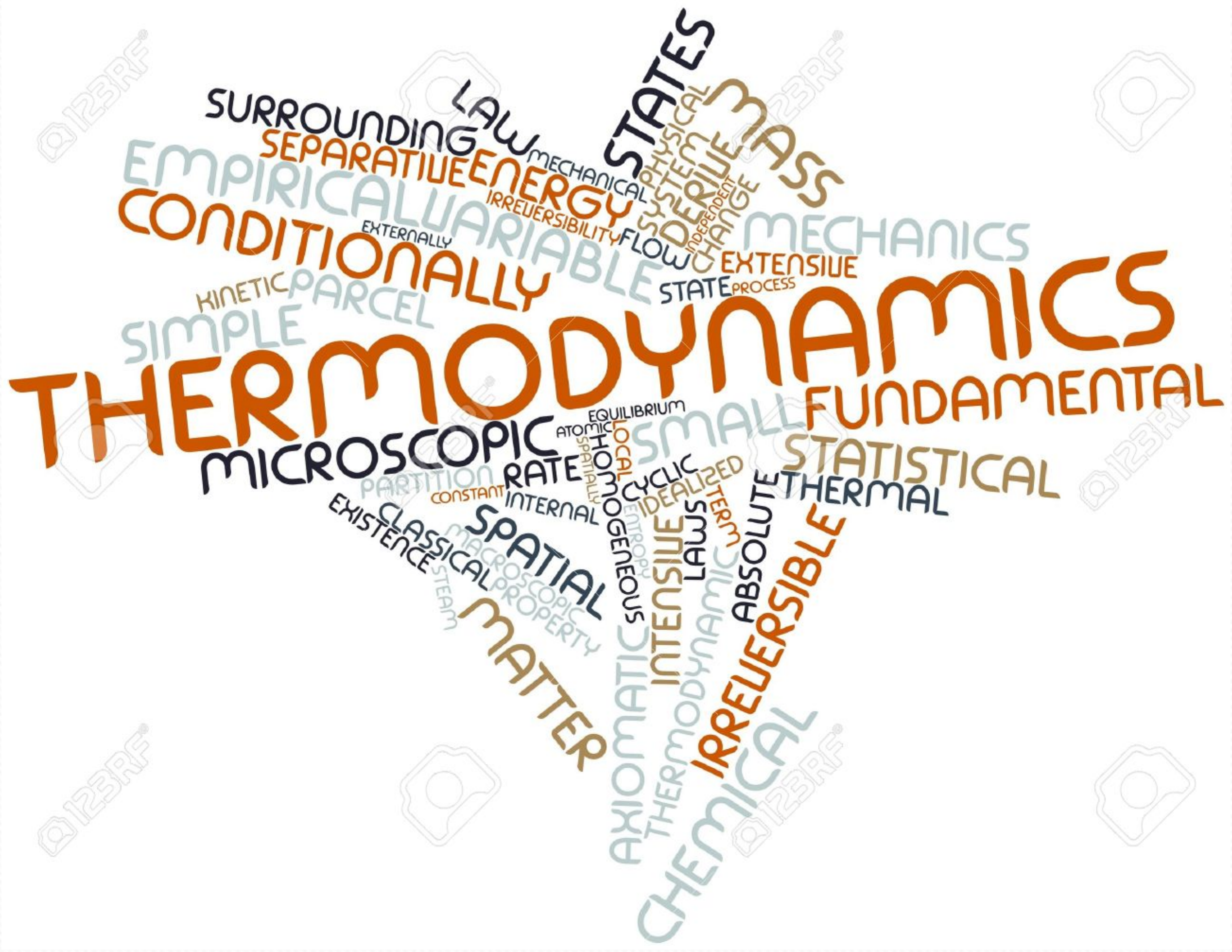


The underlying prerequisite to the application of thermodynamic principles to natural systems is that the system under consideration should be at equilibrium.

http://eps.mcgill.ca/~courses/c220/

Reversible and irreversible processes

Any natural process that proceeds at a finite rate is an irreversible process. It is called irreversible because it proceeds only in one direction. A good example of an irreversible process is radioactive decay:

$$^{226}Ra \rightarrow {}^{222}Rn + \alpha$$

Ex: oxidation of H_2S by O_2 --- $H_2S(aq) + 2O_2(aq) \rightarrow 2H^+ + SO_4^{2-}$
(in the absence of SO_4^{2-} reducing bacteria)

weathering of forsterite --- $Fe_2SiO_4 + 4H^+ \rightarrow 2Fe^{2+} + SiO_2 + 2H_2O$

decarbonation of $CaCO_3$ to wollastonite --- $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$

For chemical reactions, however, it is important to realize that the term irreversible applies only to a set of state variables (i.e., given T and P) and that the rate and direction of the reaction may change if T and P are changed.

On the other hand, a reversible process is more of an abstraction and is really an alternate view of equilibrium. One definition of a reversible process is a process that proceeds in such infinitely small steps that the system is at equilibrium at every step.

Reversible and irreversible processes

In other words, when a reaction has reached equilibrium, it must be occurring in the forward direction at the same rate as in the reverse reaction:

$$A \leftrightarrow B$$

On a macroscopic level, $dn_A/dt = dn_B/dt = 0$, there is no net change in the number of moles of A or B in the system. Nevertheless, this does not mean that there is no inter-conversion. On a microscopic scale, molecules of A are still reacting to give molecules of B and molecules of B reacting to give molecules of A. The rate of production of B = $-dn_A/dt$ is equal to the rate of decomposition of B = dn_B/dt and finite:

$$-dn_A/dt = dn_B/dt \neq 0 \quad \text{concept of microscopic reversibility}$$

Equilibrium

There are two essential conditions to satisfy the requirements of equilibrium:

-At equilibrium, system components and its properties do not change with time (regardless of how long the system is observed).

-The system will return to the same state after being disturbed (having one or more of its properties changed, then returned to their original values).

