

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 melts. In ice the molecules are in fixed positions.

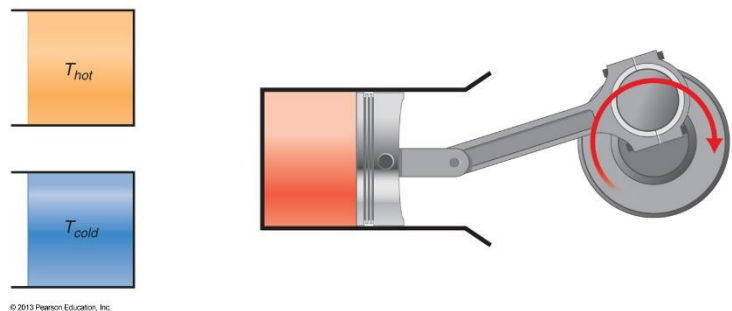
The entropy is connected to free energy. Liquid and gas phase water have very different enthalpies but in equilibrium the free energies are the same.

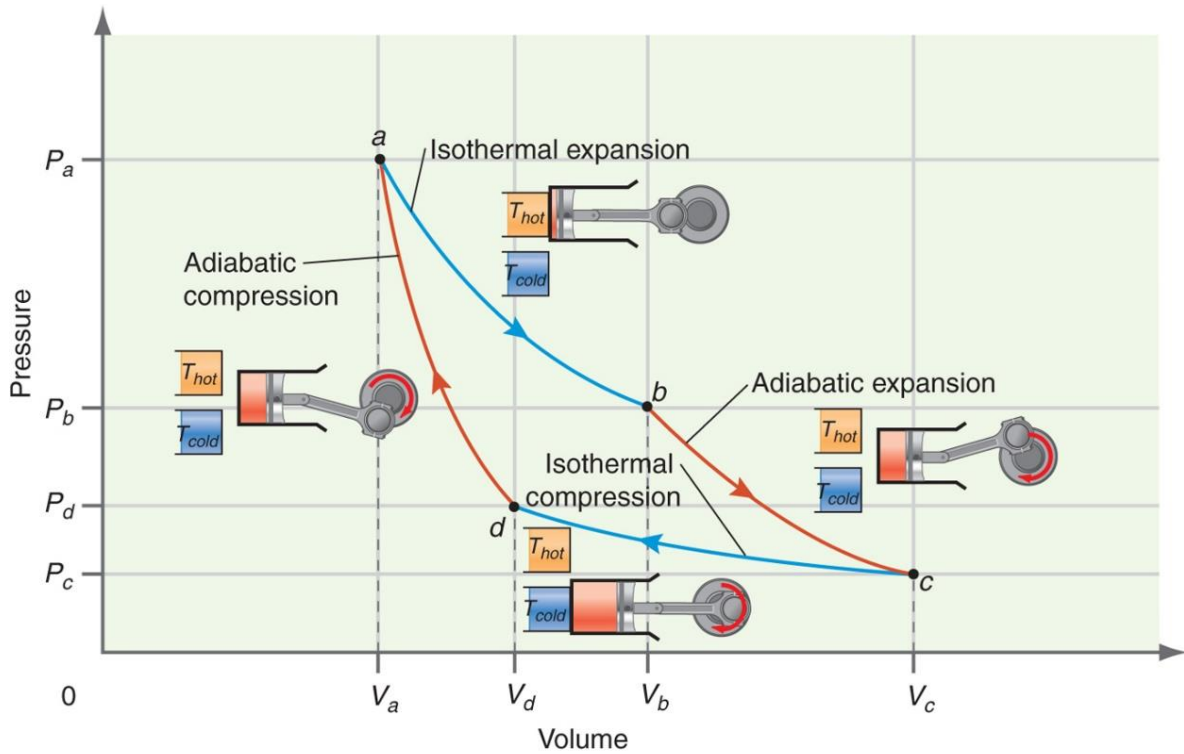
Heat engine

Engel & Reid chapter 5.10

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

The simplest model engine is the heat engine. It consists 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.





© 2013 Pearson Education, Inc.

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

TABLE 5.1 Heat, Work, and ΔU for the Reversible Carnot Cycle

Segment	Initial State	Final State	q	w	ΔU
$a \rightarrow b$	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}	$q_{ab} + q_{cd} (+)$	$w_{ab} + w_{bc} + w_{cd} + w_{da} (-)$	$\Delta U_{cycle} = 0$

© 2013 Pearson Education, Inc.

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} . This is the energy intake of the system. 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**

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.

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

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

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 the process is not adiabatic. There are temperature leaks, friction 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.

