

So far, we have concentrated to energy and enthalpy but there is also a very important quantity, **entropy**. It can be connected 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 can move freely in the gas. In liquid the molecules are 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.

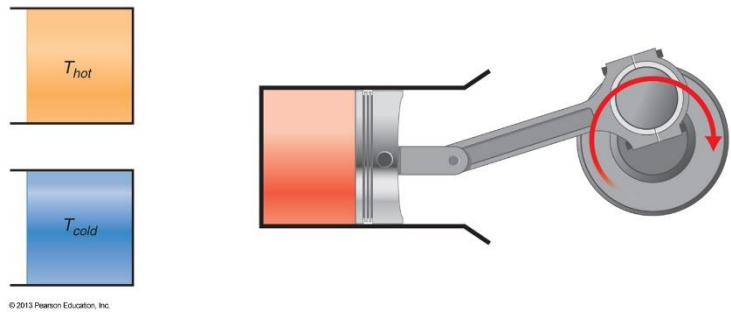
The entropy is connected to free energy. Liquid and gas phase water have very different enthalpies but in equilibrium the free energies are the same.

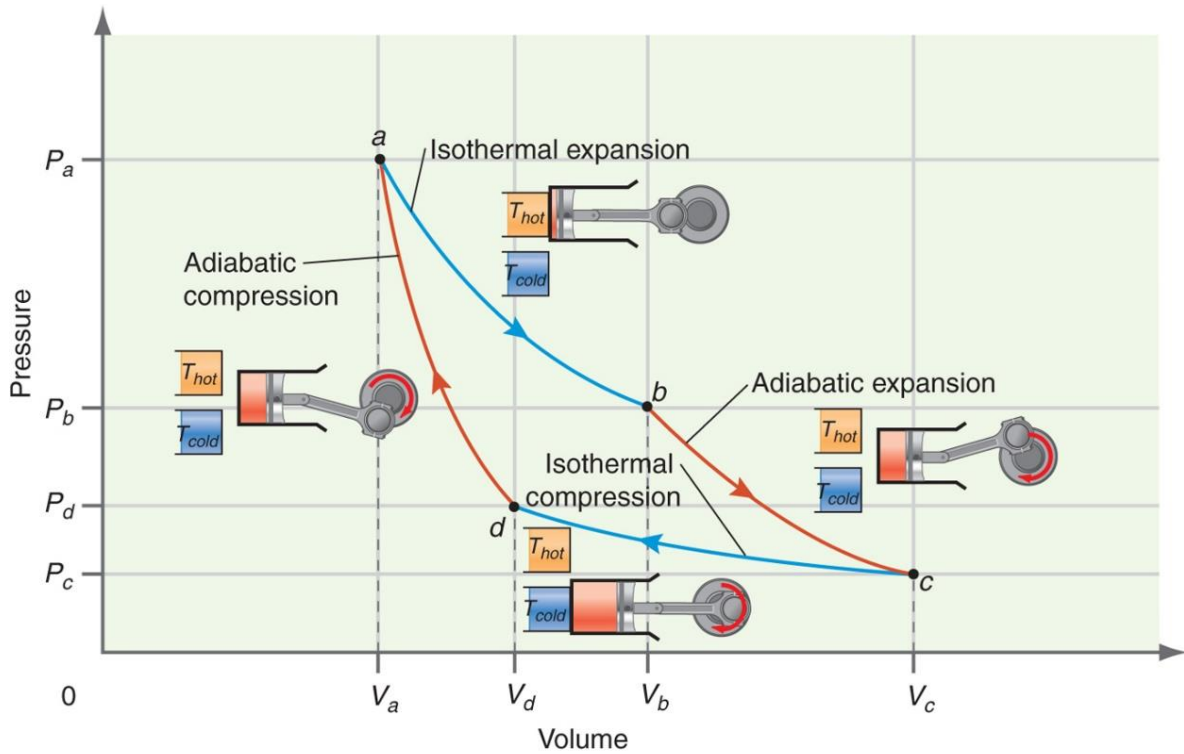
## Heat engine

## Engel & Reid chapter 5.10

WARNING: here the chapter order is different that in Engels book (4<sup>th</sup> ed.). originally I used the 3<sup>rd</sup> ed. and I do not see that the 4<sup>th</sup> is better.