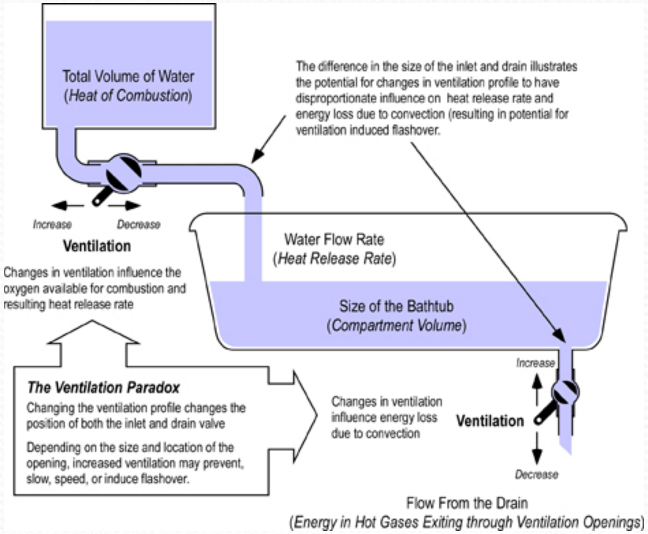
With respect to temporal variations, a system is said to be time-dependent or time-independent.

Time-dependent processes taking place within a system are called transient states (e.g., cooling melt, seasonal variations in river composition).

Whereas time-dependent processes are always in motion, time-independent processes can be dynamic or static. When they are dynamic (and show no change), the system is in a steady state. When they are static, the system is at equilibrium.

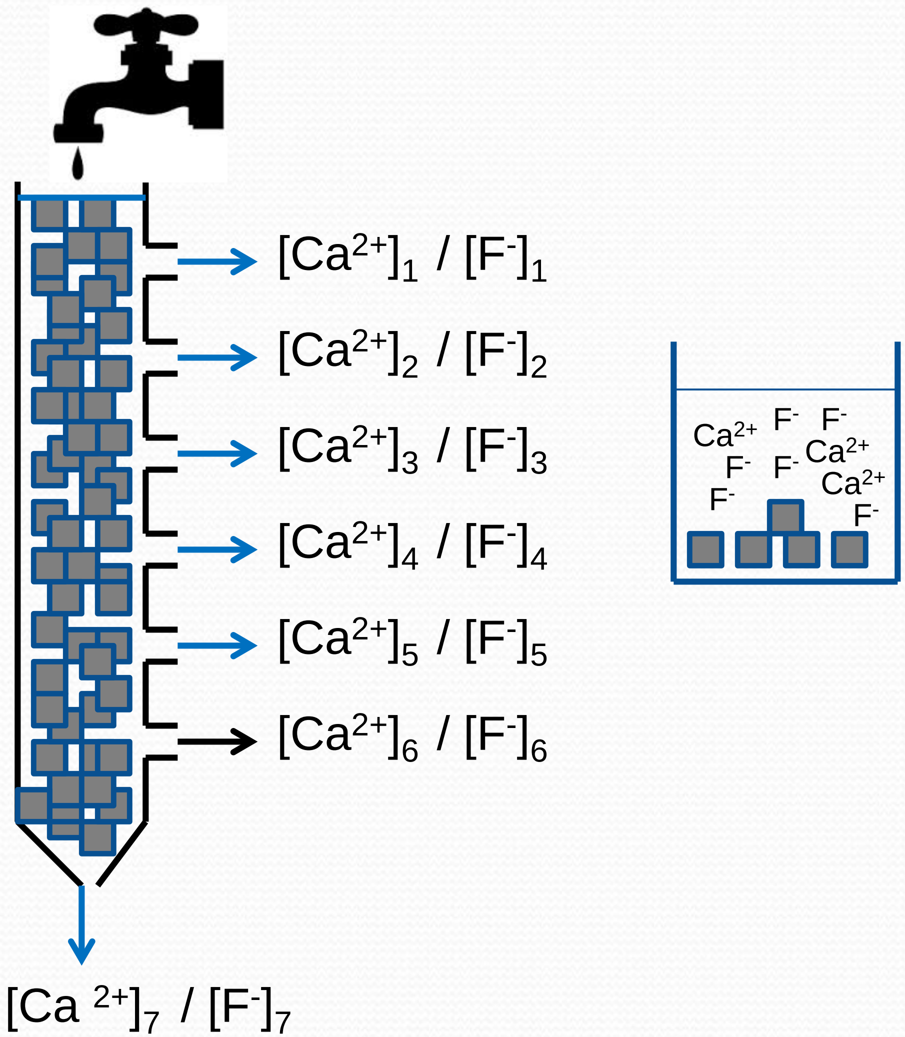
Steady state

A steady state is the time-invariant but spatially variant state (intensive variables such as P, [*i*], T) of an open or closed system.



In a steady state system, the equilibrium is apparent and determined by the spatial boundaries of the system. In other words, the steady state is fixed by the kinetics of the reactions/processes, whereas in an equilibrium system, the system has reached a state of maximum stability and is not undergoing any change.

Steady state



Local equilibrium

Even though a system is not at equilibrium as a whole, a subset or part of the system may be at equilibrium and all the thermodynamic variables and relationships can be applied to this subsystem.

