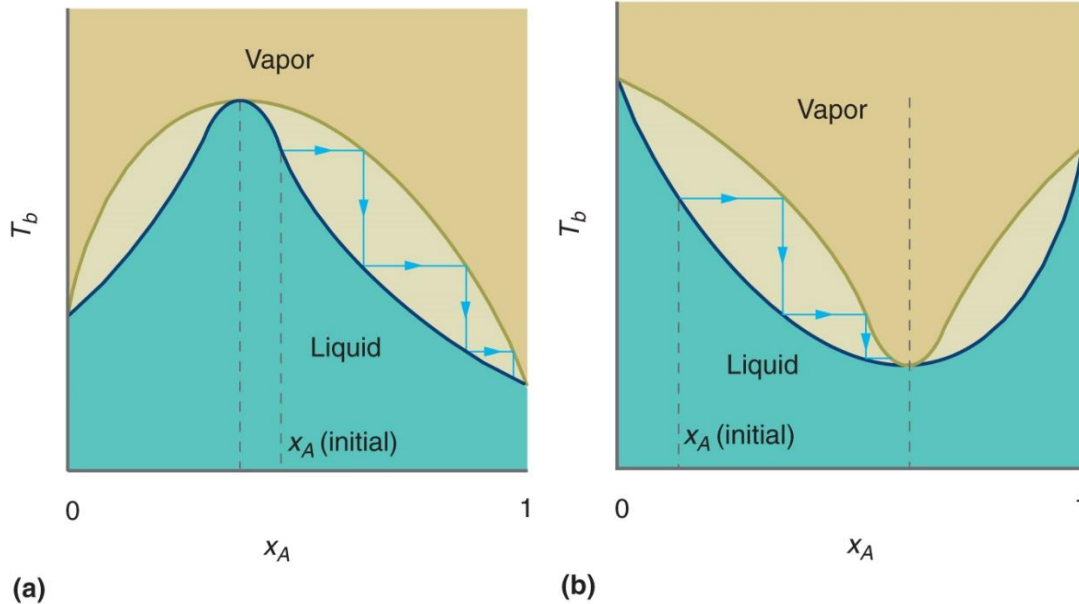
## Engel & Reid chapter 9.4

The T-Z diagram is also useful. In this diagram, the relevant temperatures are the liquids boiling temperatures with respect to Z. Also in this diagram, the liquid and gas coexist. Here the diagram is used to illustrate the fractional distillation. If we start around point a there will gas at point b that have higher benzene concentration than at a. If this gas (mixture of benzene and toluene) is collected and cooled to temperature at c and then then the gas is collected that point d with again is richer in benzene than at c. The procedure can be repeated several times and at the end, very pure benzene can obtain.



The benzene-toluene mixture is a rather rare example of almost ideal mixtures. Most real liquid mixtures have more complex boiling point. At some mixture the boiling point can be even higher or lower than the pure substances boiling points. These are called azeotropes.

See the table 9.1. In the case (b) with low boiling point around  $x=0.66$  it is not possible to get compound A richer than ca. 66 % (at this pressure).



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**TABLE 9.1** Composition and Boiling Temperatures of Selected Azeotropes

Azeotropic Mixture	Boiling Temperature of Components (°C)	Mole Fraction of First Component	Azeotrope Boiling Point (°C)
Water-ethanol	100./78.5	0.096	78.2
Water-trichloromethane	100./61.2	0.160	56.1
Water-benzene	100./80.2	0.295	69.3
Water-toluene	100./111	0.444	84.1
Ethanol-hexane	78.5/68.8	0.332	58.7
Ethanol-benzene	78.5/80.2	0.440	67.9
Ethyl acetate-hexane	78.5/68.8	0.394	65.2
Carbon disulfide-acetone	46.3/56.2	0.608	39.3
Toluene-acetic acid	111/118	0.625	100.7

Source: Lide, D. R., ed. *Handbook of Chemistry and Physics*. 83rd ed. Boca Raton, FL: CRC Press, 2002.

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## Freezing and boiling points

## Engel & Reid chapter 9.7

The next interesting thing is the effect of mixtures to freezing and boiling points. In general the mixture (solute-solvent) will have low melting point and higher boiling point. As an example, the water-ethanol will freeze at lower temperatures than pure water. The boiling point is more difficult to observe since most of the ethanol will evaporate before water boils but the mixture will have higher boiling point.

We also assume that the solid and gas are of pure compound A (solvent). The later is realistic if the compound B(solute) have higher boiling temperature. In freezing we assume that the compound A and B separates which is very often the case. It is reasonable to assume that there is much more solvent than solute.

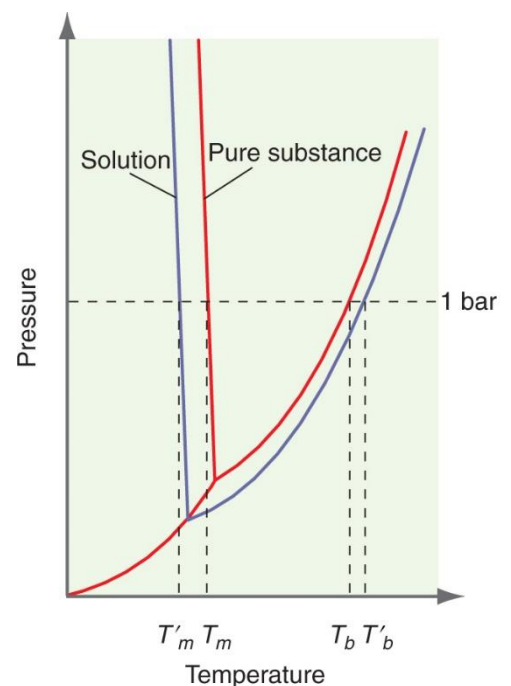
The derivation of the equations are bit tricky. The details are in the book. The final result for melting is

$$\Delta T_f = -\frac{RM_{solvent}T_{melt}^2}{\Delta H_{melt}}m_{solute} = -K_f m_{solute}$$

where the  $M_{solvent}$  is the mass of solvent molecules, the  $m_{solute}$  is the molality (moles of solute per kg of solvent). In principle the  $K_f$  do not depend on the solute. It is reasonable to assume that  $m$  is small

For boiling point an identical equation hold

$$\Delta T_b = \frac{RM_{solvent}T_{vapor}^2}{\Delta H_{vapor}}m_{solute} = K_b m_{solute}$$



(b)

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**TABLE 9.2** Freezing Point Depression and Boiling Point Elevation Constants

Substance	Standard Freezing Point (K)	$K_f$ (K kg mol <sup>-1</sup> )	Standard Boiling Point (K)	$K_b$ (K kg mol <sup>-1</sup> )
Acetic acid	289.6	3.59	391.2	3.08
Benzene	278.6	5.12	353.3	2.53
Camphor	449	40.	482.3	5.95
Carbon disulfide	161	3.8	319.2	2.40
Carbon tetrachloride	250.3	30.	349.8	4.95
Cyclohexane	279.6	20.0	353.9	2.79
Ethanol	158.8	2.0	351.5	1.07
Phenol	314	7.27	455.0	3.04
Water	273.15	1.86	373.15	0.51

Source: Lide, D. R., ed. *Handbook of Chemistry and Physics*, 83rd ed. Boca Raton, FL: CRC Press, 2002.

