Physical Chemistry for Chemical Engineering
23435

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Aim

- Chemical engineers are concerned with the rate of reactions (kinetics) and the energies involved (thermodynamics). They deal with separation processes such as distillation, crystallization and gas absorption which depend on understanding change of phase, solubility, vapor pressure etc.
- The Physical Chemistry course is the scientific basis of the chemical engineering, since fluid mechanics, heat transfer, and mass transfer can be traced back to their roots in Kinetic Theory, or Chemical Reactor Engineering is basically applied Chemical Kinetics.
- This course focuses on the chemical applications of thermodynamics.

References

- Physical Chemistry by Peter W. Atkins
- Physical Chemistry by Ira N. Levine

Course structure

Midterm exam	22 Aban	4 PM	35%
Final exam	28 Dey	3 pm	50%
TA, Assignment, quiz			15%

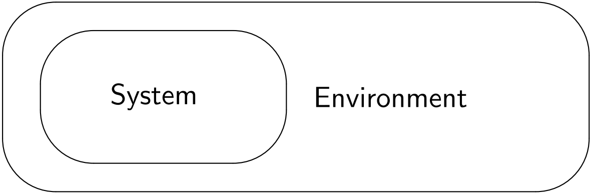
- Office hours: Sundays 9:30 AM - 12 PM

Topics

- Phase equilibrium and diagrams, Azeotrope and eutectic mixtures, pressure-Temperature diagram, colligative properties
- Chemical equilibrium
- Surface phenomena: Surface chemistry, surface between phases, surface absorption, ...
- Kinetic theory
- Electrolytes and electrochemistry: Solution conduction, ion mobility, ion mobility and electric conduction relation.

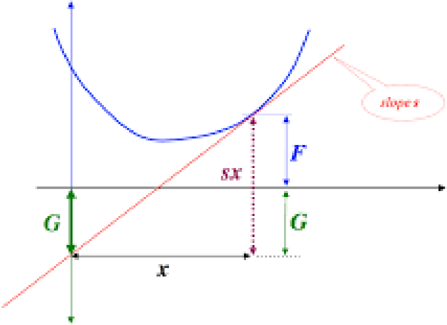
Thermodynamics

- Zeroth law of thermodynamics, first law of thermodynamics, Second law of thermodynamics.
- Universe:



- State functions vs. path functions
- $dE = dq + dw = TdS - pdV \qquad E = E(S, V)$
- $T = (\frac{\partial E}{\partial S})_V \quad p = -(\frac{\partial E}{\partial V})_S$
- Calculation of work, e.g., calculation of work of an ideal gas in a reversible adiabatic change.

Thermodynamics



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- Legendre transformation: $F = F(x), \quad s = \frac{F-G}{x-0} \quad G(s) = F - sx.$ Generally, $G(s) = F - \sum_j s_j x_j.$
- $E(S,V), \quad H(S,p) = ?, \quad A(T,V) = E - (\frac{\partial E}{\partial S})_V S = E - TS, \quad G(T,p) = ?$

Thermodynamics

- A thermodynamic potential is a scalar quantity used to represent the thermodynamic state of a system. The concept of thermodynamic potentials was introduced by Pierre Duhem in 1886. Josiah Willard Gibbs in his papers used the term fundamental functions.
- Internal energy E is the energy of configuration of a given system of conservative forces and only has meaning with respect to a defined set of references.
- Expressions for all other thermodynamic energy potentials are derivable via Legendre transforms from an expression for U.
- Grand potential or Landau free energy is defined by $\Phi_G \stackrel{\text{def}}{=} \Omega \stackrel{\text{def}}{=} F - \mu N = U - TS - \mu N$
- fundamental equation: $d\Phi_G = dU - TdS - SdT - \mu dN - Nd\mu = -PdV - SdT - Nd\mu$
- When the system is in thermodynamic equilibrium, Φ_G is a minimum.

Thermodynamics

- For homogeneous systems, one obtains $\Omega = -PV$.
- Internal energy (U) is the capacity to do work plus the capacity to release heat.
- Gibbs energy (G) is the capacity to do non-mechanical work. $dG = dq + dw + d(pV) - TdS - SdT$ for a reversible process at constant temperature $dG = dw_{rev+} + d(pV)$.
- Enthalpy (H) is the capacity to do non-mechanical work plus the capacity to release heat.
- Helmholtz energy (F), or maximum work function is the capacity to do mechanical plus non-mechanical work (a result of Clausius inequality).
- ΔU is the energy added to the system, ΔF is the total work done on it, ΔG is the non-mechanical work done on it, and ΔH is the sum of non-mechanical work done on the system and the heat given to it.
- When the entropy S and "external parameters" (e.g. volume) of a closed system are held constant, the internal energy U decreases and reaches a minimum value at equilibrium.
- the principle of minimum energy follows from the first and second laws of thermodynamics.

Thermodynamics

- The following three statements are directly derivable from this principle.
- When the temperature T and external parameters of a closed system are held constant, the Helmholtz free energy F decreases and reaches a minimum value at equilibrium.
- When the pressure p and external parameters of a closed system are held constant, the enthalpy H decreases and reaches a minimum value at equilibrium.
- When the temperature T, pressure p and external parameters of a closed system are held constant, the Gibbs free energy G decreases and reaches a minimum value at equilibrium.
- The variables that are held constant in this process are termed the natural variables of that potential

Thermodynamics

- if a thermodynamic potential can be determined as a function of its natural variables, all of the thermodynamic properties of the system can be found by taking partial derivatives of that potential with respect to its natural variables and this is true for no other combination of variables.
- If there are D dimensions to the thermodynamic space, then there are 2D unique thermodynamic potentials.
- $U[\mu_j] = U - \mu_j N_j$, $F[\mu_j] = U - TS - \mu_j N_j$, $H[\mu_j] = U + pV - \mu_j N_j$ and $G[\mu_j] = U + pV - TS - \mu_j N_j$.
- Fundamental equations: $dH =$ $dA =$ $dG =$
- If the system has more external variables than just the volume that can change, the fundamental thermodynamic relation generalizes to: $dU = T\,dS - \sum_i X_i\,dx_i + \sum_j \mu_j\,dN_j$ X_i are the generalized forces corresponding to the external variables x_i.
- Maxwell relations.