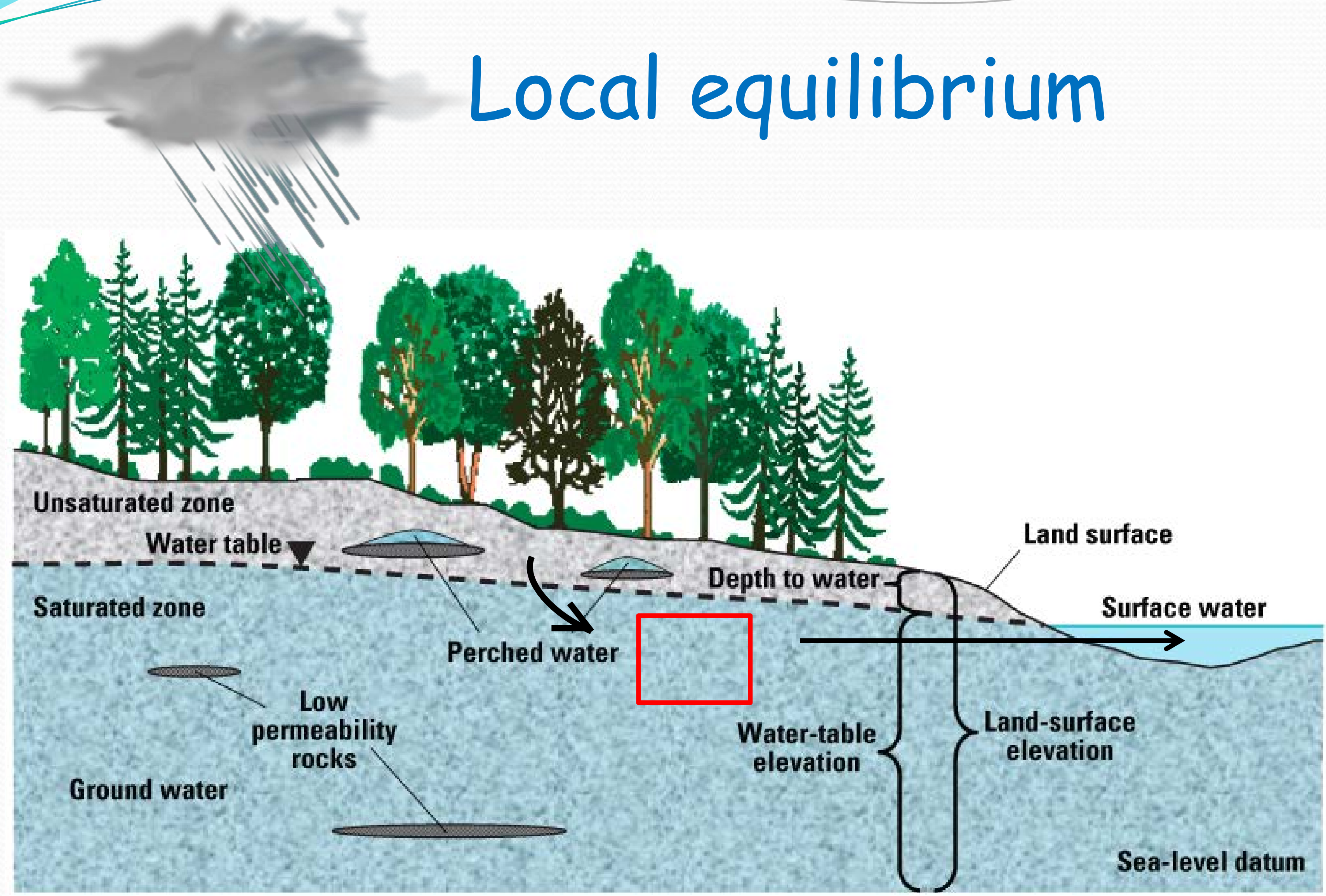
Partial equilibrium

Partial equilibrium is reached when some of the intensive variables (P, [*i*], T) in a system have reached equilibrium while others are still in a non-equilibrium state.

Metastable equilibrium

If a substance has not reached its state of maximum stability but shows no change in time, then it would be in a state of metastable equilibrium.

Local equilibrium



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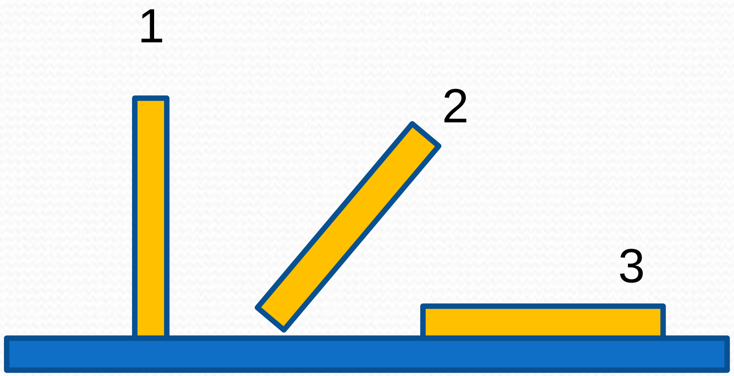
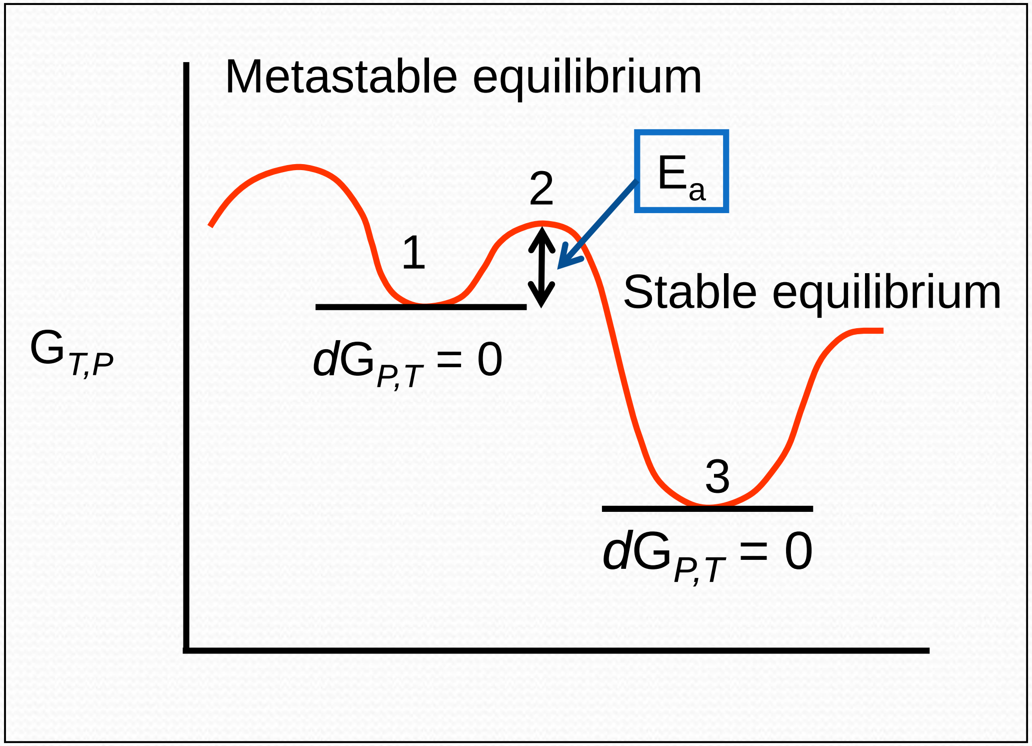




Gibbs free energy

For chemical systems, at constant temperature and pressure, the appropriate measure of energy is called the Gibbs free energy. It is related to the heat content of the system, the enthalpy, and the level of organization of the system, the entropy. The Gibbs free energy (G_i) of a substance is defined as $G_i = H_i – TS_i$, where H and S are, respectively, the enthalpy and the entropy of the substance.