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Note that for water the coefficients  $K_f$  and  $K_b$  are rather small.

## Real solutions

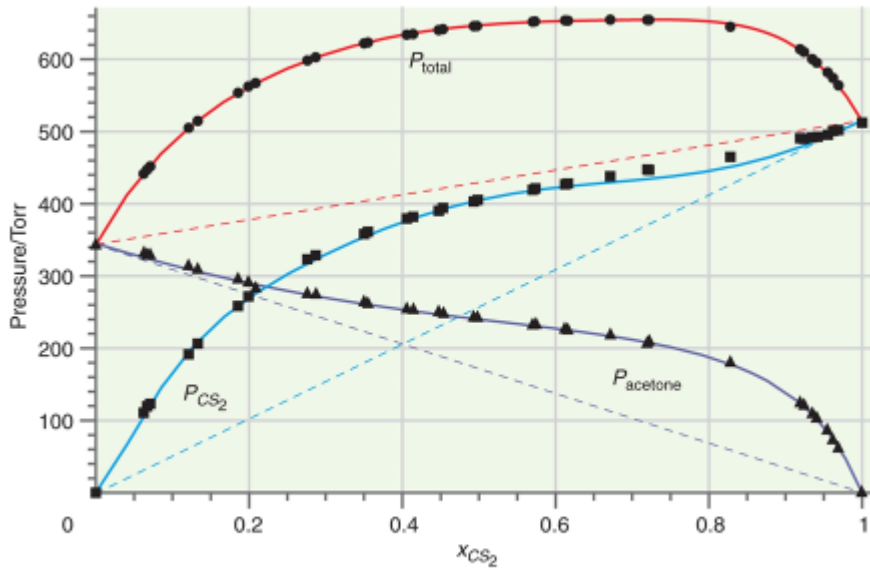
## Engel & Reid chapter 9.9

The ideal gas is a good approximation on normal pressures but the not so good at high pressures. The densities of liquids are much higher than on high pressure gases, so the molecular interactions are even more important. From this point of view the ideal solutions are rather rare. There are no unique equations that could describe the real solution properties. The modern approach is data based. There are several (usually commercial) data bases of solutions properties and reliable numerical fitting tools for the data.

Some examples of open tools. For solid systems. OpenCalphad: <http://www.openalphad.com/>

ThermoCalc have also a free student license.

Below is the partial pressures and total pressure of CS<sub>2</sub> and acetone mixture. The dashed lines are from the Raoult's law. The deviation is quite large, especially on both ends. This means that the pure substances (either CS<sub>2</sub> or acetone) do not "like" the impurity molecules very much and they are evaporated easier.

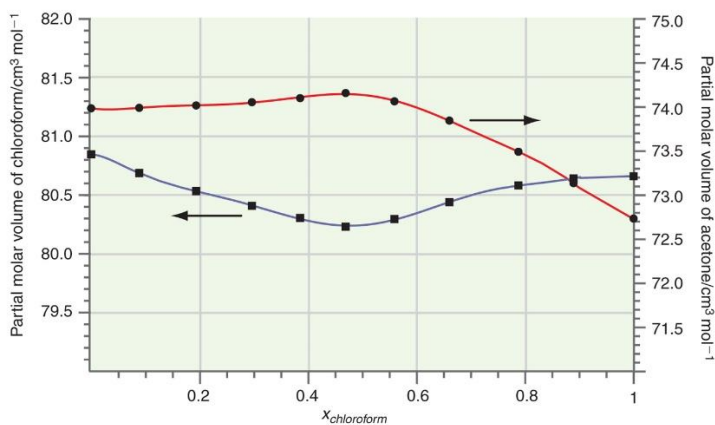


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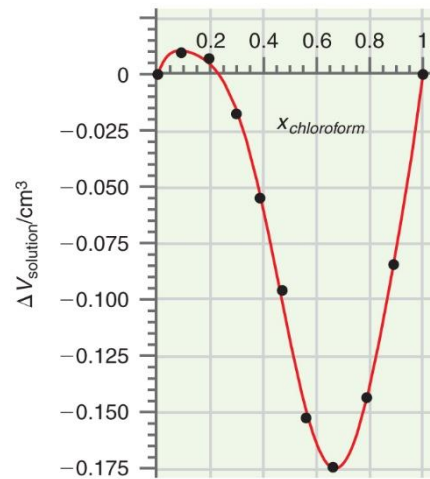
Similarly, to the partial pressure also the molar volume can deviate from the ideal. On the left there is the molar volume deviation from the ideal chloroform-acetone system.

The total molar volume will not tell the volumes of individual molecules. At small concentration interval, we can use Gibbs-Duhem equation to estimate the individual volume changes.

$$dV_1 = -\frac{x_2}{x_1} dV_2$$



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Ideal dilute solution

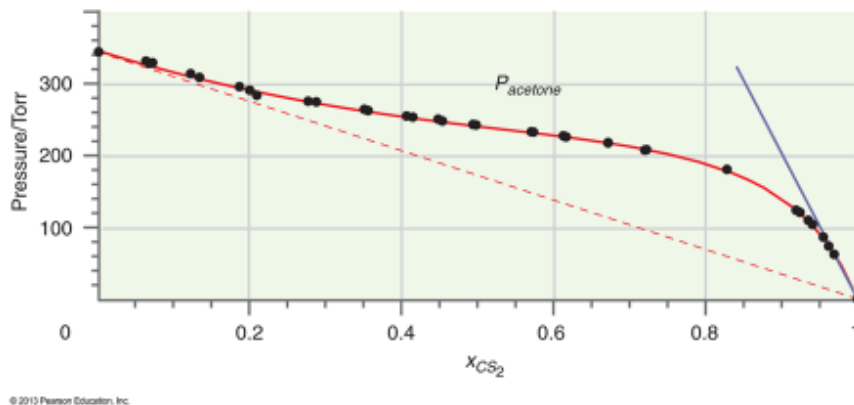
Engel & Reid chapter 9.10



Often we are interested of real solutions with one major component (solvent) and one dilute component (solute). We can compute the chemical potential as

$$\mu_{i,solution} = \mu_i^* + RT \ln P_i/P_i^*$$

remember that for non-ideal solution  $P_i \neq x_i P_i^*$  now we can define an **activity**  $a_i = P_i/P_i^*$  and activity coefficient  $a_i = \gamma_i x_i$ . The activity coefficient is an experimental parameter and at dilute system it has a simple interpretation. It is the slope of P(x) curve at low concentrations. At high acetone concentrations the acetone is close to ideal (the slope is ca. 1)



$$P_i = k_{i,H} x_i$$

this is the Henry's law and the  $k_H$  is the Henry's constant. Note that the  $\gamma$  is valid in all mixtures and  $k_H$  only on dilute systems.