Thermodynamics

- $(\frac{\partial U}{\partial V})_{N,T} - T(\frac{\partial p}{\partial T})_{N,V} = -p$
- $dU = [T(\frac{\partial p}{\partial T})_V - p]dV + C_V dT$
- $C_V = (\frac{\partial U}{\partial T})_V = T(\frac{\partial S}{\partial T})_V$ and $C_p = (\frac{\partial H}{\partial T})_p = T(\frac{\partial S}{\partial T})_p$.
- Thus, $C_p - C_v = [p + (\frac{\partial U}{\partial V})_T](\frac{\partial V}{\partial T})_p$
- Chemical potential, $\mu_j = (\frac{\partial U}{\partial N_j})_{S,V,\ldots} = (\frac{\partial H}{\partial N_j})_{S,p,\ldots} = (\frac{\partial A}{\partial N_j})_{V,T,\ldots} = (\frac{\partial G}{\partial N_j})_{p,T,\ldots}$.
- Extensive vs. intensive.
- Homogeneous of degree n, $f(\lambda x_1, \cdots, \lambda x_N) = \lambda^n f(x_1, \cdots, x_N)$
- Euler's theorem: If f is a homogeneous function of degree n, $nf(x_1, \cdots, x_N) = x_1 \frac{\partial f}{\partial x_1} + x_2 \frac{\partial f}{\partial x_2} + \cdots + x_N \frac{\partial f}{\partial x_N}$
- $n(n-1)f(x_1, \cdots, x_N) = \sum_{i,j=1}^{N} x_i x_j (\frac{\partial^2 f}{\partial x_i \partial x_j})$
- $G = \sum_j N_j (\frac{\partial G}{\partial N_j})_{T,p,\cdots} = \sum_j N_j \mu_j$

Thermodynamics

- Gibbs-Duhem equation: $\sum_j N_j d\mu_j = 0$
- For a chemical reaction $aA + bB \rightleftarrows cC + dD$ which can be represented by $\sum_j \nu_j A_j = 0$, $dG = \sum_j \mu_j dN_j = (\sum_j \mu_j \nu_j) d\lambda$
- At equilibrium: $\sum_j \mu_j \nu_j = 0$
- Phase equilibrium
- $\mu_j = \mu_j^0 + RT \ln \frac{p_j}{p^0} = \mu_j^0 + RT \ln p_j'$
- $\Delta\mu_0 = -RT \ln[\frac{(P_c')^{\nu_c}(P_d')^{\nu_d}}{(P_a')^{\nu_a}(P_b')^{\nu_b}}] = -RT \ln K_p$
- A thermodynamic free entropy is an entropic thermodynamic potential analogous to the free energy. Also known as a Massieu, Planck, or Massieu–Planck potentials (or functions), or (rarely) free information.

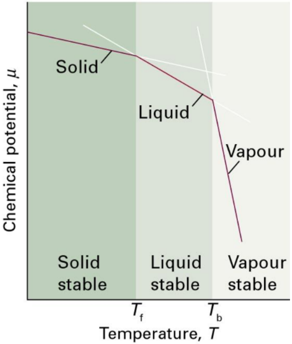
Phases

- Phase (appearance): State of matter that is uniform throughout, not only in chemical composition but also in physical state.
- Phase: a physically distinctive form of a substance or mixture, such as the solid, liquid, and gaseous states of ordinary matter also referred to as a "macroscopic state"
- Component: A species present in the system.
- Number of components: minimum number of independent species necessary to define the composition of all the phases present in the system.
- Allotrope: each of two or more different physical forms in which an element can exist. Eg. Graphite, charcoal, and diamond are all allotropes of carbon.
- Polymorphic and polyamorphic substances have multiple crystal or amorphous phases.
- The chemical potential of a sample is uniform when it is at equilibrium regardless of the number of phases present.

Phase transformation

- $(\partial\mu/\partial T)_p = -S_m$, $(\partial\mu/\partial p)_T = V_m$

Figure: Chemical potential vs. Temperature taken from `https://www.chegg.com/homework-he/`



Phase rule

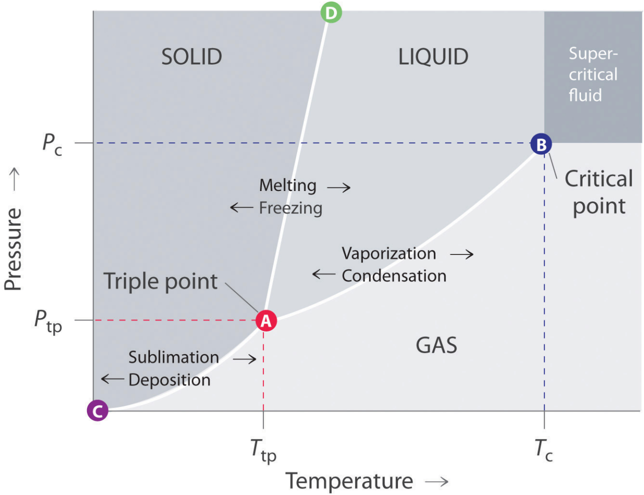
- Number of phases in a system is denoted by P, while the number of independent chemical species is denoted by C (from components).
- Number of degrees of freedom, i.e., the number of independent intensive variables are denoted by F.
- Each phase contains $C - 1$ concentration variables, so there are $p(C-1)+2$ variables.
- Chemical equilibrium implies $P - 1$ independent equations for each species, thus there are $C(P-1)$ equations.
- Phase rule states that $F = p(C-1)+2-C(P-1) = C-P+2$

Physical transformations of pure substances

- The pressure of a vapor in equilibrium with its condensed phase at a specified temperature is called the vapor pressure (VP).
- Antoine equation, $\ln P = A - \frac{B}{C+T}$
- For any phase transition of a pure substance $d\mu_\alpha = d\mu_\beta$, thus $-S_{\alpha,m}dT + V_{\alpha,m}dp = -S_{\beta,m}dT + V_{\beta,m}dp$
- Clapeyron equation: $dp/dT = \Delta S_m/\Delta V_m$
- Solid-liquid boundary $dp/dT = \Delta H_{melt,m}/T_f\Delta V_{melt,m}$
- $\int_{p^*}^{p} dp = (\Delta H_{melt,m}/\Delta V_{melt,m}) \int_{T^*}^{T} dT/T$
- $p = p^* + (\Delta H_{melt,m}/\Delta V_{melt,m}) \ln(T/T^*)$
- $p = p^* + (\Delta H_{melt,m}/T^*\Delta V_{melt,m})(T - T^*)$
- Liquid-vapor boundary $d\ln p/dT = \Delta H_{vap,m}/RT^2$
- solid-vapor boundary $d\ln p/dT = \Delta H_{sub,m}/RT^2$
- Solid-liquid-vapor equilibrium

Phase diagram

- A phase diagram is used to show conditions at which thermodynamically distinct phases occur and coexist at equilibrium.