At equilibrium and constant P:
$dH = dE + PdV$

$dE = dq + dw_{on} = dq - PdV - vdP + \Sigma\ dw'$ (other work, including chemical work, dG)

$= dq_p - PdV + \Sigma\ dw'$ at constant P

$= TdS - PdV + \Sigma\ dw'$ at constant P & T, substituting $\Sigma\ dw' = dG$

$dG = dE + PdV - TdS = dH – TdS$, since $dH = dE + PdV$

integrating, we get : $\Delta G = \Delta H - T\Delta S$

Enthalpy

Enthalpy (H) is the heat content of a substance at constant pressure ($dq_p = dH$). We cannot measure the absolute/intrinsic value of the heat of a substance, it is calculated from the heat of formation of its constituent elements at a given temperature and pressure. By convention, the enthalpy of formation of pure elements in their most stable form at 25°C and 1 bar pressure is arbitrarily assigned a value of zero ($\Delta H^o_f = 0$).

For:

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(l)$$

The enthalpy is an extensive property and a state function (irrespective of the path) and, therefore, additive.

$$\begin{aligned}\Delta H^o_r &= \Delta H^o_{products} - \Delta H^o_{reactants} \\ &= \Delta H^o_f\,(H_2O) - \Delta H^o_f\,(H_2) - \tfrac{1}{2}\,\Delta H^o_f\,(O_2) \\ &= \Delta H^o_f\,(H_2O) = -285.83 \text{ kJ mol}^{-1} \\ &\quad \text{or } -68.315 \text{ kcal mol}^{-1}\ (1 \text{ cal} = 4.184 \text{ J})\end{aligned}$$

Entropy

The entropy at 25^{o}C and 1 bar represents the heats involved in all state or phase transformations that a substance has undergone between 0K and 298.15K. Entropy values are absolute and based on a reference state defined by the third law of thermodynamics. In practice, the entropy is determined calorimetrically for solids, liquids, or gases by measuring the heat capacity of the substance of interest at a constant pressure (C_p) from 0K to a temperature T. The heat capacity is the number of calories or joules required to raise the temperature of one mole of the substance by 1K (dq_p/dT) at constant P.

$$dS = dq_{rev}/T,$$

at constant P, $dH = dq_p \rightarrow dS = dH/T$ and since $dH = C_p dT$

$$dS = C_p\, dT/T$$

Entropy

If T(1) = 0K and T(2) = T, then:

$$S_T = S_0 + \int_{T_1}^{T_2} C_p/T\,dT + \text{heat of phase change}$$

$$S = \int_{T_m} C_p dT/T + \Delta H_f/T_m + \int_{T_m}^{T_b} C_p\,dT/T + \Delta H_v/T_b + \int_{T_b}^{T} C_p\,dT/T$$

For a number of substances, heat capacities can be calculated from thermodynamic data, but more commonly, heat capacities are obtained by direct measurements and fitted to an empirical polynomial equation such as:

$$C_p = a + bT + CT^{-0.5} + dT^{-2} + \ldots$$

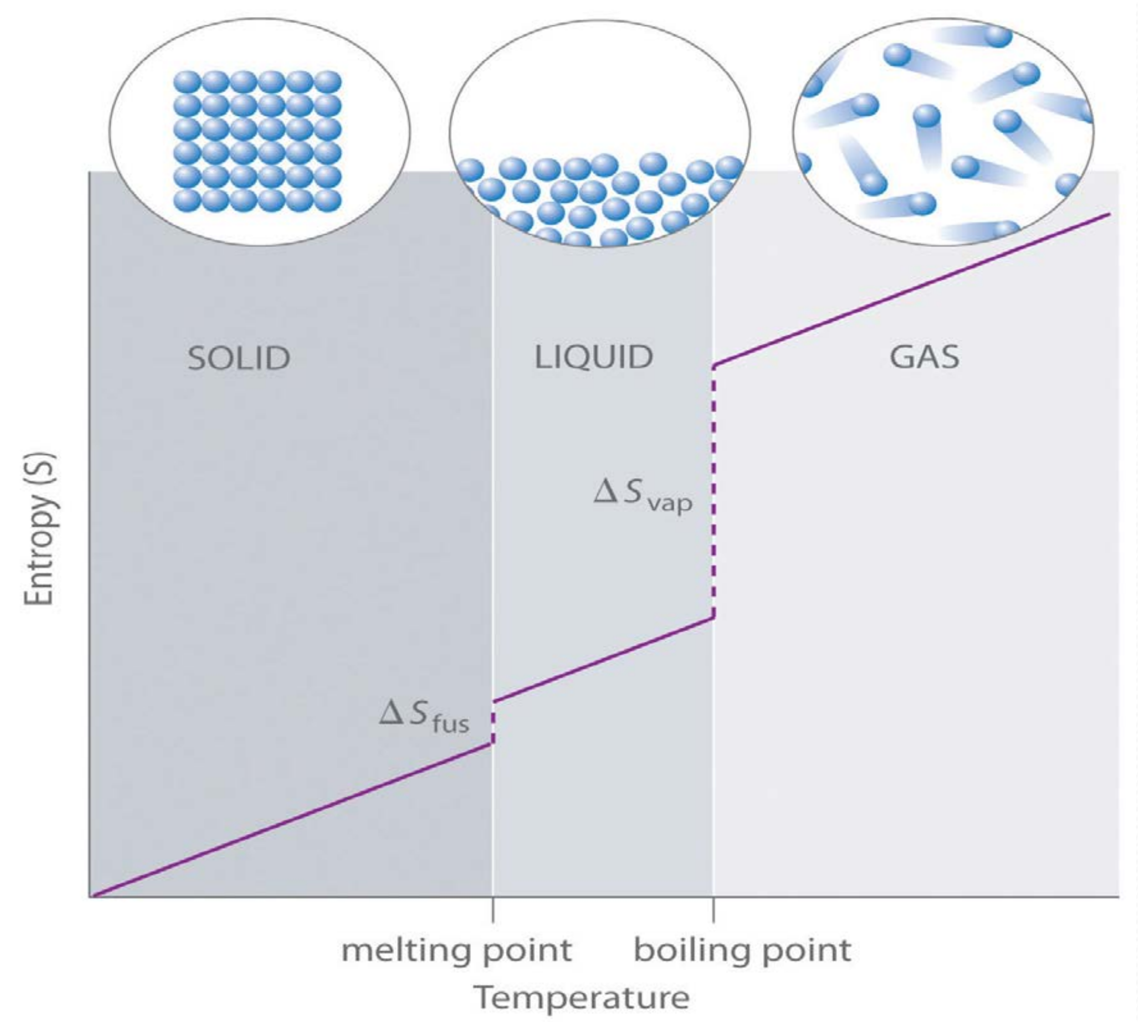
where a, b, c and d are the coefficients of the polynomial fit.