For dilute systems we can also write

$$\mu_{i,solution} = \mu_i^* + RT \ln \frac{P_i}{P_i^*} = \mu_i^* + RT \ln \frac{k_{i,H} x_i}{P_i^*} = \mu_i^H + RT \ln x_i \text{ where } \mu_i^H = RT \ln \frac{k_{i,H}}{P_i^*}$$

The activity coefficient can be much higher than 1.

Examine example 9.8.

$$\gamma_{CS_2} = 1.997$$

We can use the Henry's law to estimate the solubility of gases to liquid. An interesting example is nitrogen to water,  $N_2(\text{gas}) \leftrightarrow N_2(\text{aqueous})$  the nitrogen pressure

$$P(N_2) = k_H(N_2) x(N_2) \text{ and nitrogen do not dissolve well to water } x(N_2) = \frac{n(N_2)}{n(N_2) + n(H_2O)} \approx \frac{n(N_2)}{n(H_2O)} \text{ then}$$

$$n(N_2) = n(H_2O) \frac{P(N_2)}{k(N_2)}$$

Examine example 9.12.

70 kg human have ca. 5 L of blood. How much she/he have nitrogen in blood at 1 atm. The  $k_H$  is  $9.04 \cdot 10^4$  bar. In air the  $N_2$  concentration is ca. 80 % so at 1 atm the  $P(N_2) = 0.8$  bar.

$n(N_2) \approx 2.5$  mmol.

What is the case for a diver using compressed air at 50 bar pressure ?  $n(N_2) \approx 0.125$  mol.

At normal pressure what is the volume of this gas?  $V = 3.06$  L

This is the cause of divers' disease. The volume is a significant fraction of the blood circulation system. (ca. 5 L)

## Chemical equilibrium

## Engel & Reid chapter 9.13

As before we can write the chemical reaction equilibrium using the chemical potentials.

$$\sum_i \nu_i \mu_i = 0 \Rightarrow \sum_i \nu_i \mu_i^* + RT \sum_i \ln(a_i^{\nu_i}) = 0$$

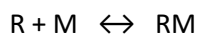
The first part of this equation is  $\Delta G_{react}$  so  $\Delta G_{react} = -RT \sum_i \ln(a_i^{\nu_i}) = -RT \ln K$

and the equilibrium constant is

$$K = \prod_i a_i^{\nu_i} = \prod_i \gamma_i^{\nu_i} \left(\frac{c_i}{c^o}\right)^{\nu_i}$$

This equation is not so simple to use since we need to know the  $\gamma$ 's for each substance. Often for most substances the  $\gamma$  is close to 1.

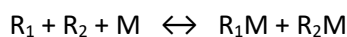
As an example we can look a simple binding reaction. We have a free molecule R and a binding site M and the bound molecule RM and they are in equilibrium. The binding site can be surface, like Pt catalyst, protein, etc.



the equilibrium constant  $K = c_{RM}/c_R c_M$  (the  $\gamma$ 's are assumed to be 1). The fraction of bound molecules

$$\nu = \frac{c_{RM}}{c_M + c_{RM}} = \frac{K c_R}{1 + K c_R}$$

this is very simple equation and it depend only on  $K$  and  $c_R$ .  $K$  has dimension of  $1/c$ . This model assumes that all the binding sites are identical and independent. This naïve model can be used in gas phase by replacing  $c$  with  $p$ . It can be generalized to multiple species adsorption. For two species



the equilibrium constants are  $K_i = c_{R_iM}/c_{R_i}c_M$

and fraction of bound molecules are (i=1,2)

$$v_i = \frac{c_{R_iM}}{c_M + c_{R_1M} + c_{R_2M}} = \frac{K_i c_{R_i}}{1 + K_1 c_{R_1} + K_2 c_{R_2}}$$

From the figure on right we can see that the adsorbed molecules fraction reach 1 rather slowly.

The model can be extended to case where several sites (N) are needed to bind a molecule.

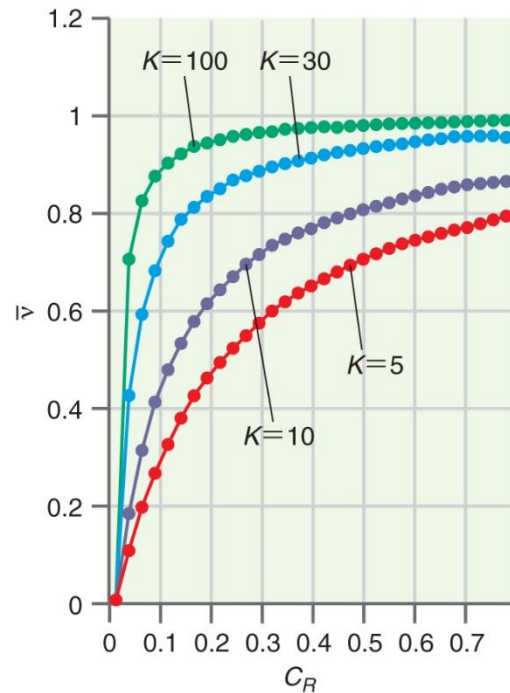
$$v = \frac{NKc_R}{1 + Kc_R}$$

This can be written in form

$$\frac{v}{c_R} = -Kv + NK$$

this has now two parameters but they are easy to fit to numerical data.

Examine the example 9.14



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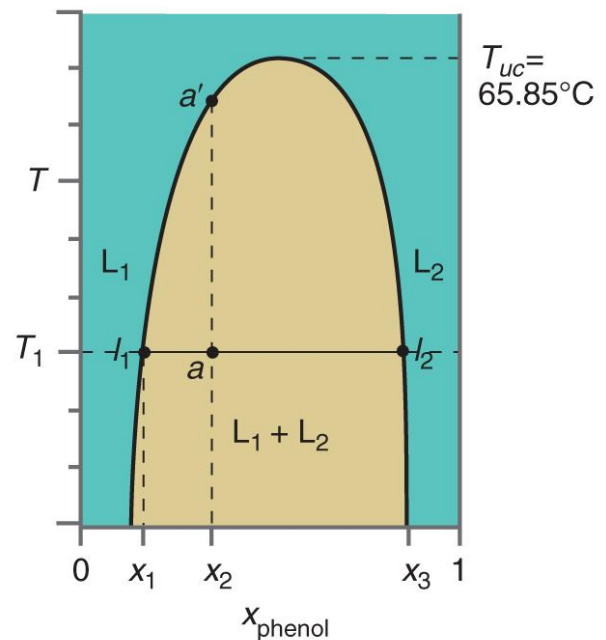
## Partially miscible liquids

So far we have assumed that the liquids will fully mix this is not always the case. If the liquids are fully immiscible, the situation is rather easy – they can be studied separately. The challenging case are the partially miscible liquids.

On the right there is phase diagram of water-phenol system. One can investigate the line at temperature  $T_1$ . If we start from 100% phenol system and add water to it we will have homogenous liquid ( $L_2$ ) up to concentration  $x_3$ . Then the water and phenol will separate to liquids  $L_1$  and  $L_2$ . At concentrations between  $x_1$  and  $x_3$  the ratio of the two liquids can be estimated with lever rule. Below the concentration  $x_1$  (quite watery system) the liquids mix again. Often the separated liquids can be below some temperature. This temperature is called the upper consolute temperature  $T_{uc}$ .