This efficiency is valid for ALL thermal processes but not e.g. electrical engines. Thus, the electric cars are much more efficient than combustion engine ones.

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

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

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

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

and

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

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, $V_i \rightarrow V_f$

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

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.

For solid systems the volume does not change much and we can use the thermal expansion coefficient (κ_T) and compressibility (β)

$$\Delta S = n \int \frac{C_{V,m} dT}{T} + \int \frac{\beta}{\kappa_T} dV \approx \frac{\beta}{\kappa_T} (V_f - V_i) + nC_{V,m} \ln \frac{T_f}{T_i}$$

See example 5.4.

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?

For solid or liquid system the volume does not change much and we can use the thermal expansion coefficient (κ_T) and compressibility (α). The T,V change

$$\Delta S = n \int \frac{C_{V,m} dT}{T} + \int \frac{\alpha}{\kappa_T} dV \approx nC_{V,m} \ln \frac{T_f}{T_i} + \frac{\alpha}{\kappa_T} (V_f - V_i)$$

the T,P change is similar

$$\Delta S = n \int \frac{C_{P,m} dT}{T} - \int V\alpha dP \approx nC_{P,m} \ln \frac{T_f}{T_i} - V\alpha(P_f - P_i)$$

See example 5.4. The detailed derivation of these equations are in chapters 5.11 and 5.12.

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.

Go through example 5.4

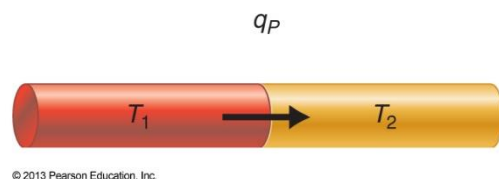
3 mol of liquid Hg is transformed from 300 K, 1 bar to 600 K, 3 bar. $C_{p,m} = 27.98$ J/(mol K)

The entropy change is $nC_{p,m} \ln \frac{T_f}{T_i} - V\alpha(P_f - P_i) = (58.2 - 1.6 \times 10^{-3})$ J/K so the pressure part is very small.

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 cold part of the rod. 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)

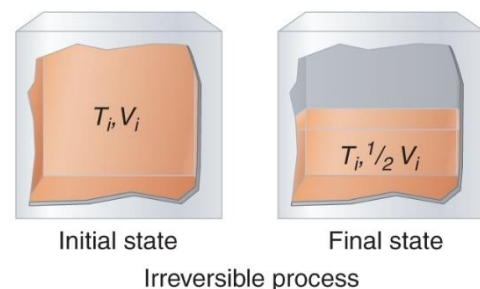
$$\Delta S = \int \frac{dq_{revert}}{T} = \frac{q_p}{T_1} - \frac{q_p}{T_2} = q_p \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

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

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

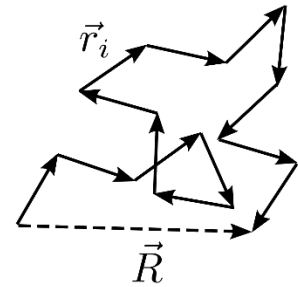
the entropy change is negative but the process is absurd. The reverse process is realistic, and its entropy change is $nR \ln 2$ which is positive.



(a)

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

A bit more complex example, random coil. Let us think a protein (or polymer) that contains rigid parts and joints that have 4 (or n) positions, forward, backward, up, down. Here we need to use the probability definition of entropy. Above is a simple example of the probability (Ω). A molecule has probability of $\frac{1}{2}$ to be on the lower part of the box (and 1 on the whole box). The entropy change is ($R=N_A k$)



$$\Delta S = k \ln(\Delta\Omega) = k \ln\left(\frac{\Omega_f}{\Omega_i}\right)^N = Nk \ln \frac{\Omega_f}{\Omega_i} = nR \ln \frac{\Omega_f}{\Omega_i}$$

If the chain is completely straight, each joint has to have the same orientation as the first one (probability = $\frac{1}{4}$). For a completely random chain the probability is 1.

The entropy difference of (long) straight and random coil is

$$\Delta S = nR \ln \frac{\Omega_f}{\Omega_i} = nR \ln \frac{1}{4} = -nR \ln 4$$

The random coil is more likely. Of course in real proteins the situation is more complex since the polymer fragments will interact and the stick-joint model is not very realistic. A very tight coil has also low entropy. Repeated forward-down-backward-up chain has entropy close to straight chain.

The main point is that entropy favors random and soft coily structures.

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, $T=300$ K.