Hence, the effect of temperature on the enthalpy at constant pressure would be given by :

$$\int_{T_r}^{T} dH = \int_{T_r}^{T} C_p dT = \int_{T_r}^{T} (a + bT + CT^{-0.5} + dT^{-2} + \ldots)\,dT$$

$$H_T - H_{Tr} = a\,(T - T_r) + b/2\,(T^2 - T_r^2) + 2c\,(T^{0.5} - T_r^{0.5}) + d(1/T - 1/T_r)$$

Entropy



SOLID
LIQUID
GAS
Entropy (S)
ΔS_{vap}
ΔS_{fus}
melting point
boiling point
Temperature

Gibbs free energy

Like enthalpy, the Gibbs free energy of a substance cannot be measured directly. Its value must be obtained from the difference in the free energy of formation of the constituent elements:

$$\Delta G_f = (G_{substance} - G_{elements}) = \Delta H_f - T\Delta S_f$$

$$\text{or} \quad \Delta G_{f(T,P)} = (G_{substance\ (T,P)} - G_{elements\ (T,P)})$$

Unlike the enthalpy of the elements, there is no convention assigning values to the free energies of the elements, $G_{elements\ (T,P)}$. …

$$CaCO_3 + SiO_2 \leftarrow\rightarrow CaSiO_3 + CO_2 \quad (Ca, C, 5O, Si)$$

The ΔG for a reaction is the maximum energy change for that reaction as useful work, measured at a constant temperature and pressure. When the state of a chemical system tends towards equilibrium, it releases energy, some combination of heat and entropy change takes place which causes a decrease in G.

Gibbs free energy

When you mix a strong acid with water, the solution heats up ($\Delta H_r < 0$, exothermic). The reaction, in this case the dissociation of the acid, releases energy in the form of heat. On the other hand, the dissolution of potassium nitrate, KNO_3, in water is endothermic but the salt still dissolves in water ($\Delta G < 0$). The energy which drives the reaction toward the dissolution of KNO_3 is mostly released through entropy in modifying the structural arrangement of the water molecules.

If: $\Delta G_r < 0$ (is negative), the reaction should occur spontaneously
$\Delta G_r = 0$, the reaction is at equilibrium
$\Delta G_r > 0$ the reaction is thermodynamically impossible. It cannot occur unless an external source of energy is applied to it (or you change the state variables).

Gibbs free energy

If an infinitesimal amount of a component i is added to the system, then the amount by which the Gibbs free energy of the system changes is given by:

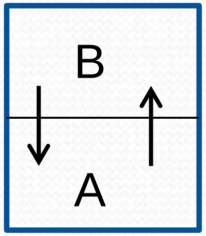
$$(dG/dn_i)_{T,P} = \text{partial molal Gibbs free energy} = \mu_i$$

where the subscript i refers to the component added to the system and n is the number of moles being added. The partial molal Gibbs free energy of a component is also called its chemical potential, μ_i.

Conversely, the Gibbs free energy of a system is given by the chemical work which depends on the composition of the system: $dG = \Sigma\, \mu_i\, dn_i$

Gibbs free energy

When two or more phases coexist at equilibrium, the chemical potential of all components in the system must be identical in each phase.
For example, if we have a closed system containing two phases, at equilibrium $(\mu_i)_A = (\mu_i)_B$



If by some way we can increase the chemical potential in phase A without changing B, then the system will be unstable and the transfer of some component i from A to B will result in the release of energy.

The chemical potential, μ_i, of a component i in an aqueous solution, a solid solution or a gas mixture is given by:

$$\mu_i = \mu^\circ_i + RT \ln a_i$$

where μ°_i is a constant under specified T and P, R is the gas constant, T is the temperature and a_i is the activity or fugacity (effective concentration of component i). μ°_i is the chemical potential of component i in its standard state or reference state.

Chemical potential

In general, for solid solutions, solutions of two miscible liquids, and for the solvent (H_2O) in an aqueous solution, the standard state is taken to be the pure substance at the same temperature and pressure as the solution of interest.

For an aqueous solution: $\mu_{H2O} = \mu°_{H2O} + RT \ln a_{H2O}$,
in a dilute solution $a_{H2O} \rightarrow 1$ and $\mu_{H2O} = \mu°_{H2O}$

For a pure solid (e.g., calcite) $a_{CaCO3} = 1$ and $\mu_{CaCO3} = \mu°_{CaCO3}$

For a solid solution (e.g., magnesian calcite; $Ca_xMg_{(1-x)}CO_3$):

$$\mu_{CaCO3} = \mu°_{CaCO3} + RT \ln a_{CaCO3} = \mu°_{CaCO3} + RT \ln \lambda_{CaCO3} X_{CaCO3}$$

where X_{CaCO3} is the mole fraction of $CaCO_3$ (X_{CaCO3} = # moles $CaCO_3$/ $CaCO_3 + MgCO_3$) in the solid solution and λ_{CaCO3} is the activity coefficient, a measure of the deviation from ideality.