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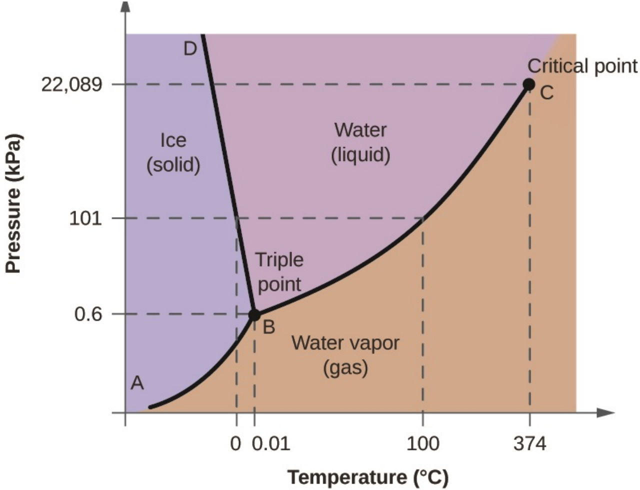
- Lines of equilibrium are called phase boundaries.

Phase diagram

- Triple points are points on phase diagrams where three distinct phases exist in equilibrium with one another (lines of equilibrium intersect).



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Phase diagram

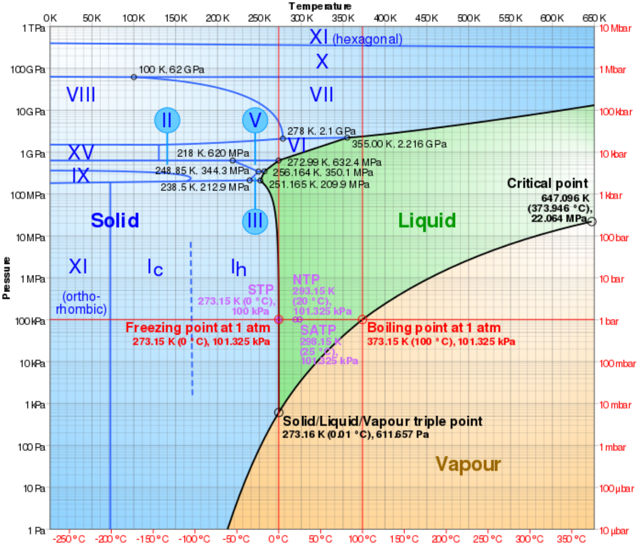


Figure: Water phase diagram taken from `https://en.wikipedia.org`

Phase diagram

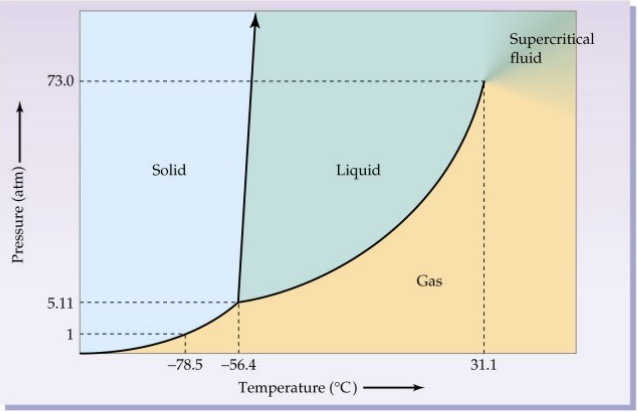
- phase boundary between liquid and gas does not continue indefinitely. It terminates at a point on the phase diagram called the critical point.
- In water, the critical point occurs at around $T_c = 647.096$ K (373.946°C), $p_c = 22.064$ MPa (217.75 atm) and $\rho_c = 356 kg/m^3$.
- 

Figure: Phase diagram for carbon dioxide

Phase diagram

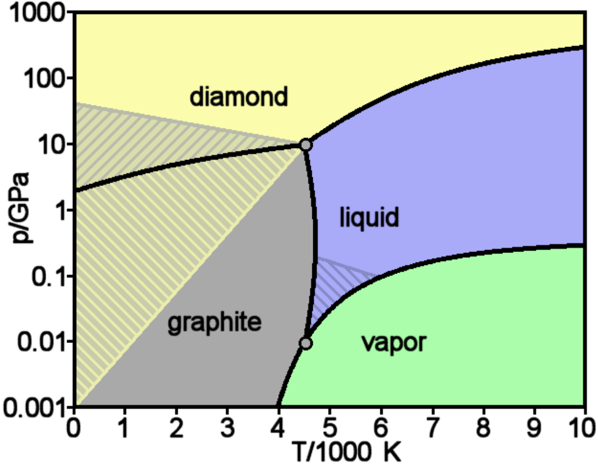


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Figure: Phase diagram for carbon taken from `https://en.wikipedia.org`

Phase diagram

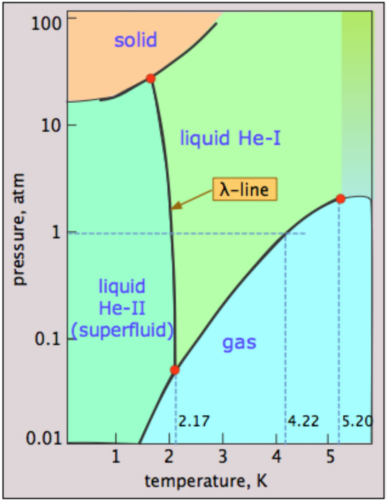
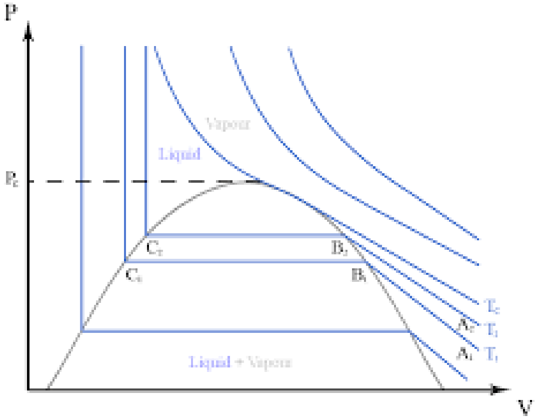


Figure: Phase diagram for ^{4}He taken from Chemistry LibreTexts

- Close to the critical point density can vary from gas density to liquid density.

Critical point



- Close to the critical point properties like solubility and dielectric constant vary almost exponentially with density.
- Such variations give rise to many applications.