If the compression 25 L to 10 L 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. $q_{\text{surroun}} = -q_{\text{system}}$ and then the entropy of the surrounding is

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

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 $w = -P\Delta V = -3.741 \text{ kJ}$. ($P=P_{\text{ext}}=2.494 \cdot 10^5 \text{ Pa}$) The system is isothermal, $\Delta U = 0$ and $q = -w$. 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)

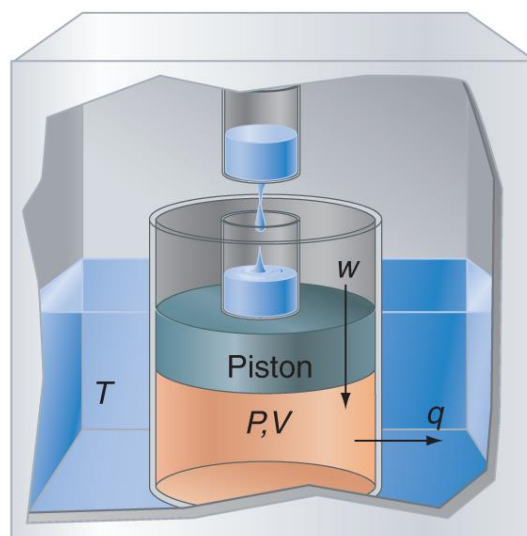
$$\Delta S_{\text{system}} = nR \ln \frac{V_f}{V_i} = -7.62 \text{ J/K}$$

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

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



© 2013 Pearson Education, Inc.

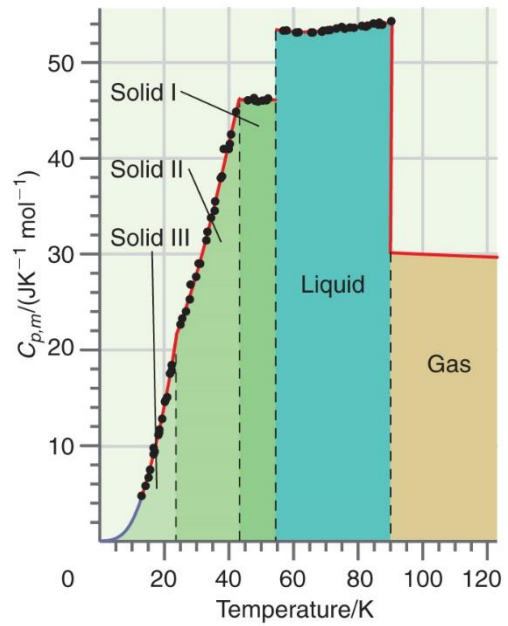
Absolute entropy

Engel & Reid chapter 5.7

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.)

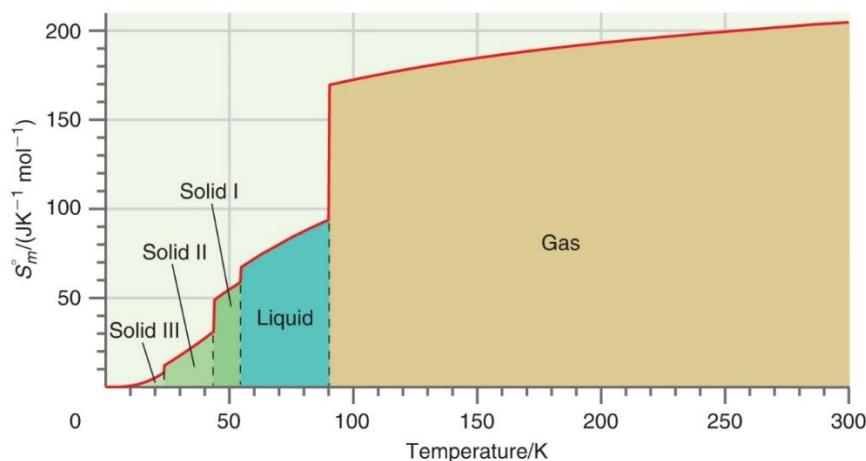


© 2013 Pearson Education, Inc.

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



© 2013 Pearson Education, Inc.

The O_2 entropy at standard conditions is 204.9 J/(mol K). The largest contribution comes from the evaporation (liquid-gas transition). See the numbers from the book.

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

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 ΔH and ΔG ref is the most stable form of a pure substance. See example 5.8 to compute reactions ΔS .

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 number are take form Table 4.1.). 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 5.8

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 (S° : CO = 197.67, O₂ = 213.74, CO₂ = 205.14 kJ/(K mol))

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 the reaction entropy is 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.