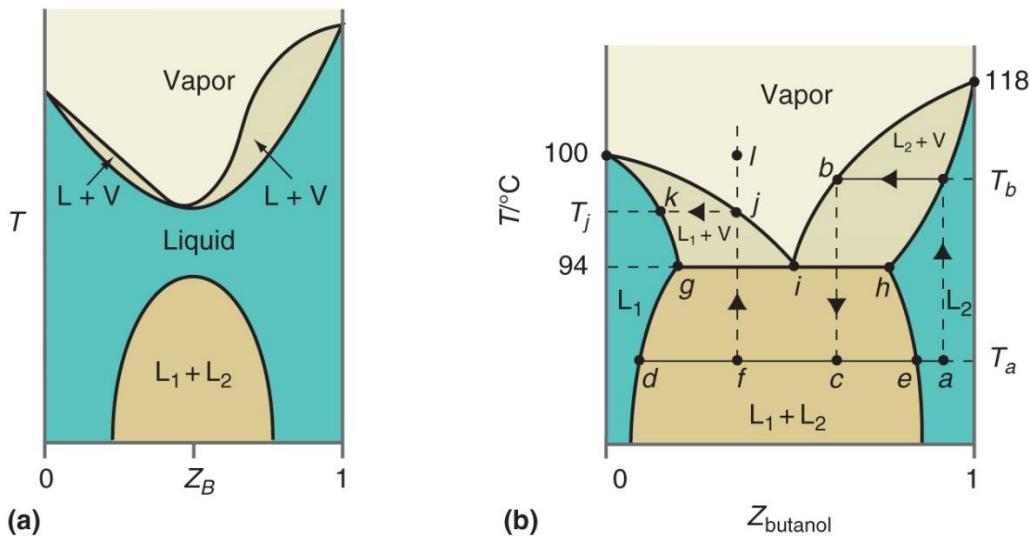
If the temperature is increased further the liquids start to boil. In the figure (a) below the  $T_{uc}$  is lower than the lowest boiling point and in figure (b) the

## Engel & Reid chapter 9.14



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boiling happen below  $T_{uc}$ . The behavior of the this type of liquids mixture is complex. You can read the book the get some idea what the lines means.



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## Chemical Kinetics

## Engel & Reid chapter 35

Everything above has related to equilibrium but in the changes will always take time. Ice don't melt instantaneously, neither the chemical reactions. We need to include the time (or kinetics) the models. So if look the time behavior of a trivial reaction  $A \rightarrow B$ . The  $A(t)$  and  $B(t)$  are rather obvious. The long time limit is the equilibrium.

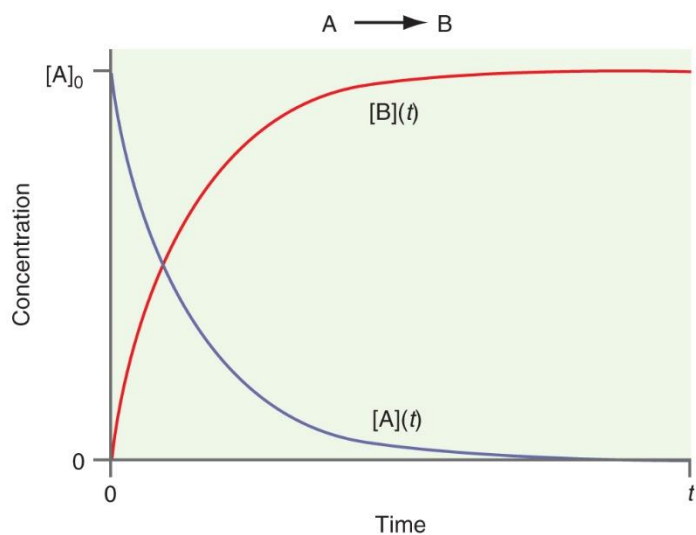
Next we need to define the rate of chemical reaction. That is how many reaction  $\xi$  happen in 1 s. This is connected to mole change

$$\frac{dn}{dt} = v \frac{d\xi}{dt}$$

The stoichiometric coefficient is needed since in a dissociation reaction on molecule broke and two are formed. So the rate is

$$Rate = \frac{d\xi}{dt} = \frac{1}{v} \frac{dn}{dt}$$

An example:  $4 \text{NO}_2 + \text{O}_2 \rightarrow 2 \text{N}_2\text{O}_5$



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$$\text{Rate} = -\frac{1}{4} \frac{dn(\text{NO}_2)}{dt} = -\frac{dn(\text{O}_2)}{dt} = \frac{1}{2} \frac{dn(\text{N}_2\text{O}_5)}{dt}$$

This definition of rate depend on the system size (the amount of matter,  $n$ ). To make it an intensive variable it can be divided by the volume of the system.

$$R_i = \frac{\text{Rate}}{V} = \frac{1}{\nu_i V} \frac{dn_i}{dt} = \frac{1}{\nu_i} \frac{d[i]}{dt}$$

where  $[i]$  is the moles of species  $i$  divided by the volume.

## Rate law

## Engel & Reid chapter 35.3

The rate of a reaction  $A + B \rightarrow X$  depend on the concentration  $[A]$ ,  $[B]$  etc.

$$R = f([A], [B]) \quad \text{often} \quad R = k[A]^\alpha[B]^\beta$$

this the **rate law**. If it is in the power form the exponents are called **the reaction order**. The rate law need to be determined experimentally.

An example  $4 \text{NO}_2 + \text{O}_2 \rightarrow 2 \text{N}_2\text{O}_5$

$$R = k[\text{NO}_2]^2[\text{O}_2]$$

this reaction is first order with respect of  $\text{O}_2$  and second order of  $\text{NO}_2$ . The total reaction order is 3.

If the rate law is known then often the reaction dynamics can be solved. The simplest case is the unimolecular first order reaction

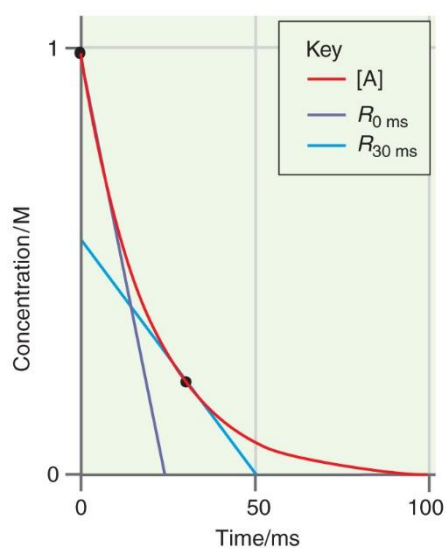
$$R = -\frac{d[A]}{dt} = k[A]$$

this is a first order differential equation and its solution is  $[A](t) = A_0 \exp(-kt)$ . So the concentration decay exponentially with coefficient  $k$ . The  $k$  need to be determined experimentally.

if the concentration in the beginning is 1 M (mol/L) and we mesure the rate to 40 M/s. The rate constant  $k = 40 \text{ 1/s}$ . The rate law can be tested at later time. If at 30 ms the concentration is 0.3 M and the rate is 12 M/s the  $k(30\text{ms}) = R(30 \text{ ms})/[A](30 \text{ ms}) = 12/0.3 \text{ 1/s} = 40 \text{ 1/k}$ . So the rate law is correct and the  $k$  is constant.