The simplest model engine is the heat engine. It 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 has 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  $\Delta U = q + w = 0$  the total work is  $-(q_{ab} + q_{cd})$ . We get always less work out of the system than the thermal processes provide. The thermal process will provide heat at a-b segment,  $q_{ab}$ . The c-d segment will consume heat and  $|q_{ab}| > |q_{cd}|$  and  $w_{cycle} < 0$

The efficiency of the Carnot engine is (total work done divided by the heat consumed)

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

The **second law of thermodynamics**

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

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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.

$$w_{cycle} = -nR(T_{hot} - T_{cold}) \ln\left(\frac{V_b}{V_a}\right), \quad q_{ab} = nRT_{hot} \ln\left(\frac{V_b}{V_a}\right)$$

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

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 diesel engine is hotter than gasoline engine and thus it is more efficient.

Example: What is the maximum efficiency of Olkiluoto 3, Nuclear power station? The temperature of the steam is 290 °C(=563 K) and the cooling water temp 10 °C (=283 K),  $\epsilon = 49.7\%$ . From the TVO web page the real efficiency is 37%.

## Entropy

## Engel & Reid chapter 5.2

The entropy is a very important concept in thermodynamics. We can use the efficiency equations to define entropy. This a bit abstract but at the end the entropy is not so complex.

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

the later part can be generalized to the reversible heat and a heat cycle we can write

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

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

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

and

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

Entropy is a state function. It is important that the reversible heat is used. The general heat is path dependent.

Some examples:

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

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

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

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

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

$$\Delta S = nR \ln \frac{V_f}{V_i} + n \int \frac{C_{V,m} dT}{T} \approx nR \ln \frac{V_f}{V_i} + nC_{V,m} \ln \frac{T_f}{T_i}$$

and  $P_i T_i \rightarrow P_f T_f$  process

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

What are the contributions from the  $\int \frac{nC_{V,m} dT}{T}$  and  $nR \ln \frac{V_f}{V_i}$  terms?

Go through example 5.2

One mole of CO is transformed from  $T_i = 320$  K and  $V_i = 80.0$  L to  $T_f = 650$  K and  $V_f = 120.0$  L.

A polynome approximation of  $C_v$  is given in the book.

The entropy change is for  $\int \frac{nC_{V,m} dT}{T} = 21.03$  J/K and  $nR \ln \frac{V_f}{V_i} = 3.37$  J/K, totally 24.4 J/K

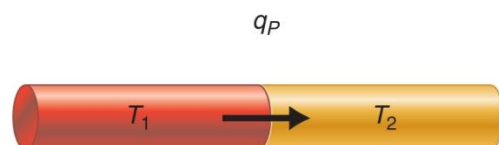
Go through example 5.3

Similar to 5.2.

In isolated system the entropy will always increase  
& Reid chapter 5.1

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. The  $T_1$  part will give  $q_p$  amount of heat.



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

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

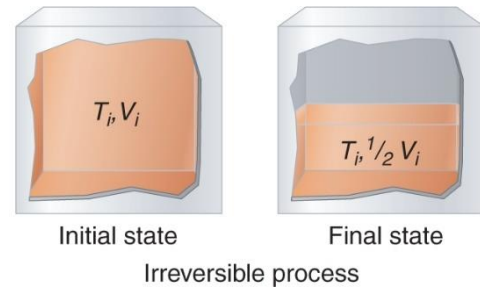
the  $q_P$  is negative because the hot part will lose heat. If  $T_1 > T_2$  the entropy increases.

Another example: we can study a gas system with initial state of  $T_1 V_1$  which will spontaneously (irreversibly) and isothermally located to half of the volume. The entropy change of this process is

$$\Delta S = nR \ln \frac{V_f}{V_i} = nR \ln \frac{1/2 V_1}{V_1} = nR \ln \frac{1}{2} = -nR \ln 2$$

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)

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## Clausius Inequality Engel & Reid chapter 5.5

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 5.6

Go through example 5.5

The total system is insulated ( $\Delta U = 0$ ) and is at (almost) constant temperature,  $T$ .

If the compression is done reversibly (slowly), in the piston the work done on the system is

$$w = -nRT \ln \frac{V_f}{V_i} = -2285 \text{ J}$$

$T = \text{const}$   $\Delta U = 0$  and  $q = -w$ .  $\Delta S_{\text{system}} = 7.62 \text{ J/K}$ .

There is heat transfer from the piston to the surrounding. Without the heat bath the gas temperature would increase.  $q_{\text{surround}} = -q_{\text{system}}$  and then the entropy of the surrounding is

$$\Delta S_{\text{surround}} = -\Delta S_{\text{system}}$$

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

Is the heat bath temperature exactly constant?

Go carefully through example 5.6

Here the compression is done isothermally and at constant pressure. The process is irreversible.