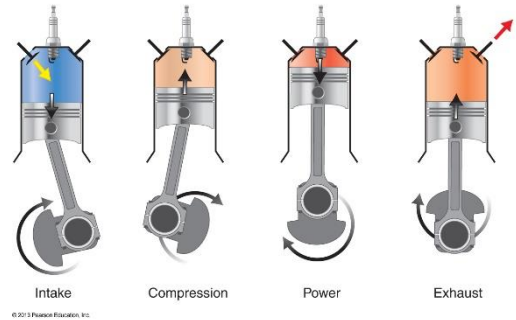
The refrigerator is a good example of a heat engine. It uses electricity to keep its interior cool. Or more general. it uses work to transport heat. Its performance (or efficiency) can be computed as

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

the typical temperatures are $T_{cold} = 277 \text{ K}$ and $T_{hot} = 294 \text{ K}$ 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 $T_{cold} = 277 \text{ K}$ and $T_{hot} = 294 \text{ K}$ 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)

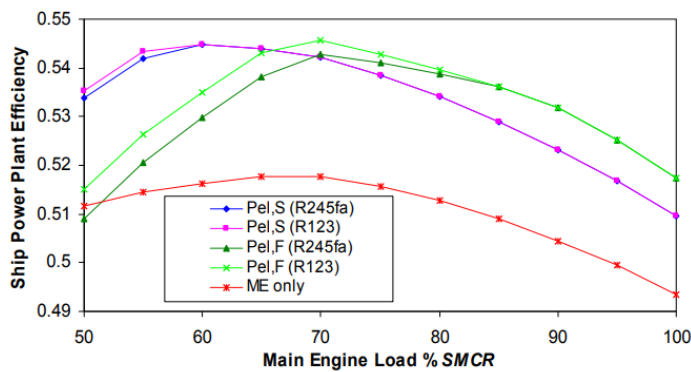


Figure 19. Ship Power Plant Efficiency with organic fluids— $\eta_{p,ship}$ (power only).

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.

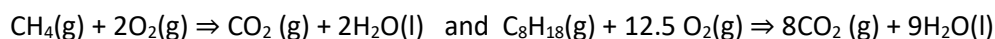
The entropy can be combined to thermodynamical energy. We know from the Clausius inequality that $TdS > dq$. In a constant temperature process, we can write

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

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 describes 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:

$$\Delta G_{\text{comb}}(\text{CH}_4, \text{g}) = -818 \text{ kJ/mol}, \quad \Delta G_{\text{comb}}(\text{C}_8\text{H}_{18}, \text{g}) = -5296 \text{ kJ/mol},$$

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

Gibbs energy is the most important "energy" in chemistry.

Now 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 non-expansion 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 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.

The most important relation is $dG(T, P) = -SdT + VdP$

Temperature and pressure dependence of G chapter 6.3

Engel & Reid

At constant temperature from chapter 6.2 we can get the pressure dependence

$$\int_{P^0}^P dG = \int_{P^0}^P VdP'$$

for liquids and solids V is close to constant

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

for ideal gas

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

from Gibbs-Helmholtz equation we have the temperature dependence

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

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**, μ

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

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.

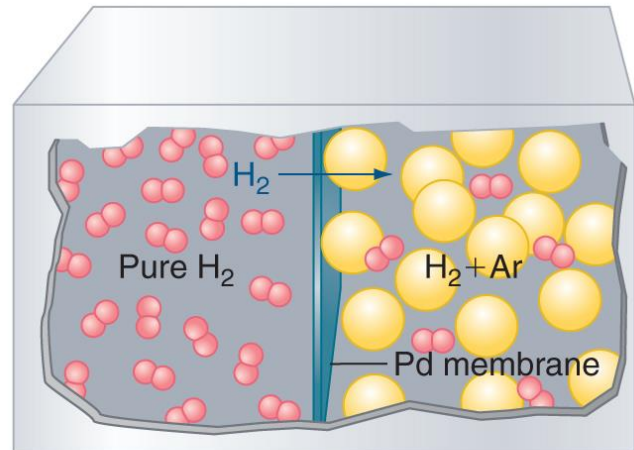
The chemical potential is a very intuitive quantity. Let us assume a specie to have chemical potential μ^I in one part of the system and μ^{II} in the other. If $\mu^I > \mu^{II}$ and the molecules can flow (change of dn) from one system to another the Gibbs energy change

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

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 is the Gibbs energy of this system and the final pressure of H₂?



© 2013 Pearson Education, Inc.