First order phase transition

- Phase transitions occur when the thermodynamic free energy of a system is non-analytic for some choice of thermodynamic variables
- Phase transition is a statistical phenomena typically involving a symmetry breaking or formation.
- According to Ehrenfest classification, order of a phase transition is determined by the order of the first discontinuous derivative of the free energy.
- In a first order phase transition, the first derivative of chemical potential is discontinuous.
- $(\frac{\partial \mu_\beta}{\partial p}) - (\frac{\partial \mu_\alpha}{\partial p}) = V_{\beta,m} - V_{\alpha,m} = \Delta V$
- $(\frac{\partial \mu_\beta}{\partial T}) - (\frac{\partial \mu_\alpha}{\partial T}) = -S_{\beta,m} + S_{\alpha,m} = -\Delta S = -\frac{\Delta H}{T}$
- Enthalpy is discontinuous around a first order phase transition which results in the heat capacity diverging at a first order phase transition.

First order phase transition

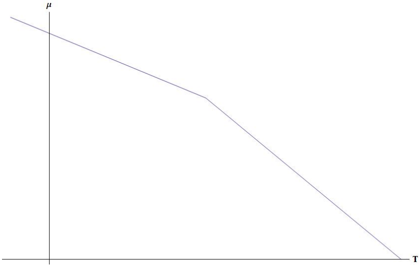


Figure: Example of μ vs. T for a first order phase transition (discontinuity in the first derivative)

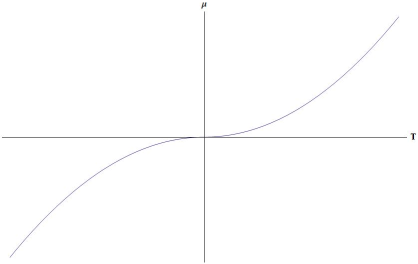


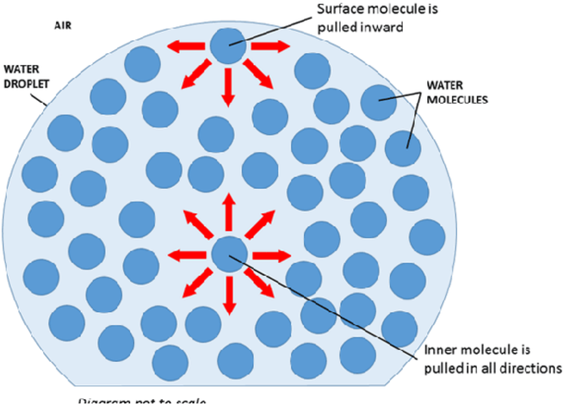
Figure: Example of μ vs. T for a second order phase transition (discontinuity in the second derivative)

Second order and λ phase transition

- The first derivative of chemical potential is continuous while the second is discontinuous. Thus volume and entropy does not change during the phase transition.
- E.g., order-disorder transition in alloys, paramagnetic-ferromagnetic transition and fluid-super fluid transition.
- Phase transitions at which heat capacity diverges are lambda transitions.
- In the modern classification scheme first order transitions involve latent heat.
- Second order or continuous phase transitions exhibit a divergent susceptibility, infinite correlation length and a power law decay of correlations near criticality.
- E.g., ferromagnetic transition, super conducting transition and superfluid transition. Also the liquid-gas transition becomes second order at the critical point.

Liquid-gas surface: Surface tension

- The difference between the average number of interactions of a molecule in the bulk and that of the same molecule in the surface of a liquid suggest that a liquid is stabilized by minimizing its surface.
- Surface tension depends on intermolecular forces.



Liquid-gas surface: Surface tension

- The energy (work) required for increasing liquid surface by unit surface area is called surface tension (in J/m^2), $dw = \gamma d\sigma$.
- $du = dq + dw = TdS - pdV + \gamma d\sigma$. Thus $dA = -pdV + \gamma d\sigma - SdT$, at constant volume and temperature $dA = \gamma d\sigma$.
- Bubbles, cavities and droplets are spherical in the absence of external fields.
- Work in a differential change of radius, $dw = 8\pi\gamma r dr$
- Surface tension force resisting enlargement, $F = 8\pi\gamma r$
- $4\pi r^2 p_{in} = 4\pi r^2 p_{out} + 8\pi\gamma r$. Laplace equation: $p_{in} = p_{out} + \frac{2\gamma}{r}$
- Vapor pressure depends on pressure, i.e. $\mu_l(p, T) = \mu_g^0(T) + RT \ln \frac{p^*}{p^0} \rightarrow \frac{p^*}{p^0} = e^{\frac{\mu_l(p,T) - \mu_g^0(T)}{RT}}$
- Substituting $\mu_l(p + \Delta p, T) = \mu_l(p, T) + V_m \Delta p$ one derives Kelvin equation for the VP of a droplet $p = p^* e^{\frac{2\gamma V_m}{RTr}}$

Liquid	Temperature (°C)	Surface tension, γ [mN/m]
Acetic acid	20	27.60
Acetic acid (45.1%) + Water	30	40.68
Acetone	20	23.70
Blood	22	55.89
Diethyl ether	20	17.00
Ethanol	20	22.27
Ethanol (40%) + Water	25	29.63
Glycerol	20	63.00
n-Hexane	20	18.40
Isopropanol	20	21.70
Liquid nitrogen	-196	8.85
Liquid oxygen	-182	13.2
Mercury	15	487.00
Methanol	20	22.60
n-Octane	20	21.80
Sucrose (55%) + water	20	76.45
Water	0	75.64
Water	25	71.97
Water	50	67.91
Water	100	58.85
Toluene	25	27.73

Table: Surface tension of various liquids in dyn/cm (millinewton per meter)

Liquid-gas surface: Surface tension

Figure: A manifestation of surface tension taken from
`https://en.wikipedia.org`

Liquid-gas surface: Surface tension

- VP inside of a cavity, $p = p^* e^{-\frac{2\gamma V_m}{RTr}}$
- This increase in droplet vapor pressure results in supersaturation.
- Surfaces from small particles end supersaturation.
- E.g., artificial cloud insemination and cloud chamber.
- Surface tension also inhibits bubble formation and thus causes superheating of fluid.
- Capillary effect: $\Delta p = \rho g h = 2\gamma/r$. Thus $h = \frac{2\gamma}{\rho g r}$.
- Compare a glass capillary in water with a glass capillary in Mercury.