The rate law determination is easy. Consider a simple reaction  $A + B \rightarrow C$

$$R = k[A]^\alpha[B]^\beta$$



We can use isolation method in which one concentration is much higher than the other and then the major component are not essentially consumed. Choose  $[B] \gg [A]$  then  $[B]$  is almost constant  $B_0$ .

$R = k[A]^\alpha[B]^\beta \approx k B_0^\beta [A]^\alpha = k' [A]^\alpha$  now  $\alpha$  is easy to determine. The experiments can be done with reversed conditions,  $[A] \gg [B]$  and the  $\beta$  can be determined.

Another method is initial rate method. In it concentration of one component is kept constant, the other is varied and the initial rate is measured.

$$\frac{R_1}{R_2} = \frac{k[A]_1^\alpha [B]_0^\beta}{k[A]_2^\alpha [B]_0^\beta} = \left(\frac{[A]_1}{[A]_2}\right)^\alpha \Rightarrow \ln \frac{R_1}{R_2} = \alpha \ln \frac{[A]_1}{[A]_2}$$

### Study the Example 18.2

The equations are quite simple but the measurements of the concentration of fast reaction are not easy. Sometimes physical quantities like pressure can be used to follow the reaction. Usually some spectroscopical methods are convenient. IR adsorption can be measured in ms.

## Integrated rate laws

## Engel & Reid chapter 35.5

As shown above the time dependence of the reaction components can be solved when the rate law is known. In simple cases the solution can be written with simple function and the general solution maybe obtained only numerically.

The first order reaction,  $A \rightarrow P$

$$R = -\frac{d[A]}{dt} = k[A] \Rightarrow [A](t) = [A]_0 e^{-kt}$$

where the  $[A]_0$  is the initial concentration. The product concentration is  $[P]+[A]=[A]_0$

and  $[P](t) = [A]_0(1-\exp(-kt))$

The second order reaction  $2A \rightarrow P$  is also easy

$$R = -\frac{1}{2} \frac{d[A]}{dt} = k[A]^2 \Rightarrow \frac{1}{[A](t)} - \frac{1}{[A]_0} = 2kt = k_{eff}t$$

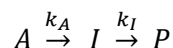
the more general reaction  $A + B \rightarrow P$  is more complex, see the derivation from the book

$$R = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \Rightarrow \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]/[A]_0}{[B]/[B]_0} = kt$$

## Sequential first order reactions

## Engel & Reid chapter 35.7

In chemical reactions there are sometimes intermediate compounds. In fact there almost always several intermediate steps and the total rate of the reaction chain depend on these intermediate steps. In this case, the reaction can be written as



for first order reaction (and no backward reactions) the equations can be written as

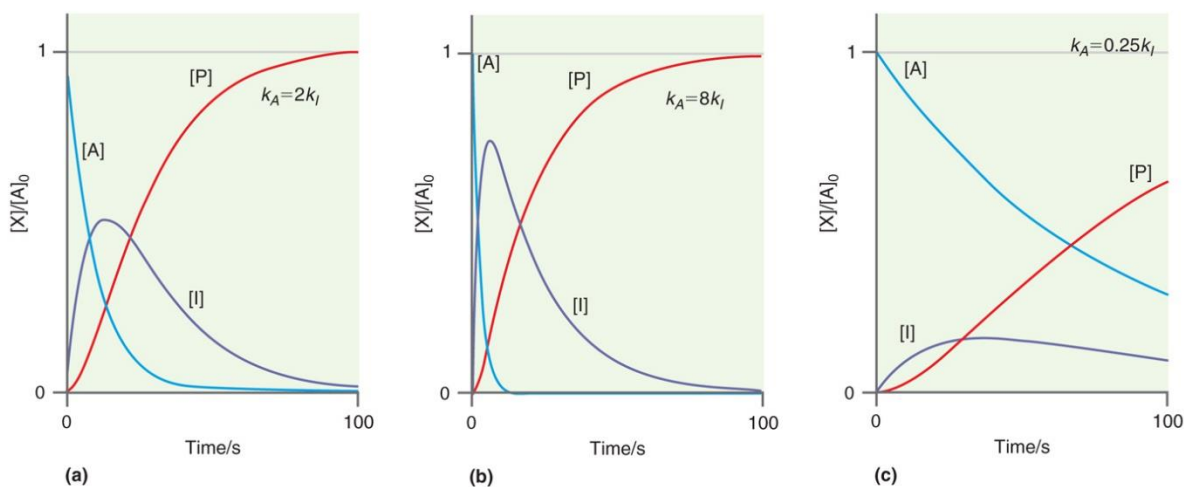
$$\frac{d[A]}{dt} = -k_A[A], \quad \frac{d[I]}{dt} = k_A[A] - k_I[I], \quad \frac{d[P]}{dt} = k_I[I]$$

We assume that the initial concentrations of I and P are = 0. The solutions are quite easy

$$[A](t) = [A]_0 e^{-k_A t},$$

$$[I](t) = [A]_0 \frac{k_A}{k_I - k_A} (e^{-k_A t} - e^{-k_I t}), \quad [P](t) = [A]_0 \left( \frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1 \right)$$

With different rate constant, the concentrations are shown below. The intermediate compound concentration is never very high.



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Even this model is very simple it contain many important features of chemical reactions.

## The rate limiting step

we can look the time dependence of the product at two limits, a) when  $k_A \gg k_I$  and  $\exp(-k_A t) \ll \exp(-k_I t)$  then

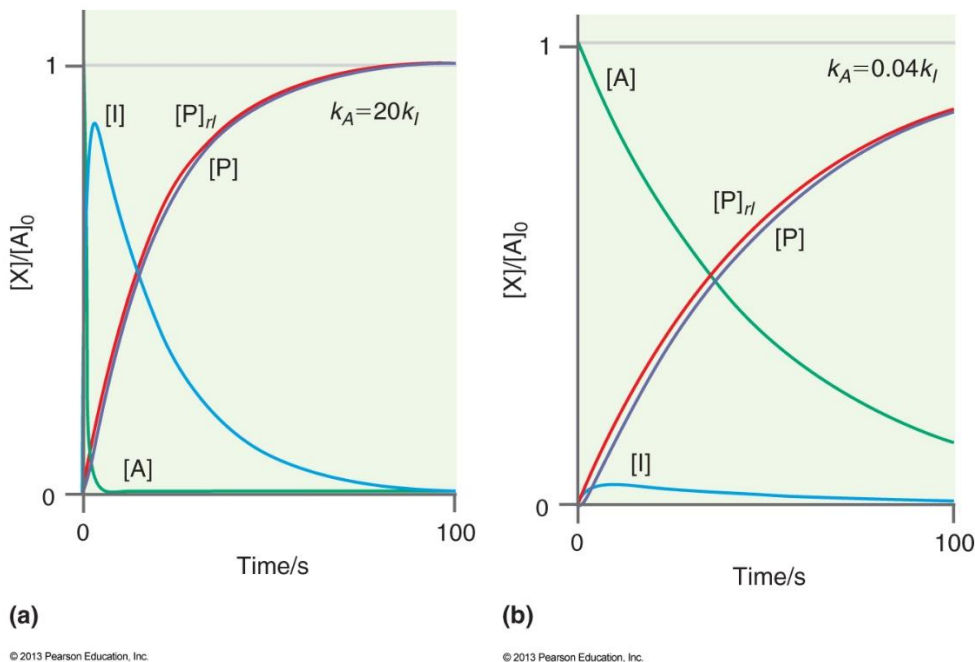
$$[P](t) = [A]_0 \left( \frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1 \right) \rightarrow (1 - e^{-k_I t}) [A]_0$$