At equilibrium

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

the chemical potential of the pure H₂ gas at pressure P_{H_2} is (P° is 1 atm, $n_{H_2} = 1$ mol)

$$\mu_{\text{pure.H}_2} = \mu_{H_2}^\circ + RT \ln \frac{P_{H_2}}{P^\circ}$$

in the mixture the H₂ pressure is $x_H P$ where x_H is the mole fraction of hydrogen in the Argon side. The chemical potential is

$$\mu_{\text{mixt.H}_2} = \mu_{H_2}^\circ + RT \ln \frac{x_H P}{P^\circ} = \mu_{H_2}^{\text{pure}}$$

in equilibrium $P_{H_2} = x_H P$ 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.

$$\begin{aligned} \Delta G &= \mu_{H_2}^\circ + RT \ln \frac{P_{H_2, \text{final}}}{P^\circ} - \left(\mu_{H_2}^\circ + RT \ln \frac{P_{H_2, \text{init}}}{P^\circ} \right) \Rightarrow \\ \Delta G &= RT \ln \frac{P_{H_2, \text{final}}}{P_{H_2, \text{init}}} = RT \ln \frac{V_{H_2, \text{init}}}{V_{H_2, \text{final}}} < 0 \end{aligned}$$

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

G of gas mixing

Engel & Reid chapter 6.5

For two gas mixture the Gibbs energy is

$$\mu_A^{\text{mixt}} = \mu_A^{\text{pure}} + n_A RT \ln \frac{P_A}{P} = \mu_A^{\text{pure}} + n_A RT \ln x_A = n_A G_{A,m} + n_A RT \ln x_A$$

where μ_A^{pure} is molar Gibbs energy of pure A and x_A is the fraction of gas A, $P_A = x_A P$.

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.)

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

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

$$= n_{He}G_{m,He} + \dots + nRT(x_{He} \ln x_{He} + \dots)$$

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 $(1-x)$

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

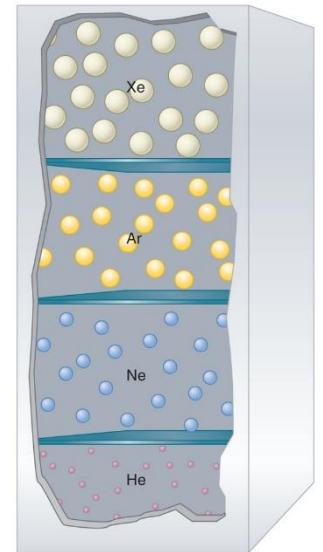
The mixing entropy can be computed as

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

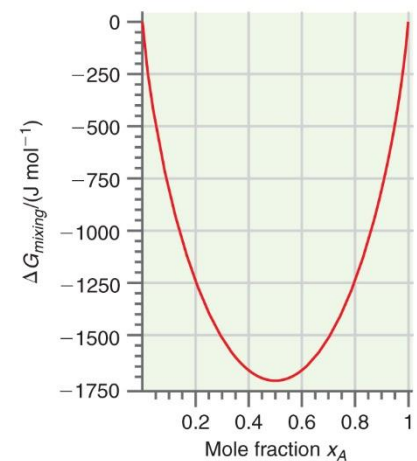
In ideal systems the mixing Gibbs energy is purely entropic.

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

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



© 2013 Pearson Education, Inc.



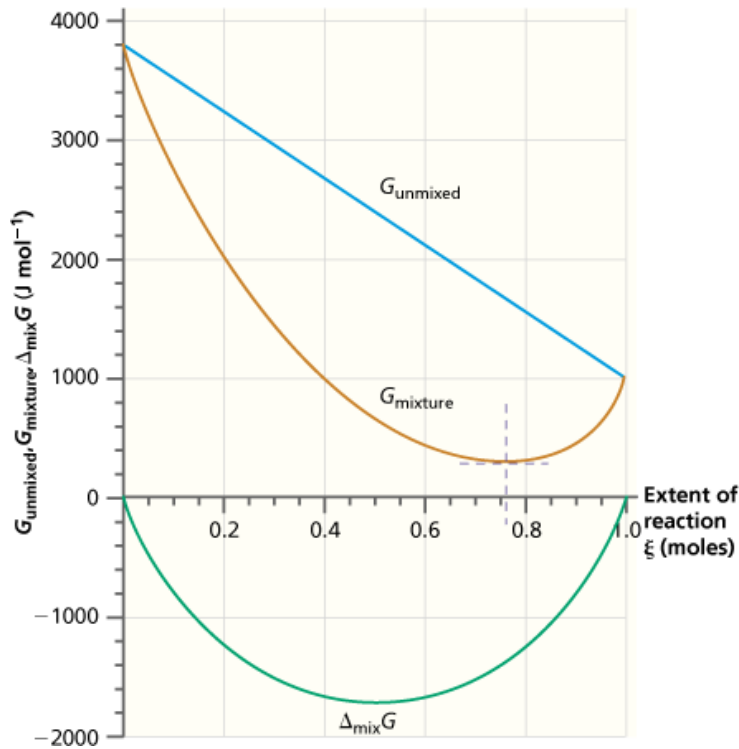
© 2013 Pearson Education, Inc.