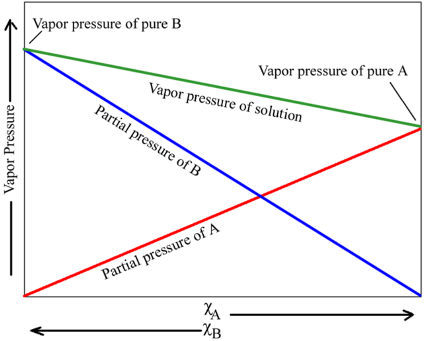
Gas Mixtures

- Partial molar volume $V_J = (\frac{\partial V}{\partial n_J})_{p,T,n'}$
- $dV = (\frac{\partial V}{\partial n_A})_{p,T,n_B} dn_A + (\frac{\partial V}{\partial n_B})_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B$
- $V = V_A n_A + V_B n_B$
- Partial molar Gibbs free energy, $\mu_J = (\frac{\partial G}{\partial n_J})_{p,T,n'}$
- $G = \mu_A n_A + \mu_B n_B$
- Gibbs-Duhem equation: $\sum_J n_j d\mu_J = 0$
- Analogously, $\sum_J n_J dV_J = 0$.
- At infinite dilution $V_{MgSO_4} = -1.4 cm^3/mol$
- For two ideal gases with the same initial and final pressures, $\Delta G_{mix} = nRT(x_A \ln x_A + x_B \ln x_B)$.
- $\Delta S_{mix} = -(\frac{\partial \Delta G_{mix}}{\partial T})_{p,n_A,n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$
- $\Delta V_{mix} = (\frac{\partial \Delta G_{mix}}{\partial p})_{T,n_A,n_B}$
- For an ideal gas $\Delta V_{mix} = \Delta H_{mix} = \Delta U_{mix} = 0$
- We should digress into a study of liquid solutions to write expressions for their thermodynamics. quantities.

Ideal solution

- Raoult law: $p_i = x_i p_i^*$.
- $P_t = P_A + P_B = x_A P_A^* + x_B P_B^*$
- Ideal solutions: $P_i = x_i P_i^*$, $\quad P_t = P_B^* + (P_A^* - P_B^*) x_A$

  ideal solution

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- Examples of Ideal solutions are Benzene-Toluene, Octane-Heptane, Chloroethane-Bromoethane and Tetraethylsilane-Pentane.

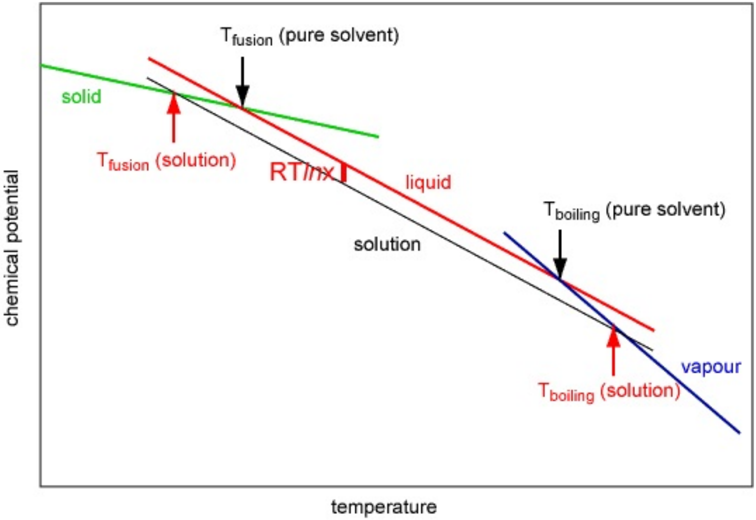
Mixtures

- Phase equilibrium with a single component, $\mu_A^*(l) = \mu_A(g) = \mu_A^0(g) + RT\ln\frac{p_A^*}{p^0}$
- Phase equilibrium with multi components, $\mu_A(l) = \mu_A^0(g) + RT\ln\frac{p_A}{p^0}$
- $\mu_A(l) = \mu_A^*(l) - RT\ln\frac{p_A^*}{p^0} + RT\ln\frac{p_A}{p^0} = \mu_A^*(l) + RT\ln\frac{p_A}{p_A^*}$
- $\mu_A(l) = \mu_A^*(l) + RT\ln x_A$
- For liquids: $\Delta G_{mix} = nRT(x_A\ln x_A + x_B\ln x_B)$.
- $\Delta S_{mix} =?, \quad \Delta V_{mix} =?$
- The difference between observed thermodynamic functions of mixing and the function for an ideal solution is called **excess function**.
- $S^E = \Delta S_{mix} + nR(x_A\ln x_A + x_B\ln x_B)$
- For a regular solution $H^E \neq 0$ while $S^E = 0$

Colligative properties: depending on the collection

- Colligative properties arise from solutes present in the liquid phase but absent from gas and solid phases.
- E.g., vapor pressure reduction, boiling point elevation, freezing point reduction and the osmosis phenomena.
- Consider non-electrolyte solutions.
- $P_t = P_A = X_A P_A^* = (1 - x_B) P_A^*$, change in vapor pressure is a colligative property because it does not depend on the nature of solute.
- Reduction in vapor pressure give rise to an increase in boiling point.
- $d\mu = V_m dP - S_m dT \quad (\frac{\partial \mu}{\partial T})_{P,n} = -S_m \quad (\frac{\partial \mu}{\partial P})_{T,n} = V_m$

Colligative properties



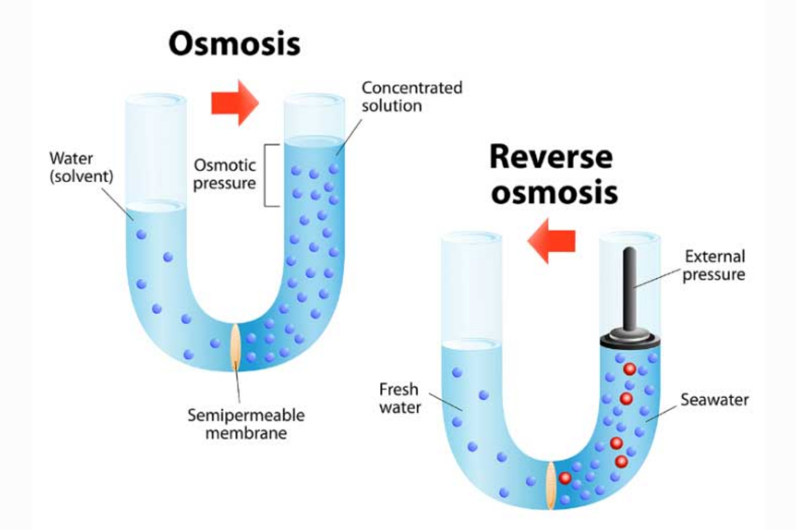
- Liquid (concentration x_A) $\leftrightharpoons$ vapor (1 atm)
- $\mu_A^0(g) = \mu_A^*(l) + RT\ln x_A$, i.e., $\ln(1 - x_B) = \frac{\mu_A^0(g) - \mu_A^*(l)}{RT} = \frac{\Delta G_{m,vap}}{RT}$.