so the production rate depend on the rate constant  $k_I$ . In other word the first step is fast and the second is slow,  $A \xrightarrow{k_A} I \xrightarrow{k_I} P$ . The slow step is called the rate limiting step. This is trivial in such a simple reaction but if there are more than 5 steps.

The second limit is b) when  $k_I \gg k_A$  and  $\exp(-k_I t) \ll \exp(-k_A t)$

$$[P](t) = [A]_o \left( \frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1 \right) \rightarrow (1 - e^{-k_A t}) [A]_o$$

in both cases the approximate equations describe the product behavior. In base b) is easy to miss the intermediate state. Its concentration is low.



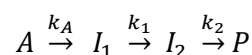
## The steady state approximation

In the case of multiple chemical reactions the reaction kinetics can in principle be solved from set of coupled differential equations. This will usually require numerical methods and this is not very convenient. There some ways to approximate the rate equations. The most convenient approximation is the steady-state approximation. In this approximation the *intermediate* concentrations are assumed to rather constant or

$$\frac{d[I_A]}{dt} = 0$$

Mathematically this would simplify the differential equations to ordinary equation and very complex reactions can be solved.

We can study a reaction path with two intermediate states





in steady-state

$$\frac{d[I_1]}{dt} = k_A[A] - k_1[I_1] = 0, \quad [I_1] = \frac{k_A}{k_1}[A], \quad \frac{d[I_2]}{dt} = k_1[I_1] - k_2[I_2] = 0, \quad [I_2] = \frac{k_1}{k_2}[I_1] = \frac{k_A}{k_2}[A]$$

the product forming rate is

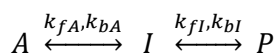
$$\frac{d[P]}{dt} = k_2[I_2] = k_A[A], \quad [A] = [A]_0 e^{-k_A t} \Rightarrow \frac{d[P]}{dt} = k_A[A]_0 e^{-k_A t}$$

the last equation can be integrated

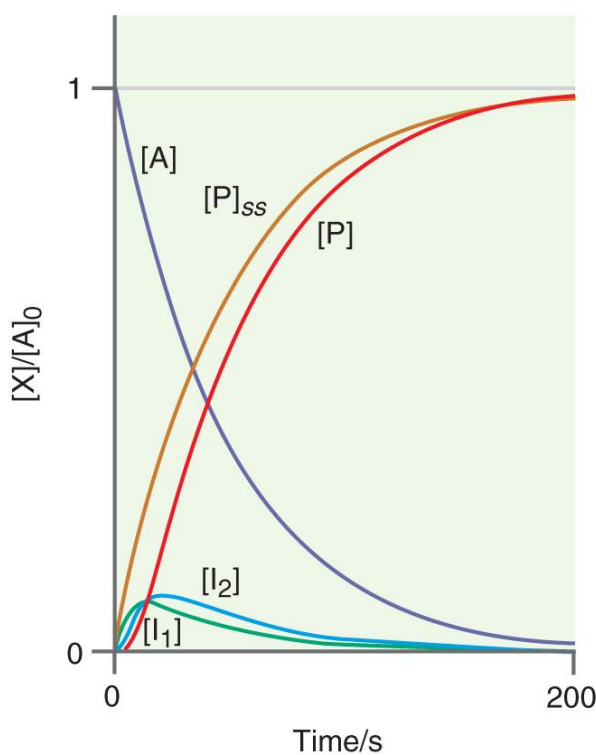
$$[P] = [A]_0(1 - e^{-k_A t})$$

The s-s approximation works well if the intermediate rate constant  $k_1$  and  $k_2$  are large compared to  $k_A$  (case b) above.

The steady-state approximation work also if the backward reactions are included



This will be discussed later in the book so we will come back to this later. Overall the steady-state approximation is very powerful tool to analyze complex reactions.

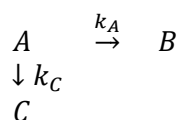


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## Parallel reactions

## Engel & Reid chapter 35.8

Reactions can have several reaction channels



$$\frac{d[A]}{dt} = -k_B[A] - k_C[A], \quad \frac{d[B]}{dt} = k_B[B], \quad \frac{d[C]}{dt} = k_C[C]$$

$$[B] = \frac{k_B}{k_B + k_C} [A]_0 (1 - e^{-(k_B+k_C)t}), \quad [C] = \frac{k_C}{k_B + k_C} [A]_0 (1 - e^{-(k_B+k_C)t})$$

so the concentrations of B and C depend on the reaction constants  $k_B$  and  $k_C$

$$\frac{[B]}{[C]} = \frac{k_B}{k_C}$$

## Temperature dependence of rate constant chapter 35.9

Engel & Reid

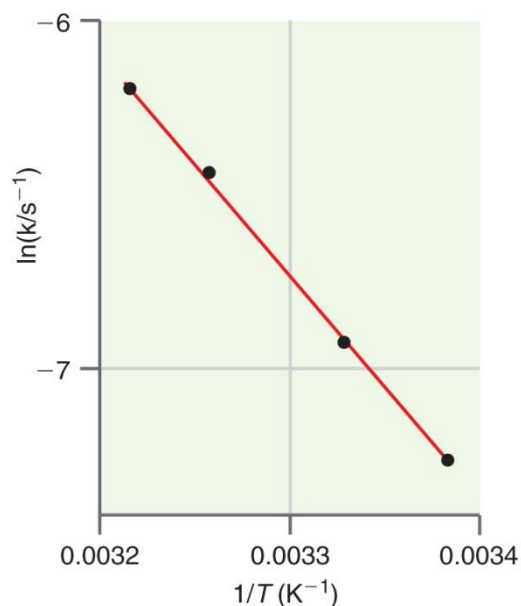
One of the key observation of reactions is the temperature dependence of rate constant. It is the famous Arrhenius law

$$k = Ae^{-E_a/RT}$$

here the  $E_a$  is the activation energy and A is a prefactor that contain often frequency attempt factor. It is clear that the reaction rates will increase rapidly with respect of temperature.