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:

$$\Delta G_R^0 = \sum_i \nu_i G_i^0 + \nu_i RT x_i \ln x_i$$

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_{unmixed} . The stable system have $x_B = 0.756$ mol. The reaction does not got to the end. Without the mixing term every reaction would be 100 % either on the reaction or product side.



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 .

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

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

$$\Delta G_R^0 = -RT \ln K_P \quad \text{or} \quad K_P = \exp(-\Delta G_R^0 / RT)$$

the ΔG_R^0 depend only on temperature (see example 6.7) and thus the K_P also depend only on 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 6.7

$2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$ at 298 K and partial pressures $P(\text{N}_2\text{O}_4) = P(\text{NO}_2) = 0.5$ bar and 1 mol of product. Is the system in equilibrium?

Get the ΔG_R^0 values from table 4.2. (99.8 kJ/mol and 51.3 kJ/mol) and compute the pressure term.

$\Delta G = -1.08$ kJ/mol NOT in equilibrium. The reaction goes towards N_2O_4

An example

$2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$ 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.

$$\text{Use } \Delta G_R = \Delta G_R^0 + RT \ln Q_P \quad \text{and} \quad Q_P = \frac{P_B}{P^0} \left(\frac{P_A}{P^0} \right)^{-2} = P_B P^0 / P_A^2$$

$\Delta G = 1.33$ kJ/mol NOT in equilibrium. The reaction goes towards NO_2 . Compare to above. We are close to equilibrium. (At equilibrium $P(\text{NO}_2) = 0.43$ bar, $P(\text{N}_2\text{O}_4) = 0.57$ bar.)

Go through example 6.8

$2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g})$ at 525 K and pressures $P(\text{N}_2\text{O}_4) = P(\text{NO}_2) = 0.5$ bar and 1 mol of product. Is the system in equilibrium? Use the $\Delta G(298 \text{ K})$ from example 6.7.

Get also the ΔH_R^0 values from table 4.2. (9.16 kJ/mol and 33.2 kJ/mol). Use eq

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H^0(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

for $\Delta G(298 \text{ K}) = -1.08$ kJ/mol and $\Delta G(T_2) = 41.6$ kJ/mol NOT in equilibrium. The reaction goes strongly towards NO_2 . I got a bit different value than in the book. There is a sign error in the book.

Example 6.11

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. Here $Q=1$ and $\ln Q = 0$.

$$\Delta G_R^0 = -RT \ln K$$

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

$K_P = 3320$, equilibrium is strongly on the CO_2 side.

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

Go through example 6.12

Reaction $\text{Cl}_2 \leftrightarrow 2\text{Cl}$. Compute the degree of dissociation $\alpha = \delta_{eq}/n_0$, $K_p = \left(\frac{P(\text{Cl})}{P_0}\right)^2 / \left(\frac{P(\text{Cl}_2)}{P_0}\right)$ Why the mole fractions are $(n_0 - \delta_{eq})/(n_0 + \delta_{eq})$ and $2\delta_{eq}/(n_0 + \delta_{eq})$

$$\alpha = \sqrt{\frac{K_p}{K_p + \frac{4P}{P_0}}}$$

Temperature dependence of K_p

Engel & Reid chapter 6.9

The equilibrium constant has strong temperature dependence due to the exp function $K_p = \exp(-\Delta G_R^0/RT)$. How is the temperature dependence of Gibbs energy, $\Delta G_R^0 = \Delta H_R^0 - T\Delta S_R^0$ or $\Delta G_R^0/T = \Delta H_R^0/T - \Delta S_R^0$ here the main temperature dependence comes from the H/T, both H and S do not vary much over temperature. (Figure (a) Ammonia synthesis)