Colligative properties: elevation of the boiling point

- $\ln(1 - x_B) = \frac{\Delta H_{vap}}{RT} - \frac{\Delta S_{vap}}{R}$, Thus $\ln 1 = \frac{\Delta H_{vap}}{RT_b} - \frac{\Delta S_{vap}}{R}$.
- $\ln(1 - x_B) = \frac{\Delta H_{vap}}{R}(\frac{1}{T} - \frac{1}{T_b})$.
- $-x_B = \frac{\Delta H_{vap}}{R}(\frac{T_b - T}{TT_b})$.
- $x_B = \frac{\Delta H_{vap}}{RT_b^2}\Delta T$
- $\Delta T_b = \frac{RT_b^2}{\Delta H_{vap}} x_B \quad x_B \approx \frac{M_A}{1000} m$
- $\Delta T_b = (\frac{RT_b^2 M_A}{1000\Delta H_{vap}})m = K_b m$, K_b is the ebullioscopic constant.
- Ebullioscopy is the determination of molar mass by measuring a solvents ebullioscopic constant.
- Freezing point depression:
- $\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$ result in $\Delta T_f = \frac{RT_f^2}{\Delta H_{vap}} x_B$
- $\Delta T_f = -K_f m_B$ where K_f is the cryoscopic constant.
- Cryoscopy is the determination of molar mass by measuring a solvents cryoscopic constant.

Colligative properties: Osmosis

- A semipermeable membrane, permeable to some molecules (e.g., solvent) but impermeable to other molecules (e.g., solute), gives rise to the osmosis phenomena.



Colligative properties: Osmosis

- Cell membrane is an example of semipermeable membranes.
- $\mu_A^*(p) = \mu_A(x_A, p + \Pi)$ thus $-RT \ln x_A = \int_p^{p+\Pi} V_m dp$. Osmotic pressure $\pi = C_B RT$: van't Hoff equation.
- For non-ideal solutions $\Pi = [B]RT\{1 + B[B] + \cdots\}$
- Reverse osmosis is used to extract drinking water from sea water.
- Osmometry is used for the measurement of macromolecules masses.
- Colligative properties for electrolyte solutions are $\Delta P = -iX_B P_A^*, \quad \Delta T_b = iK_b m \quad \Delta T_f = -iK_f m \quad \pi = iC_B RT$, i is the Van Hoff coefficient.
- Strong electrolytes dissociate completely in solution.

Colligative properties: Electrolytes

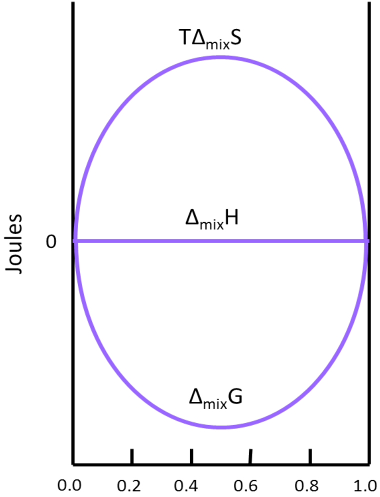
- $\lim_{m_B \to 0} i = \nu$ where ν is the number of particles resulting from dissociation.
- At higher concentration electrostatic interaction prevent independent effect of ions.
- For a weak electrolyte i depends on the dissociation multiple, α.
- $A_aB_b \rightleftarrows aA^{b+}(aq) + bB^{a-}(aq)$
- $\#$ of particles $= m - m\alpha + am\alpha + bm\alpha = m[(1-\alpha) + (a+b)\alpha]$. Thus $i = 1 - \alpha + \alpha\nu$.

Solubility

- At equilibrium $\mu_B^*(s) = \mu_B^*(l) + RT \ln x_B$
- $\ln x_B = -\frac{\Delta H_{fus}}{RT} + \frac{\Delta S_{fus}}{R}$
- $\ln x_B = -\frac{\Delta H_{fus}}{R}(\frac{1}{T} - \frac{1}{T_{fus}})$
- Exponential decrease of solubility with temperature coming down from its melting point.
- Solubility change by temperature: $\ln \frac{x_B'}{x_B} = -\frac{\Delta H_{fus}}{R}(\frac{1}{T'} - \frac{1}{T})$.

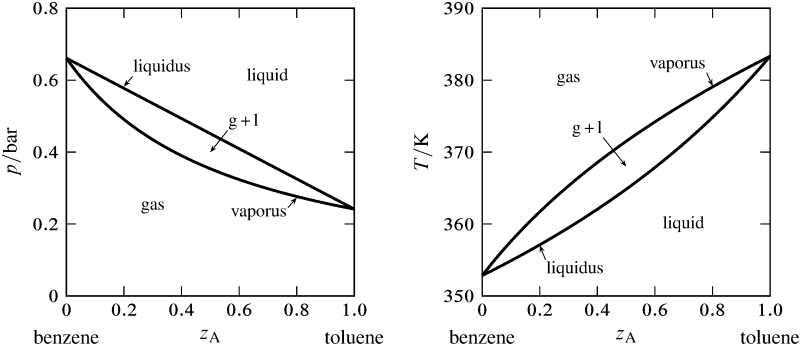
Ideal solution

- In an ideal solution inter-molecular interactions and fluid structure are similar thus $\Delta E_{mix} = 0$ for an ideal solution. Also $\Delta V_{mix} = 0$ and $\Delta H_{mix} = \Delta E_{mix} + P\Delta V_{mix} = 0$
- $\Delta S_{mix} > 0$, $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0$



Ideal solution

- Dalton's law yield mole fractions in the gaseous phase: $P_i = y_i P_t \rightarrow y_i = \frac{X_i P_i^*}{\sum_j X_j P_j^*}$
- a is a pressure composition phase diagram while b is a temperature composition phase diagram.