If the system behaves ideally, i.e., $\lambda_i = 1$ or $X_i = a_i$.

Chemical potential

For a real system, in the presence of very small amounts of $MgCO_3$, the solvent ($CaCO_3$) behaves according to Raoult's law (ideally) when X_{MgCO3} ~ 0, in other words $\lambda(CaCO_3) \rightarrow 1$ so that:

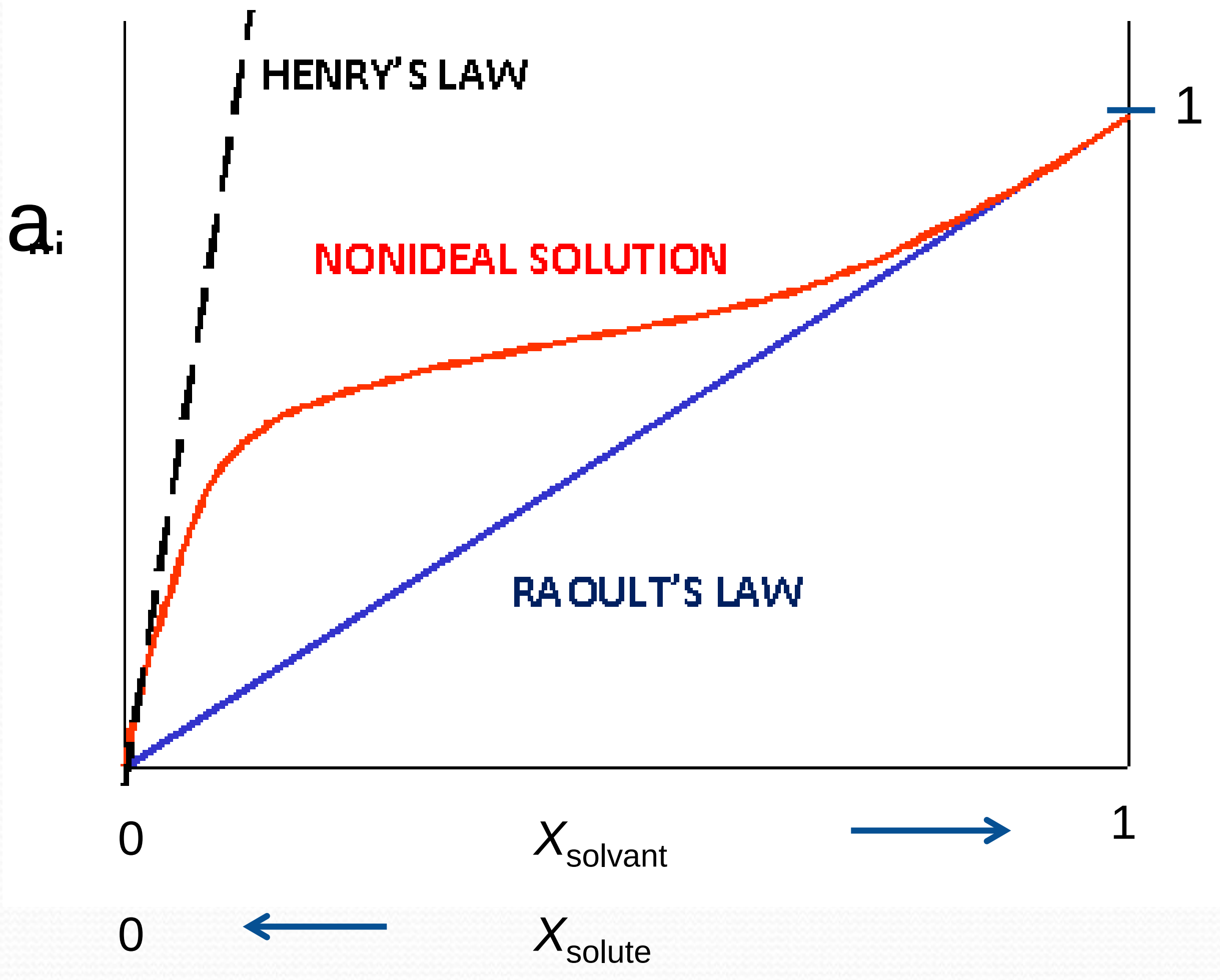
$$\mu_{CaCO3} = \mu°_{CaCO3} + RT \ln X_{CaCO3}$$ --- Raoult's law approximation

whereas the solute ($MgCO_3$) behaves according to Henry's law ($a_i = h\, X_{MgCO3}$) when $X_{MgCO3} \rightarrow 0$

$$\mu_{MgCO3} = \mu°_{MgCO3} + RT \ln hX_{MgCO3}$$ --- Henry's law approximation

where h = f(nature of the solute & solvent, T, P)

Chemical potential



Chemical potential

For solutes in aqueous solutions, the pure solute does not make a convenient standard state, and the most commonly used convention is the infinite dilution convention. According to this convention, the activity of a solute approaches its concentration as the total concentration of all dissolved species approaches zero. In other words,

$$\mu_i = \mu°_i + RT \ln a_i = \mu°_i + RT \ln \gamma_i [i] = \mu°_i + RT \ln [i] + RT \ln \gamma_i$$

as $\Sigma[i] \rightarrow 0$, $\gamma_i \rightarrow 1$ and $a_i \rightarrow [i]$

under this convention, the standard state is a hypothetical ideal 1 molal solution.