The parameters of Arrhenius law are easy to determine  $\ln(k)$  vs  $1/T$  plot. The slope is the activation energy and the interception give the prefactor.

Examine the problem 36.8

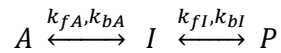


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## Reversible reactions

Engel & Reid chapter 35.10

It is important to remember that every reaction will have forward and backward reaction constants



the kinetics is

$$\frac{d[A]}{dt} = -k_{fA}[A] + k_{bA}[I],$$

$$\frac{d[I]}{dt} = k_{fA}[A] - k_{bA}[I] - k_{fI}[I] + k_{bI}[P],$$

$$\frac{d[P]}{dt} = k_{fI}[I] - k_{bI}[P]$$

this is quite complex, so let us look reaction  $A \xrightleftharpoons[k_b]{k_f} B$ , the kinetics is

$$\frac{d[A]}{dt} = -k_f[A] + k_b[B], \quad \frac{d[B]}{dt} = k_f[A] - k_b[B]$$

the material is conserved  $[A]_0 = [A] + [B]$  the kinetic can be solved (detail are in the book)

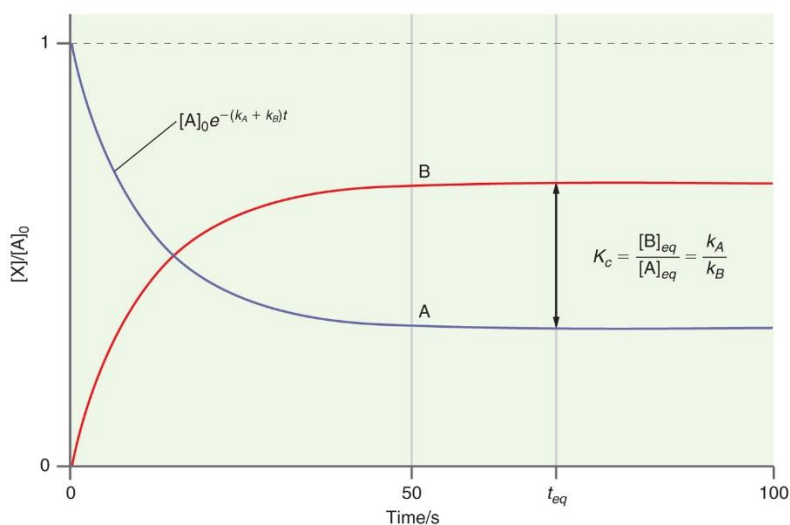
$$[A](t) = [A]_0 \frac{k_f + k_b e^{-(k_f+k_b)t}}{k_f + k_b}, \quad [B](t) = [A]_0 - [A](t)$$

The equilibrium constant is  $K=[B]/[A]$  the

$$[A]_{eq} = [A]_0 \frac{k_f}{k_f + k_b}, \quad [B]_{eq} = [A]_0 \left(1 - \frac{k_f}{k_f + k_b}\right)$$

and now (easy to derive at  $d[A]/dt=0$ ):  $\frac{d[A]}{dt} = -k_f[A]_{eq} + k_b[B]_{eq} = 0 \Rightarrow k_f[A]_{eq} = k_b[B]_{eq}$

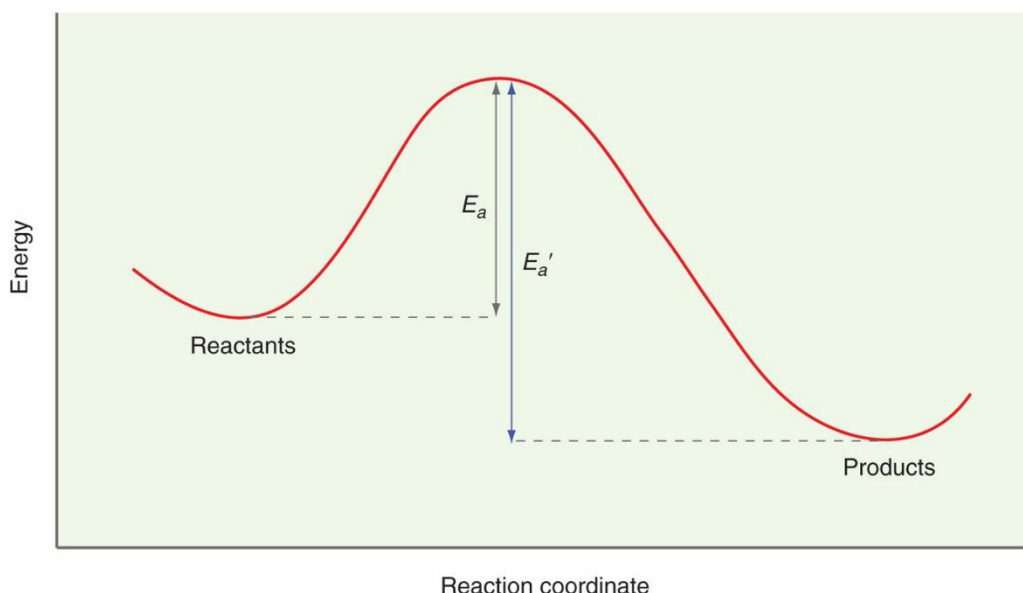
$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_f}{k_b}$$



## Reaction Free energy profile

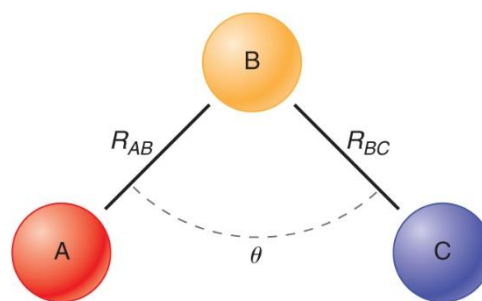
## Engel & Reid chapter 35.14

The reactions can be understood using the (free) energy profile. The reaction proceeds via a reaction coordinate. We discuss later the reaction coordinate and here we focus on the energy profile. The reaction free energy is the energy difference  $\Delta G_r$  of reactants and products. (not in the figure). This will determine the equilibrium constant  $K = \exp\left(-\frac{\Delta G_r}{RT}\right)$ . The forward rate constant is determined by the energy barrier  $E_a$ ,  $k_f = A \exp\left(-\frac{E_a}{RT}\right)$  and the backward rate constant with barrier  $E'_a$   $k_b = A' \exp\left(-\frac{E'_a}{RT}\right)$ . Here the activation energy and free energy are mixed and this is a bit confusing. A precise derivation of these equations uses the activated complex theory (chapter 35.14), which is a bit outside the course.