(a) (b)

-

Ideal solution

- b is called a "boiling diagram." Notice that at the edges we have points representing the boiling points of the pure components. The lower curve gives the boiling point of the liquid mixture as a function of composition.
- $y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A}$, also $p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A}$
- A point inside the two phase region does not give us the composition of either the liquid or the vapor phase, it does give the overall composition of the whole system.
- The tie line is a horizontal line through the composition point which intersects the two boundary lines of the two phase region.

Lever rule

- The intersection of the tie line with the boundary line on the liquid side of the region tells us the composition of the liquid
- the intersection of the tie line with the boundary curve on the vapor side tells us the composition of the vapor phase.
- $nx_A = n_\alpha x_{A,\alpha} + n_\beta x_{A,\beta}$, also $nx_A = n_\alpha x_A + n_\beta x_A$
- $n_\alpha(x_{A,\alpha} - x_A) = n_\beta(x_A - x_{A,\beta})$ or $n_\alpha l_\alpha = n_\beta l_\beta$.
- Called lever rule since in a lever $ml = m'l'$.

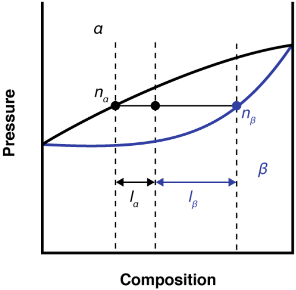


Figure: Phase diagram for a two component two phase system taken from `https://en.wikipedia.org`

Real solution

- Ideal solutions form a first approximation to solution behavior as does ideal gas to real gas behavior.
- Real solutions: $\begin{cases} \text{Positive deviation solution} \\ \text{Negative deviation solution} \end{cases}$
- In a positive deviation solution, vapor pressure is greater than that of ideal solution, e.g., carbondisulfide-Acetone.
- In a negative deviation solution, vapor pressure is smaller than that of ideal solution, e.g., Acetone-Chloroform.
- In negative deviation solutions $f_{AB} > \frac{1}{2}(f_{AA} + f_{BB})$, Also $\Delta V_{mix} < 0$ and $\Delta H_{mix} = \Delta E_{mix} + P\Delta V_{mix} < 0$. E.g., aqueous electrolyte solutions, chloroform and benzene, chloroform and diether, Acetone and aniline, nitric acid and water and acetic acid and pyridine.

Henry's law

- In positive deviation solutions $f_{AB} < \frac{1}{2}(f_{AA} + f_{BB})$, Also $\Delta V_{mix} > 0$ and $\Delta H_{mix} > 0$. E.g., Water and oil mixture, acetone and carbon disulphide, Acetone and benzene, carbon tetrachloride and toluene or chloroform, methyl alcohol and water and acetone and ethanol.
- As $X_i \to 1$ for each component in a binary mixture the vapor pressure of that component obeys Raoult's law.
- for small mole fractions, P_i becomes proportional to X_i, but the proportionality constant is not P_i^*. $P_i = K_i X_i$: Henry's law.
- In a concentration region where one component obeys Raoult's law the other will necessarily obey Henry's law.
- Henry's law is most often used to describe the solubility of gases in liquids.
- Distillation is the process of separating the components or substances from a liquid mixture by using selective boiling and condensation.

Distillation

- Distillation may result in essentially complete separation, or it may be a partial separation that increases the concentration of selected components in the mixture.
- the process exploits differences in the relative volatility of the mixture's components.
- Idealized distillation model
- Batch or differential distillation
- Continuous distillation
- Both batch and continuous distillations can be improved by making use of a fractionating column on top of the distillation flask.
- The device used in distillation, a still, consists at a minimum of a reboiler or pot, a condenser, and a receiver.
- It is not possible to completely purify a mixture of components by distillation, as this would require each component in the mixture to have a zero partial pressure.
- Use an example where $P_A^* = 800 torr$ $P_B^* = 600 torr$ $x_A = 0.8$ to analyze fractional distillation.

Distillation

- Strong deviations from ideal solution can give rise to an azeotrope or constant boiling point solution.
- An azeotrope is when the vapor phase and liquid phase contain the same composition.

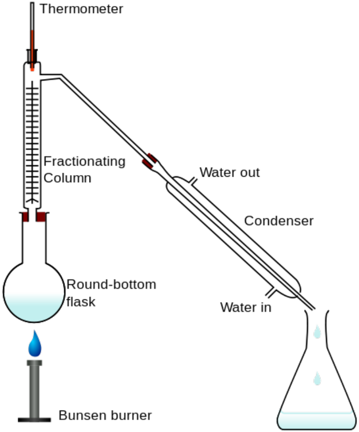
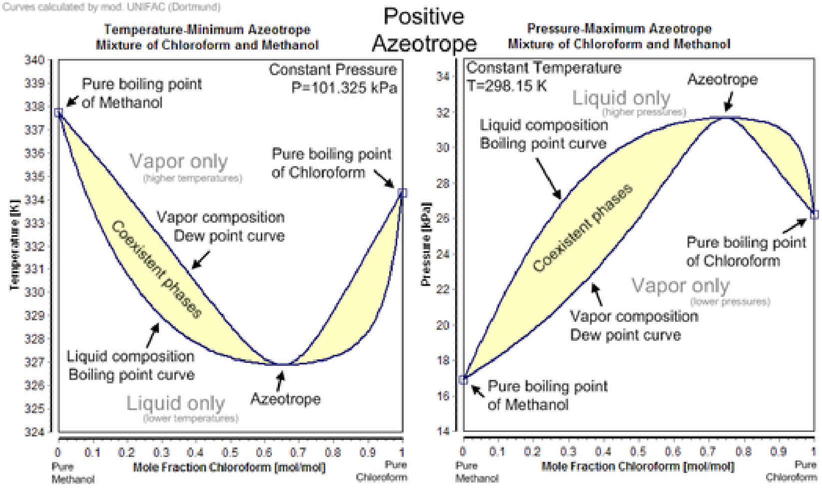


Figure: Fractional distillation taken from `en.wikipedia.org`

Azeotrope: boiling without changing

Figure: Negative azeotrope mixture of chloroform and ethanol taken from `en.wikipedia.org`