The work done is  $w = -P\Delta V = -3.741 \text{ kJ}$ . The system is isothermal  $q = -w$ . This heat is transformed to the surrounding and entropy change is  $+12.47 \text{ J/K}$ . Now the trick is that the systems (piston) entropy change is same as above. (Entropy is a state variable)

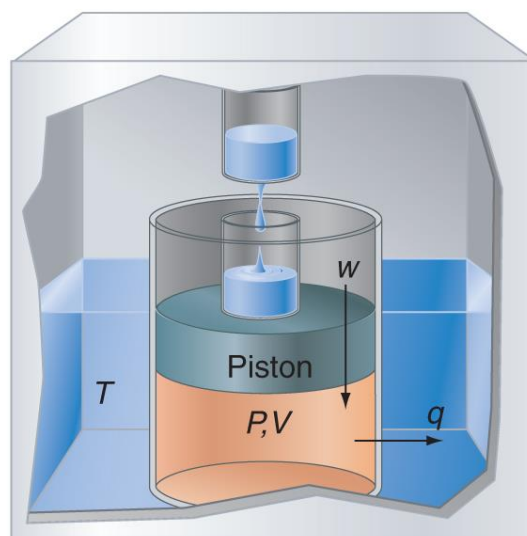
$$\Delta S_{\text{system}} = nR \ln \frac{V_f}{V_i} = -7.62 \text{ J/K}$$

Thus, the total entropy is positive =  $(+12.47 - 7.62) \text{ J/K} = 4.85 \text{ J/K}$ .

This is a delicate point. Think the differences carefully.

In any real process

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

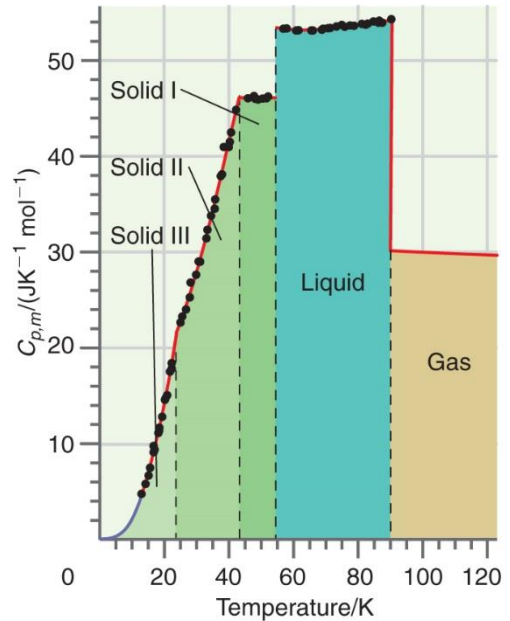


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We can also compute the absolute entropy by integrating the heat capacity. At constant pressure the entropy is

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

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. (Figure 5.8. data of  $O_2$  see details for the book.)

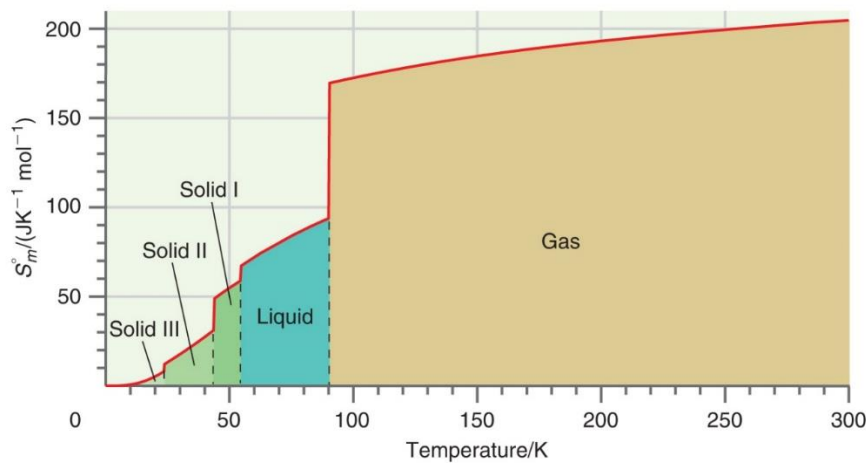


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At low temperatures the solid heat capacity is close to 0 also at 0K the entropy is =0. This is the **third law of thermodynamics**

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

Go through example 5.7



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The O<sub>2</sub> entropy at standard conditions is 204.9 J/(mol K). The largest contribution comes from the evaporation (liquid-gas transition). See the number from the book.