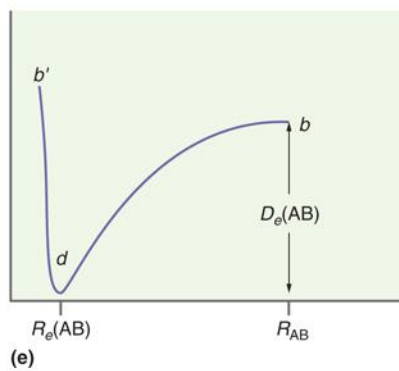
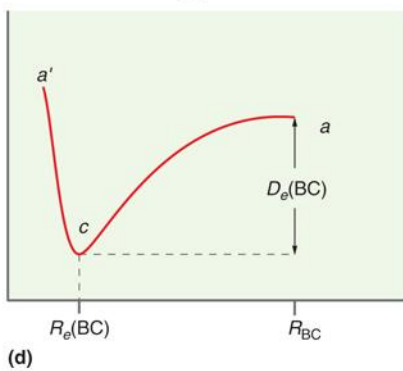
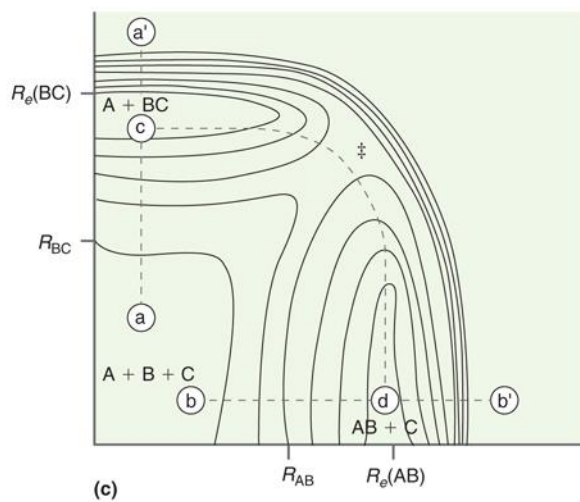
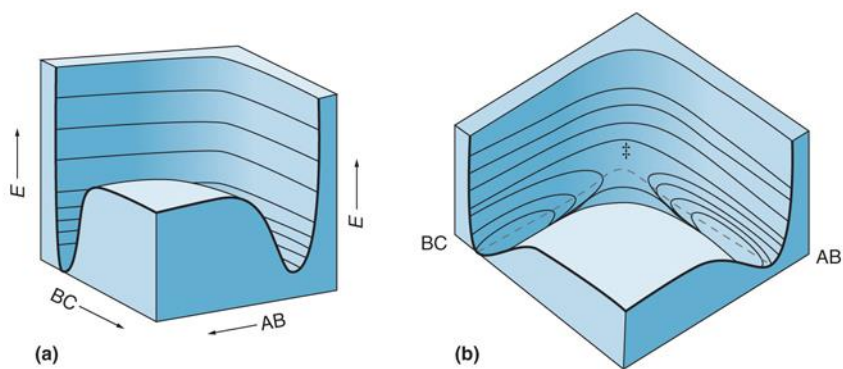
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The reaction coordinate is quite concrete. It describes the movement of all atoms in the reaction. On the right there is three atoms of reaction  $AB + C \rightarrow A + BC$ . In the beginning the distance AB is short (there is a chemical bond between them). The reaction proceeds, and at some point the bonds AB and BC are rather similar. At this point the reaction energy is at its maximum. This is the **transition state**. After it the energy will go down and the bond BC become short.



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The total potential energy surface will describe the (free) energy at every atom position. This is very complex function. For 10 atoms it is 24 dimensional function, which is very difficult to measure. It can be computed using quantum chemical methods but only in few dimensions. See subfigure (c) below.



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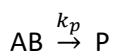
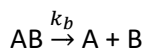
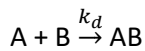
The reaction path is the lowest possible energy path from reactants to products. The transition state is the highest point in the reaction path and its position will determine the reaction rates.

The activated complex theory will derive the precise equations and if you are interested of the details read the book.

Diffusion controlled reactions

Engel & Reid chapter 35.15

Any reaction to happen need that the reaction molecules are very near (close to a chemical bond) to each other. In gas phase this happen with molecular collision and in liquid via diffusion. Here we concentrate on the liquid phase. We note with AB the case where the molecules are near each other (this is not the transition state) and we can see the state AB as an intermediate state. Next the state AB can either broke (to A+B) or form the product P. The reaction steps are



we can use the steady-state approximation

$$\frac{d[AB]}{dt} = k_d[A][B] - k_b[AB] - k_p[AB] = 0$$

and  $[AB] = \frac{k_d}{k_b+k_p} [A][B]$  the reaction product

rate is  $k_p[AB] = \frac{k_p k_d}{k_b+k_p} [A][B]$  if the rate constant  $k_p \gg k_b$  (or most of the AB complexes will react further to product), the effective rate constant is  $k_d$ . In this case the diffusion will limit the reaction rate. This is called the **diffusion limited reaction**.

The other limit  $k_b \gg k_p$  where most of the AB complexes broke back to A and B. Then the rate is

$$\frac{k_p k_d}{k_b} [A][B].$$

The diffusion rate constant can be estimated as  $k_d = 4\pi N_A (r_A + r_B) D_{AB}$  where  $D_{AB}$  is the intermolecular diffusion constant,  $D_{AB} = D_A + D_B$  and  $r_A$  is the estimate of the radius of molecule A (or B).

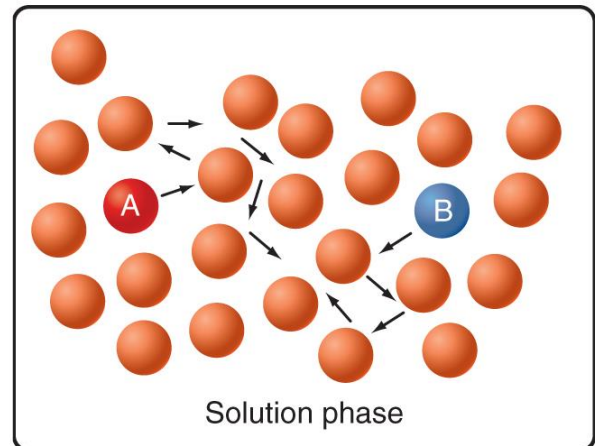
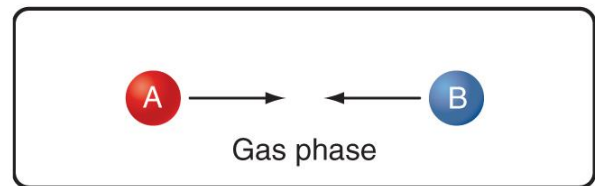
For many molecules, the diffusion coefficient and rough estimation of the size are known.

**See problem 35.11**

The oxygen binding to hemoglobin rate constant is  $4 \cdot 10^7$  1/(Ms). What is the diffusion rate. The diffusion coefficients are  $7.6 \cdot 10^{-7}$  cm<sup>2</sup>/s (hemog) and  $2.2 \cdot 10^{-5}$  cm<sup>2</sup>/s (oxygen). The sizes (radius) are 35 Å (hemog) and 2 Å (oxygen). Is the reaction diffusion limited?

with these we can compute the  $k_d = 6.4 \cdot 10^{10}$  1/(Ms). This is much larger than the observed rate so the rate is limited by the reaction.

Note that the diffusion rate estimation is only estimation. So only, if the rates differ significantly conclusion can be made.



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