Instead of mole fractions, the concentration of an environmental solution is typically reported in molality: moles solute/ 1000g of solvent

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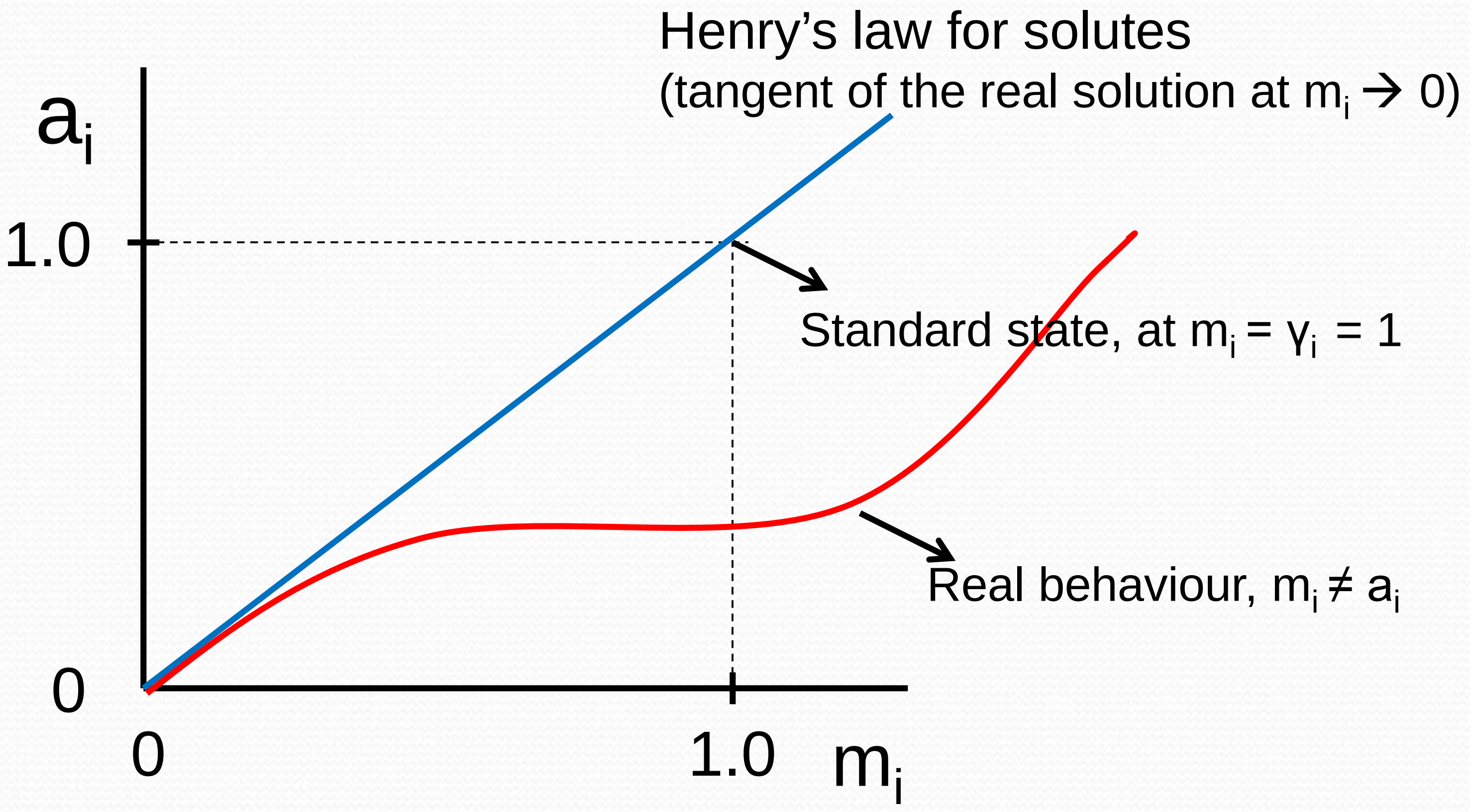
We use the molal scale (m = mol kg^{-1} solvent) instead of the molar scale (M = mol l^{-1} solution) because it is independent of T and P. The difference between molarity and molality is small in dilute solutions.

Chemical potential of solutes



Chemical potential

For gases,

$$\mu_i = \mu°_i + RT \ln f_i$$

where f_i is the fugacity of the gas = $p_i * \Gamma_i$
where Γ_i is the osmotic coefficient and $\Gamma_i = 1$ for an ideal gas.

$f_i/P \rightarrow 1$ as $P \rightarrow 0$ for a pure gas at low pressures, such as Earth surface conditions

$f_i/p_i \rightarrow 1$ as $P \rightarrow 0$ for a gas mixture

Gibbs free energy

Following from the definition of chemical potential and the general condition for chemical equilibrium in an isothermal (constant T), isobaric (constant P) one component system:

At equilibrium, dG = 0, since $(dG/dn_i)_{T,P} = \mu_i$ → $dG = \mu_i \, dn_i = 0$

For a multi-component system (since the Gibbs free energy is an extensive property and additive):

$$dG = \Sigma \, \mu_i \, dn_i = 0$$

For a chemical reaction such as:

$$aA + bB \rightarrow cC + dD$$

The Gibbs free energy per mole of reaction, ΔG_r , is the difference between the Gibbs free energy of formation of the products and the reactants:

$$\Delta G_r = \Sigma \Delta G_{f\text{- products}} - \Sigma \Delta G_{f\text{- reactants}} = \Sigma \, v_i \, \mu_i$$

Gibbs free energy

$$aA + bB \rightarrow cC + dD$$

$$\Delta G_r = \Sigma \Delta G_{f\text{- products}} - \Sigma \Delta G_{f\text{- reactants}} = \Sigma\, v_i\, \mu_i$$

$$= c\, \mu_C + d\, \mu_D - a\, \mu_A - b\, \mu_B$$

$$= c\, \mu°_C + c\, RT \ln a_C + d\, \mu°_D + d\, RT \ln a_D - a\, \mu°_A - a\, RT \ln a_A - b\, \mu°_B - b\, RT \ln a_B$$

$$= c\, \mu°_C + d\, \mu°_D - a\, \mu°_A - b\, \mu°_B + RT \ln\ ((a^c_C\, a^d_D)/(a^a_A\, a^b_B))$$

$$= \Sigma\, v_i\, \mu°_i + RT \ln\ Q \ \ \text{(reaction quotient)}$$

$$= \Delta G°_r + RT \ln\ Q$$

where $\Delta G°_r$ is the standard Gibbs free energy of the reaction when the reactants and products are both in their standard states.