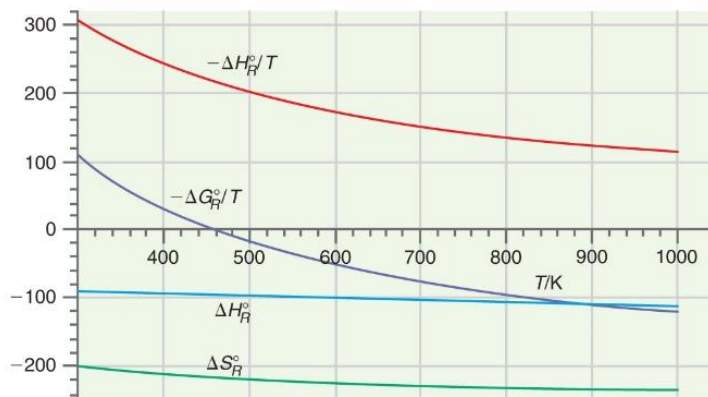
Note it is better to estimate the ΔG_R^0 temperature dependence from equation

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

than $\Delta G_R^0 = \Delta H_R^0 - T\Delta S_R^0$

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)

© 2013 Pearson Education, Inc.

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

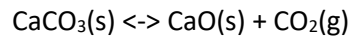
Note the very large differences of K_p , $K_p(800\text{K}) = 4.22 \times 10^{-11}$, $K_p(1500\text{K}) = 1.03 \times 10^{-3}$ and $K_p(2000\text{K}) = 0.134$. The Cl-Cl bond is quite strong.

The α 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. At room temperature

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

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

so the gas pressure depend on the ΔG_R° (note ΔG_R° depend on all the components.)

at higher temp

$$\ln K(T_2) = \ln K(T_0) - \frac{\Delta H(T_0)}{R} \left(\frac{1}{T_2} - \frac{1}{T_0} \right) = -\frac{\Delta G_R^\circ}{RT_0} - \frac{\Delta H(T_0)}{R} \left(\frac{1}{T_2} - \frac{1}{T_0} \right)$$

Go through example 6.14

At room temperature this reaction ΔG_R° is 131.1 kJ/mol and $\Delta H_R^\circ = 178.5$ kJ/mol. Compute the equilibrium constant at 1000 K and CO_2 pressure at 1000, 1100 and 1200 K.

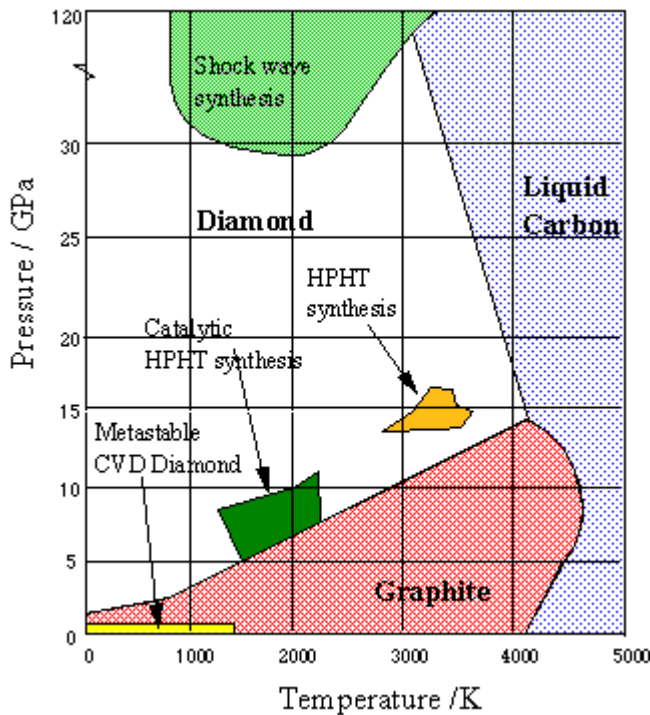
Answer: at 1000 K $K_p = -2.348$ and $P(\text{CO}_2, 1000\text{K}) = 0.0956$ bar, $P(\text{CO}_2, 1100\text{K}) = 0.673$ bar, $P(\text{CO}_2, 1200\text{K}) = 3.42$ bar. Note the very rapid pressure change.

The reverse reaction is interesting since it is one of the possible reactions to store CO_2 in solid form. At room temperature the CO_2 partial pressure is very low.

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 very slow. ("Diamonds are NOT forever", sorry Shirley Bassey and De Beers)

Go through example 6.15

The pressure is 1.5×10^4 bar = 1.5 GPa.



From Waikato Journal of Education 19 (2014), DOI:10.15663/wje.v19i2.103

An example: water vapor pressure, $\Delta H_f^0(\text{liq}) = -285.8 \text{ kJ/mol}$, $\Delta H_f^0(\text{gas}) = -241.8 \text{ kJ/mol}$, $\Delta G_f^0(\text{liq}) = -237.1 \text{ kJ/mol}$, $\Delta G_f^0(\text{gas}) = -228.8 \text{ kJ/mol}$.