$$\begin{aligned}
 S_m^\ominus(298.15\text{ K}) &= S_m^\ominus(0\text{ K}) + \overbrace{\int_0^{12.97\text{ K}} \frac{C_{P,m}^{\text{solid,III}} dT}{T}}^{\text{heating solid phase III to 12.97 K}} + \overbrace{\int_{12.97\text{ K}}^{23.66\text{ K}} \frac{C_{P,m}^{\text{solid,III}} dT}{T}}^{\text{heating solid phase III}} + \overbrace{\frac{93.80\text{ J}}{23.36\text{ K}}}^{\text{transition III} \rightarrow \text{II}} \\
 &+ \overbrace{\int_{23.66\text{ K}}^{43.76\text{ K}} \frac{C_{P,m}^{\text{solid,II}} dT}{T}}^{\text{heating solid phase II}} + \overbrace{\frac{743\text{ J mol}^{-1}}{43.76\text{ K}}}^{\text{transition II} \rightarrow \text{I}} + \overbrace{\int_{43.76\text{ K}}^{54.39\text{ K}} \frac{C_{P,m}^{\text{solid,I}} dT}{T}}^{\text{heating solid phase I}} \\
 &+ \overbrace{\frac{445.0\text{ J mol}^{-1}}{54.39\text{ K}}}^{\text{fusion}} + \overbrace{\int_{54.39\text{ K}}^{90.20\text{ K}} \frac{C_{P,m}^{\text{liquid}} dT}{T}}^{\text{heating liquid}} + \overbrace{\frac{6815\text{ J mol}^{-1}}{90.20\text{ K}}}^{\text{vaporization}} \\
 &+ \overbrace{\int_{90.20\text{ K}}^{298.15\text{ K}} \frac{C_{P,m}^{\text{gas}} dT}{T}}^{\text{heating gas}} \\
 &= 0 + 1.534\text{ J mol}^{-1}\text{ K}^{-1} + 6.649\text{ J mol}^{-1}\text{ K}^{-1} \\
 &+ 3.964\text{ J mol}^{-1}\text{ K}^{-1} + 19.61\text{ J mol}^{-1}\text{ K}^{-1} \\
 &+ 16.98\text{ J mol}^{-1}\text{ K}^{-1} + 10.13\text{ J mol}^{-1}\text{ K}^{-1} \\
 &+ 8.181\text{ J mol}^{-1}\text{ K}^{-1} + 27.06\text{ J mol}^{-1}\text{ K}^{-1} \\
 &+ 75.59\text{ J mol}^{-1}\text{ K}^{-1} + 35.27\text{ J mol}^{-1}\text{ K}^{-1} \\
 &= 204.9\text{ J mol}^{-1}\text{ K}^{-1}
 \end{aligned}$$

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

For ideal gas

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

note that at very low pressures the entropy become very large. For liquid or solid the pressure variation is small (see example 5.7)

WARNING: The tabulated entropy values are referenced to 0 K but the  $\Delta H$  and  $\Delta G$  ref is the most stable form of a pure substance. See example 5.8 to compute reactions  $\Delta S$ .



## Reaction entropy

## Engel & Reid chapter 5.10

As we know the absolute entropies of any compound 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, the numbers are taken from Table 4.1.). This is strongly negative since the hydrogen gas has 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 5.8

What is the reaction entropy of reaction  $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$  at 298.15 K and 475 K

Answer: at 298.15 K  $\Delta S_R^0 = -86.5 \text{ J}/(\text{K mol})$  and at 475 K  $\Delta S_R^0 = -88.3 \text{ J}/(\text{K mol})$ .

Why is the reaction entropy negative?

## Heat pumps, car engines etc.

## Engel & Reid chapter 5.13

There are several interesting examples of real application in chapter 5.13. Read it.

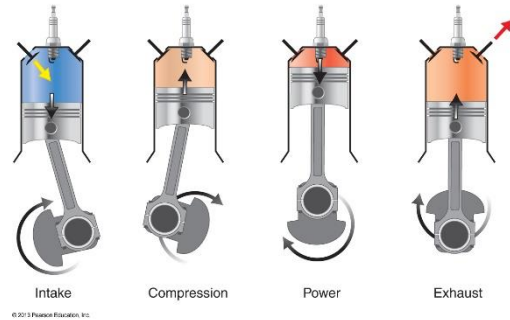
The refrigerator is a good example of a heat engine. It uses electricity to keep its interior cool. Or more general, it uses work to transport heat. Its performance (or efficiency) can be computed as