Gibbs free energy

$$aA + bB \rightarrow cC + dD$$

For a system at equilibrium, $\Delta G_r = 0$

$$\Delta G_r = \Delta G°_r + RT \ln Q \quad \text{when } Q = K$$

$$-\Delta G°_r = RT \ln K = RT \ln (a^c_C\, a^d_D / a^a_A\, a^b_B) = -\Sigma\, v_i\, \mu°_I$$

$$\exp(-\Delta G°_r/(RT)) = (a^c_C\, a^d_D / a^a_A\, a^b_B) = K = \pi\, a_i^{vi}$$

where K is the equilibrium constant for the reaction at a given temperature and pressure.

According to this relationship, one can determine the equilibrium constant of the reaction either from the standard free energy of the reactants and products of the reaction or by measuring the activity of the species involved in the reaction after the system has reached equilibrium, or from the standard enthalpy and entropy of the reaction since:

$$\Delta G°_r = \Delta H°_r - T\,\Delta S°_r$$

Effect of pressure on an equilibrium constant

The variation of the chemical potential of a chemical species with pressure is given by:

$$(d\mu_i/dP)_T = \bar{V}_i \qquad \text{since} \quad dG_i = V_i\, dP - S_i\, dT \;\; \text{and } dG/dn_i = \mu_i$$

where $\bar{V}_i$ is the partial molal volume ($cm^3\ mol^{-1}$).

For a solid, $\bar{V}_i$ is simply equal to the ratio of its molecular weight to its density, $\bar{V}_i = M_i/\rho$.

For a gas, $\bar{V}_i$ is equal to the ratio of the total volume of gases, V_g, divided by the total number of moles of gas, n_g. $\bar{V}_i = V_g/n_g$ and since $PV = nRT$ for an ideal gas, $\bar{V}_i = RT/P$ and is therefore the same for all gases in the same phase.

For a solute, $\bar{V}_i$ is related to the variation in the total volume of a solution after one mole of solute has been added. Partial molal volumes of solutes can be positive or negative.

Effect of pressure on an equilibrium constant

Under standard state conditions,

$$(d\mu^\circ_i/dP)_T = \overline{V}^o_i$$

where $\overline{V}^o_i$ is the standard state partial molal volume and the standard state is again chosen to be the infinite dilution state.

At equilibrium,

$$\Delta G_r = 0 \text{ and } \Delta G^o_r = -RT \ln K = \Sigma\, v_i\, \mu^\circ_i$$

therefore, the influence of pressure on the equilibrium constant of a reaction is given by:

$$d\ln K/dP = -1/RT\, d\,(\Sigma\, v_i\, \mu^\circ_i)/dP = -\Delta V^o/RT$$

where $\Delta V^o = \Sigma\, v_i\, \overline{V}^o_i$ (do not forget that v_i is positive for the products and negative for the reactants).

$$\ln K_P/K_{P0} = -(\Delta V^o/RT)\,(P - P_0) + [\,0.5\,(\Delta K^o/RT)\,(P - P_0)^2]$$

where ΔK^o is the change in compressibility ($\Sigma\, v_i\, \overline{K}^\circ_i$)

Effect of pressure on the solubility of $CaCO_3$

Variations of the solubility of calcite and aragonite as a function of pressure (depth) can be calculated according to:

$$\ln\left[\frac{K^{P}_{(C\ or\ A)}}{K^{o}_{(C\ or\ A)}}\right] = -\left[\frac{\Delta V_{(C\ or\ A)}}{RT}\right](P-1) + \left[\frac{0.5\,\Delta K_{(C\ or\ A)}}{RT}\right](P-1)^2$$

where P is the absolute pressure (in atmosphere or bar)

ΔV and ΔK are, respectively, the change in volume and compressibility following the ionization of the solid

R is the gas constant ($83.15\ cm^{-3}\ bar\ K^{-1}\ mole^{-1}$ or $82.06\ cm^{-3}\ atm\ K^{-1}\ mol^{-1}$)

T is the absolute temperature (K)

$\Delta V = \Sigma\overline{V}_i$ (products) $- \Sigma\overline{V}_i$ (reactants) $= \overline{V}_{Ca^{2+}} + \overline{V}_{CO_3^{2-}} - \overline{V}_{CaCO_3(s)}$

$\Delta K = \Sigma\overline{K}_i$ (products) $- \Sigma\overline{K}_i$ (reactants) $= \overline{K}_{Ca^{2+}} + \overline{K}_{CO_3^{2-}} - \overline{K}_{CaCO_3(s)}$

$\Delta V_C = -16.00 + 13.18 - 36.93 = -39.75\ cm^3\ bar\ mole^{-1}$ at $S_p = 35$, $t = 25^oC$

$\Delta V_A = -37.02\ cm^3\ mole^{-1}$

$\Delta K_C = \Delta K_A = -10.59 \times 10^{-3}\ cm^3\ bar^{-1}\ mole^{-1}$

ex: at 5000 m, $K_C^P/K_C^1 = 2.55$

Effect of temperature on an equilibrium constant

The effect of temperature variations on the equilibrium constant of a reaction is typically much greater than changes in pressure.

$$(d\mu^\circ_i/dT)_P = -\bar{S}^o_i \text{ since } dG_i = V_i dP - S_i\, dT\ (+\, dW')$$

where $\bar{S}^o_i$ is the partial molal entropy. However, …

$$\Delta G^o_r = -RT \ln K = \Delta H_{298}{}^o - T\,\Delta S_{298}{}^o$$

$$\Delta G^o_r/T = \Delta H_{298}{}^o/T - \Delta S_{298}{}^o$$

$$d(\Delta G^o_r/T)/dT)_P = -\Delta H^o/T^2 \text{ or } d \ln K/dT = \Delta H^o/RT$$

Integrating between 298K and T:

$$\int_{298}^{T} d \ln K = -\Delta H_{298}{}^o/R \int_{298}^{T} d(1/T)$$

$$\ln K_T - \ln K_{298} = \ln K_T/K_{298}$$
$$= (+\Delta H_{298}{}^o/R)(1/T_{298} - 1/T) + [(\Delta C_P/R)(T_{298}/T - 1 - \ln(T_{298}/T)]$$

Assuming that ΔH^o is independent of T,

$$\ln K_T/K_{298} = (+\Delta H_{298}{}^o/R)(1/T_{298} - 1/T) \rightarrow \text{van't Hoff equation}$$