At room temp. $\mu^o(w, \text{liq}) = \mu^o(w, \text{gas}) + RT \ln \frac{P_w}{P^o} \Rightarrow \frac{P_w}{P^o} = \exp\left(\frac{\Delta\mu}{RT}\right)$ insert the numbers

$p(\text{gas}) = 0.0324 \text{ atm}$. (exp 0.0313 atm)

At 350 K, $G(\text{liq}) = -228.6 \text{ kJ/mol}$, $G(\text{gas}) = -226.3 \text{ kJ/mol}$ and $p(\text{gas}) = 0.845 \text{ atm}$ (this is not very close to exp, exp ca. 0.44 atm)

At 370 K (=96.9 C), $p(\text{gas}) = 1.004 \text{ atm}$. Very good results since we assumed that the enthalpies does not change.

Ethanol vapor pressure, $\Delta H_f^0(\text{liq}) = -277.6 \text{ kJ/mol}$, $\Delta H_f^0(\text{gas}) = -234.8 \text{ kJ/mol}$, $\Delta G_f^0(\text{liq}) = -174.8 \text{ kJ/mol}$, $\Delta G_f^0(\text{gas}) = -167.9 \text{ kJ/mol}$.

At room temp. $\mu^o(w, \text{liq}) = \mu^o(w, \text{gas}) + RT \ln \frac{P_w}{P^o} \Rightarrow \frac{P_w}{P^o} = \exp\left(\frac{\Delta\mu}{RT}\right)$ insert the numbers

$p(\text{gas}) = 0.0618 \text{ atm}$.

At 350 K, $G(\text{liq}) = -156.92 \text{ kJ/mol}$, $G(\text{gas}) = -156.26 \text{ kJ/mol}$ and $p(\text{gas}) = 0.798 \text{ atm}$

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.

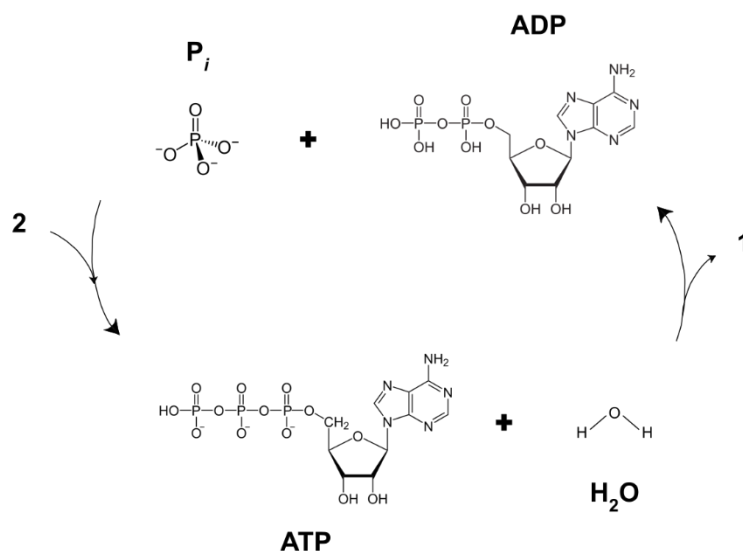
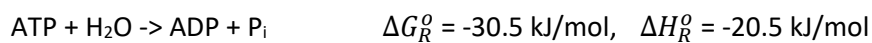
Ammonia synthesis

Engel & Reid chapter 6.13

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

ATP cycle (Not in the E&R book)

Adenosine triphosphate (ATP) is the key short term energy provider in cells. The first reaction is



What is the equilibrium constant at room temp and at 37 C

$$K = \exp(-\Delta G_R^0/RT) = 2.20 * 10^5$$

$$\text{at } 310 \text{ K} \quad \frac{\Delta G(T_2)}{310} = \frac{-30.5}{298.15} - 20.5 \left(\frac{1}{310} - \frac{1}{298.15} \right), \quad \Delta G_R^{310} = -30.9 \text{ kJ/mol}, \quad \text{and } K = 1.61 * 10^5$$

The equilibrium is strongly on the ADP side but in cells the ATP is more common. ATP need to be produces constantly.

The total quantity of ATP in the human body is about 0.1 mol/L. The energy used by human cells in an adult requires 100 to 150 mol/L of ATP reactions daily, which means a human will typically use their body weight worth of ATP over a day. Each ATP molecule is recycled 1000–1500 times during a single day.