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

the typical temperatures are  $T_{cold} = 277$  K and  $T_{hot} = 294$  K then the theoretical efficiency is 16.3. This is far from real refrigerators. The book quote factor 1.5 but the European refrigerators should be better. The heat pumps have similar efficiency,

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

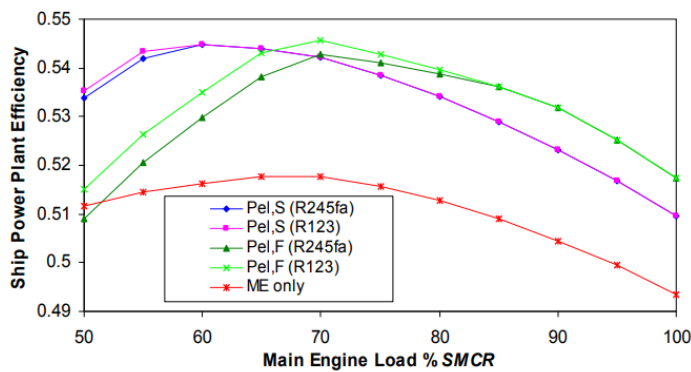
and in autumn, are  $T_{cold} = 277$  K and  $T_{hot} = 294$  K then the theoretical efficiency is 17.3. This is an overestimation and the best real efficiency is around 4-5. Overall average efficiency is a bit more than 2.



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 °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 – 25 %.

The diesel engine will operate at much higher temperatures. The diesel fuel will be injected to a hot cylinder at the end of compression. The maximum temperature is ca. 950 K. The efficiency is  $1 - 370/950 = 61\%$ . The book (chapter 5.13) has more complex analysis and with that the efficiency of 64 %. These are again 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 around 90%. It is not a heat engine. That is very good since the battery (or energy storage) is the main cost in electric cars.

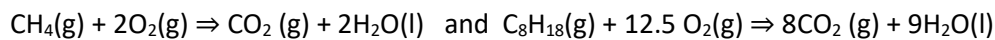
The entropy can be combined to thermodynamical energy. We know from the Clausius inequality that  $TdS > dq$ . In a constant temperature process, we can write

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

the  $w_{expansion}$  is the expansion work done to the system (and  $w_{nonexpansion}$  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

Methane and octane combustion:



(see the Table 4.1 for the numbers)

$\Delta A_{\text{comb}}(\text{CH}_4, \text{g}) = -814 \text{ kJ/mol}$ ,  $\Delta A_{\text{comb}}(\text{C}_8\text{H}_{18}, \text{g}) = -5285 \text{ kJ/mol}$ , If you take the mass of the molecules into account:  $\Delta A_{\text{comb}}(\text{CH}_4, \text{g}) = -50.6 \text{ kJ/g}$ ,  $\Delta A_{\text{comb}}(\text{C}_8\text{H}_{18}, \text{g}) = -46.3 \text{ kJ/g}$ . These are almost equal. The energy density of different hydrocarbons does not differ much.

Above the temperature was assumed to be constant.  $dT=0$ , if we choose the volume to be constant,  $dV=0$  then the  $dw_{expansion} = 0$  and if the  $dw_{nonexpansion} = 0$  then 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  $G = H - TS$ .

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

The Gibbs energy is the maximum non-expansion work the system can do

Go through example 6.2

Gibbs energy for methane and octane combustion:



Look the differences of the results in 6.1 and 6.2. Comments?  $\Delta A_{\text{comb}} \approx \Delta G_{\text{comb}}$

Now we can define Gibbs reaction energy

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

usually in chemical reaction no non-expansion work is done so for spontaneous reactions

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

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

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

The Gibbs reaction energy is probably one of the most important equations in chemistry. It will tell the equilibrium state of any chemical reaction. The equilibrium will define the yield of the reaction.

Again several Gibbs reaction energy values can be found from tables 4.2 and 4.3.

Go through Engel & Reid chapter 6.2

## Temperature and pressure dependence of G chapter 6.3

Engel & Reid

From chapter 6.2 we can get

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

for liquids V is mostly constant

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

for ideal gas

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

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 does not change much. Often a good approximation and if needed the heat capacity can be used to estimate the enthalpy at different temperatures.

With these equations we can get the Gibbs energy in other than standard conditions (pressure = 1 atm, temperature = 25 C).

Go through example 6.4

## G and concentration changes

Engel & Reid chapter 6.4

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

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

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

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

The flow occurs as long as the two chemical potentials are equal. Or in other words, in equilibrium all chemical potentials are the same.

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

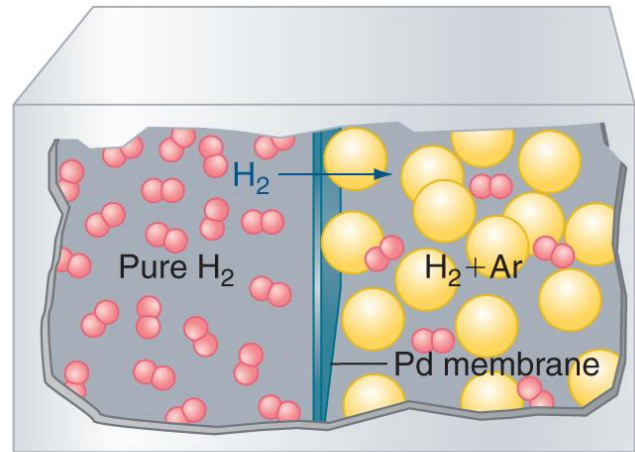
Let us look a system where a gas (here hydrogen) will penetrate through a membrane to right to gas b (here argon). The argon cannot go to left. What are the Gibbs energy of this system and the final pressure of H<sub>2</sub>?

At equilibrium

$$\mu_{\text{pure.H}_2} = \mu_{\text{mixt.H}_2}$$

the chemical potential of the pure H<sub>2</sub> gas at pressure  $P_{\text{H}_2}$  is ( $P^\circ$  is 1 atm,  $n_{\text{H}_2} = 1$  mol)

$$\mu_{\text{pure.H}_2} = \mu_{\text{H}_2}^\circ + RT \ln \frac{P_{\text{H}_2}}{P^\circ}$$



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in the mixture the H<sub>2</sub> pressure is  $x_H P$  where  $x_H$  is the mole fraction of hydrogen and the chemical potential is

$$\mu_{\text{mixt.H}_2} = \mu_{\text{H}_2}^\circ + RT \ln \frac{x_H P}{P^\circ} = \mu_{\text{H}_2}^{\text{pure}} + RT \ln x_H$$

in equilibrium  $P_{\text{H}_2} = x_H P$  so the hydrogen pressure is the same on both sides.

The Gibbs energy change in this process is  $\mu_{\text{pure.H}_2}(\text{final}) - \mu_{\text{pure.H}_2}(\text{initial})$  and we assume that the temperature is constant and ideal gas behavior.

$$\Delta G = \mu_{\text{H}_2}^\circ + RT \ln \frac{P_{\text{H}_2, \text{final}}}{P^\circ} - \left( \mu_{\text{H}_2}^\circ + RT \ln \frac{P_{\text{H}_2, \text{init}}}{P^\circ} \right) \Rightarrow$$

$$\Delta G = RT \ln \frac{P_{\text{H}_2, \text{final}}}{P_{\text{H}_2, \text{init}}} = RT \ln \frac{V_{\text{H}_2, \text{init}}}{V_{\text{H}_2, \text{final}}} < 0$$

The Gibbs energy change is negative and the process is spontaneous.

For two gas mixture the Gibbs energy is

$$\mu_{mixt.A} = \mu_A^{pure} + n_A RT \ln x_A = n_A G_{A,m} + n_A RT \ln x_A$$

where  $\mu_A^{pure}$  is molar Gibbs energy of pure A and  $x_A$  is the fraction of gas A.

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.)

$$G_{tot,not-mixed} = n_{He}G_{m,He} + n_{Ne}G_{m,Ne} + \dots$$

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

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.

For two components, the fractions are x and (1-x)

$$G_{mix} = nRT [x \ln x + (1-x) \ln(1-x)]$$

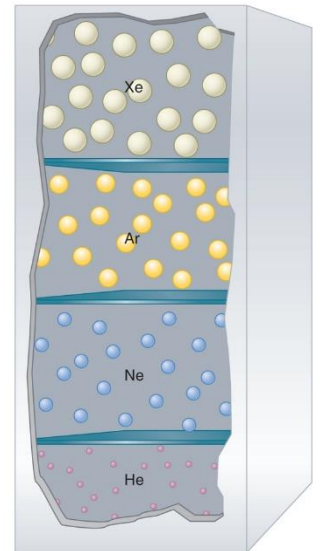
The mixing entropy can be computed as

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

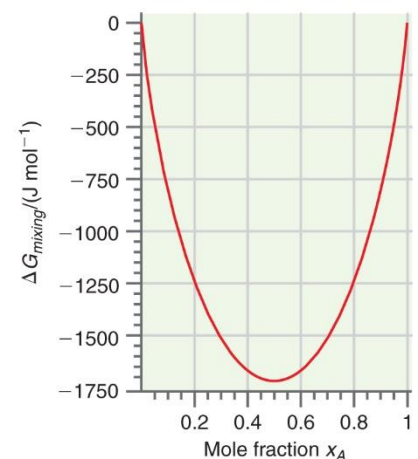
In ideal systems the mixing Gibbs energy is purely entropic.

$$G_{mix} = -TS_{mix}$$

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



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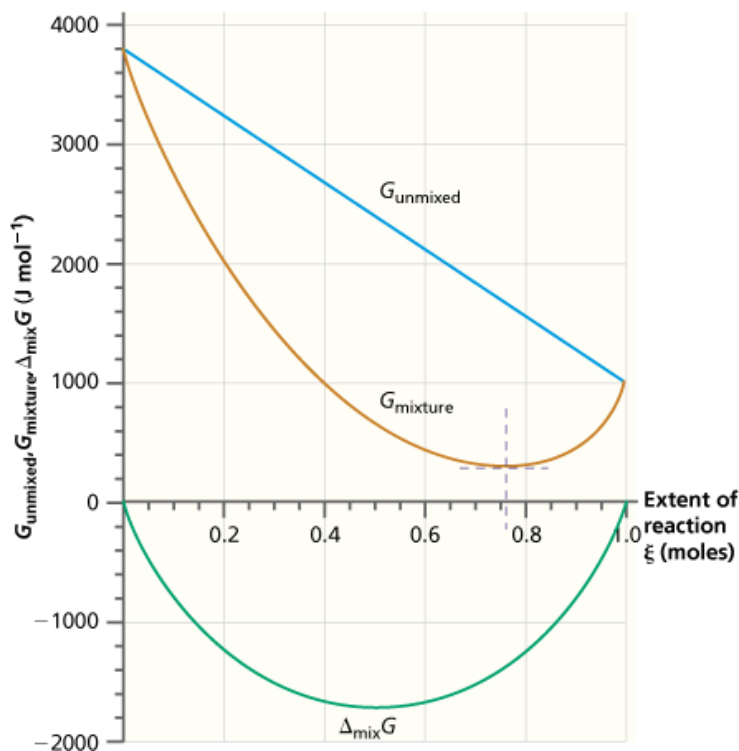
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## Gibbs energy for chemical reaction    Engel & Reid chapter 6.6

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

$$\Delta G_R^o = \sum_i \nu_i G_i^o + \nu_i RT \ln x_i$$

The equation above include also the mixing term. For a simple reaction  $A \rightarrow B$  ( $x_A = 1 - x_B$ ) and  $G_{A,m}^o = 3.8$  kJ/mol and  $G_{B,m}^o = 1.00$  kJ/mol. It is useful to see the  $G_{\min}$  and  $G_{\text{unmixed}}$ . The stable system have  $x_B = 0.756$  mol. The rection does not got to the end.



## Chemical equilibrium    Engel & Reid chapter 6.7 - 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 a very simple reaction  $\alpha A(g) \leftrightarrow \beta B(g)$  (a more complex reaction is in the book). At equilibrium the gases have partial pressures of  $P_A$  and  $P_B$ .



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

**In equilibrium**  $\Delta G_R = 0$  or  $\Delta G_R^\circ = -RT \ln Q_P$ . NOTE the difference of  $\Delta G_R$  and  $\Delta G_R^\circ$ . In this case the  $Q_P$  can be called the equilibrium constant  $K_P$

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

the  $\Delta G_R^\circ$  depend only on temperature (see example 6.7) 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 if 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.

If the system is NOT in equilibrium  $\Delta G_R \neq 0$  and  $Q \neq K$ . See example 6.7

**Go through example 6.6**

$2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$  at 298 K and pressures  $P(\text{N}_2\text{O}_4) = P(\text{NO}_2) = 1.0$  bar and 1 mol of product. Is the system in equilibrium?

Get the  $\Delta G_R^\circ$  values form table 4.2.

$\Delta G = -2.80$  kJ/mol NOT in equilibrium. The reaction goes towards  $\text{N}_2\text{O}_4$

**Go through example 6.7**

$2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$  at 325 K and pressures  $P(\text{N}_2\text{O}_4) = P(\text{NO}_2) = 1.0$  bar and 1 mol of product. Is the system in equilibrium?

Get also the  $\Delta H_R^\circ$  values form table 4.2. Use eq

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

for  $\Delta G(T_2)$ .  $\Delta G = 1.92$  kJ/mol NOT in equilibrium. The reaction goes towards  $\text{NO}_2$

**Go through example 6.8**

$2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$  at 298 K and pressures  $P(\text{NO}_2) = 0.350$  bar and  $P(\text{N}_2\text{O}_4) = 0.650$  bar and 1 mol of product.

Use  $\Delta G_R = \Delta G_R^\circ + RT \ln Q_P$  and  $Q_P = \frac{P_B}{P^\circ} \left( \frac{P_A}{P^\circ} \right)^{-2}$

$\Delta G = 1.33$  kJ/mol NOT in equilibrium. The reaction goes towards  $\text{NO}_2$

**Example 6.9**

Equilibrium constant for  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \leftrightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$  at 298 K

$$\Delta G_R^\circ = -RT \ln K$$

$\Delta G_R^\circ = (-394.4 - 0 + 237.1 + 137.2)$  kJ/mol = -20.1 kJ/mol

$K_P = 3320$ , equilibrium is strongly on the  $\text{CO}_2$  side.

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

Go through example 6.10

Reaction  $\text{Cl}_2 \leftrightarrow 2\text{Cl}$ . Compute the degree of dissociation  $\alpha = \delta_{eq}/n_0$

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

$$\alpha = \sqrt{\frac{K_p}{K_p + \frac{4P}{P^\circ}}}$$

## Temperature dependence of $K_p$

Engel & Reid chapter 6.9

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

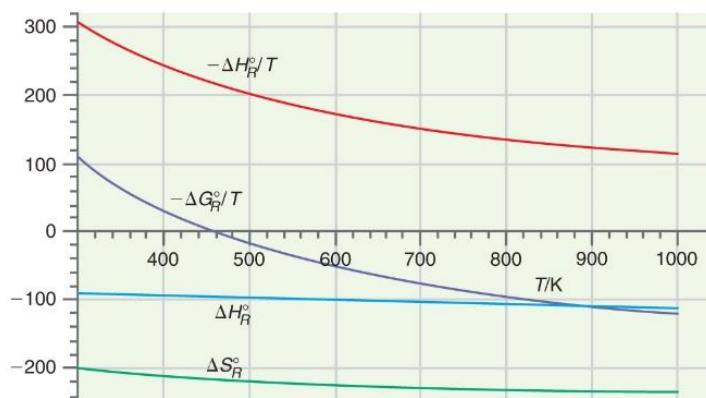
Note it is better to estimate the  $\Delta G_R^\circ$  temperature dependence from equation

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

than  $\Delta G_R^\circ = \Delta H_R^\circ - T\Delta S_R^\circ$

from equation (GT) one can derive

$$\ln K(T_2) = \ln K(T_1) - \frac{\Delta H(T_1)}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$



(a)

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Go through example 6.13 (Reaction  $\text{Cl}_2 \leftrightarrow 2\text{Cl}$  at  $P = 0.01$  bar)

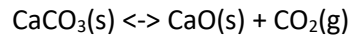
Note the very large differences of  $K_p$ ,  $K_p(800\text{K}) = 4.22 \times 10^{-11}$ ,  $K_p(1500\text{K}) = 1.03 \times 10^{-3}$  and  $K_p(2000\text{K}) = 0.134$ . The Cl-Cl bond is quite strong.

The  $\alpha$  values are at 2000 K = 0.878,  $\alpha(1500\text{K}) = 0.159$  and  $\alpha(800\text{K}) = 3.23 \times 10^{-5}$ .

## Liquid/solid-gas equilibrium

## Engel & Reid chapter 6.10

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 has 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  $\Delta G_R^o$  (note  $\Delta G_R^o$  depend on all the components.)

[Go through example 6.14](#)

At room temperature this reaction  $\Delta G_R^o$  is 131.1 kJ/mol and  $\Delta H_R^o = 178.5$  kJ/mol. Compute the equilibrium constant at 1000 K and  $\text{CO}_2$  pressure at 1000, 1100 and 1200 K.

Answer: at 1000 K  $K_p = -2.348$  and  $P(\text{CO}_2, 1000\text{K}) = 0.0956$  bar,  $P(\text{CO}_2, 1100\text{K}) = 0.673$  bar,  $P(\text{CO}_2, 1200\text{K}) = 3.42$  bar. Note the very rapid pressure change.

The problem 6.15 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 6.15](#)

## Expressing U, H, and $C_v$ solely in terms of measurable quantities

## Engel chapter 6.12

Nice to know chapter but we leave it out form the course.

## Ammonia synthesis

## Engel & Reid chapter 6.13

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