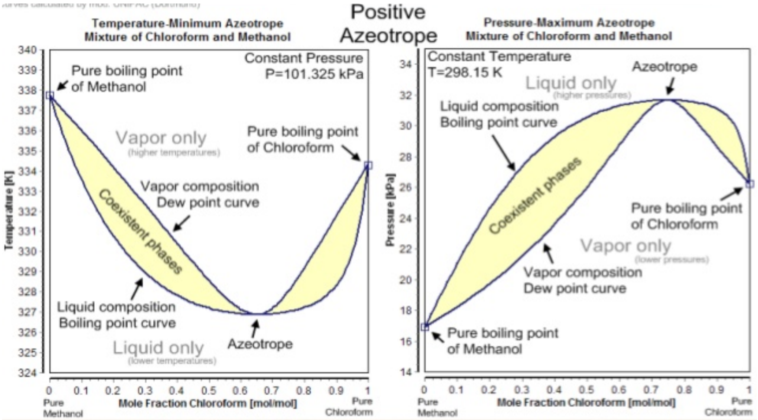


Azeotrope: boiling without changing

- Negative deviation solutions may give rise to a maximum in the phase boundary of the temperature vs. composition graph. $G^E < 0$
- E.g., chloroform-aceton, nitric acid-water.
- If the constituents of a mixture are completely miscible in all proportions with each other, the type of azeotrope is called a homogeneous azeotrope.
- An azeotrope can be found inside the miscibility gap. This type of azeotrope is called heterogeneous azeotrope or heteroazeotrope. Heteroazeotropes are always minimum boiling mixtures.
- Positive deviation solutions may give rise to a minimum in the phase boundary of the temperature vs. composition graph. $G^E > 0$
- E.g., dioxane-water, ethanol-water.
- Simple distillation can be used in cases with large difference in boiling point.
- for separating compounds with smaller boiling point difference fractional distillation is used.

Distillation

- Azeotropic vapor and liquid phases have the same composition, thus an azeotropic solution's composition cannot be altered by distillation.
- Positive deviations from Raoult's law result in a minimum boiling point azeotrope.



Distillation

- E.g., 95.6% by volume ethanol+4.4% water mixture boils at 78.2°C. Ethanol boils at 78.4°C.
- Negative deviations from Raoult's law result in a maximum boiling point azeotrope.
- E.g., 68% nitric acid (boiling at 356 K) and 32% water by mass boils at 393.5 K.
- The distillation of two immiscible liquids can be regarded as the joint distillation of the separated components, and boiling occurs when the sum of partial pressures equals 1 atm.

Solvent activity

- $\mu_A(l) = \mu_A^*(l) + RT\ln\frac{p_A}{p_A^*} = \mu_A^*(l) + RT\ln a_A$
- a_A activity of A is a kind of effective mole fraction as the fugacity is an effective pressure.
- $a_A \to 1 \quad as \quad x_A \to 1$
- $a_A = \gamma_A x_A \quad \gamma_A \to 1 \quad as \quad x_A \to 1$
- Ideal dilute solutes obey Henry's law, $\mu_B(l) = \mu_B^*(l) + RT\ln\frac{p_B}{p_B^*} = \mu_B^*(l) + RT\ln\frac{K_B}{p_B^*} + RT\ln\frac{p_B}{K_B} = \mu_B^\dagger(l) + RT\ln x_B$
- $\mu_B = \mu_B^\dagger(l) + RT\ln a_B \quad a_B = \frac{p_B}{K_B} \quad a_B = \gamma_B x_B$
- $a_B \to x_B \quad and \quad \gamma_B \to 1 \quad as \quad x_B \to 0$
- $x_B \approx \frac{n_B}{n_A} = \frac{n_B M_A}{n_A M_A} = M_A\frac{n_B}{m_A} = M_A m_B = \frac{k m_B}{m^0}$
- For an ideal dilute solution $\mu_B = \mu_B^\dagger + RT\ln k + RT\ln\frac{m_B}{m^0} = \mu_B^0 + RT\ln\frac{m_B}{m^0}$
- For a real solution $\mu_B = \mu_B^0 + RT\ln a_B$ where $a_B = \frac{\gamma_B m_B}{m^0}$

Liquid-Liquid phase diagrams

- Phase separation: creation of two distinct phases from a single homogeneous mixture.
- Upper critical temperature: The upper critical solution temperature (UCST) or upper consolute temperature is the critical temperature above which the components of a mixture are miscible in all proportions.
- Hexane-nitrobenzene mixtures have a UCST of 19 C
- Lower critical temperature: The lower critical solution temperature (LCST) or lower consolute temperature is the critical temperature below which the components of a mixture are miscible for all compositions.
- e.g., water-triethylamine.

Liquid-Liquid phase diagrams

- Nicotine-water are partially miscible between 61°C and 210°C.

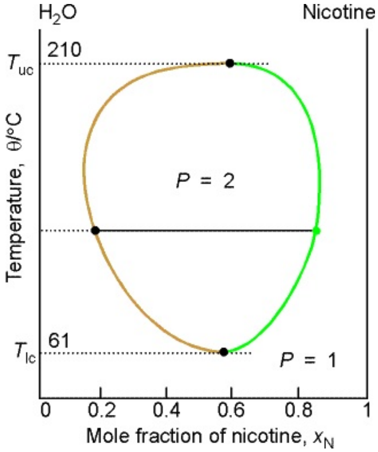
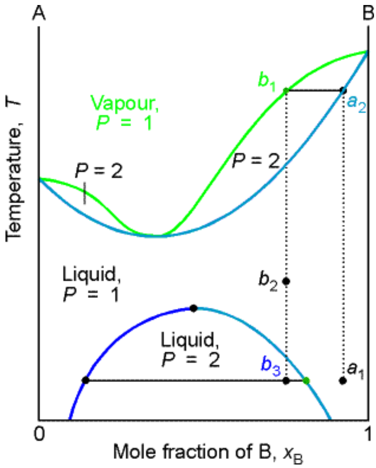


Figure: Upper and lower critical temperatures, credit belongs to Prof. Tecklenburg

Liquid-Liquid phase diagrams

- Distillation of partially miscible liquids
- Partially miscible liquids are Likely to form a low boiling azeotrope
- Miscible before boiling

Figure: Temperature-composition diagram of immiscible liquids, credit belongs to Prof. Tecklenburg



Liquid-Liquid phase diagrams

- Boiling before full miscibility

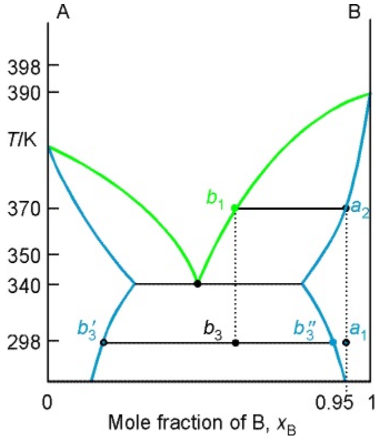


Figure: Temperature-composition diagram of immiscible liquids, credit belongs to Prof. Tecklenburg

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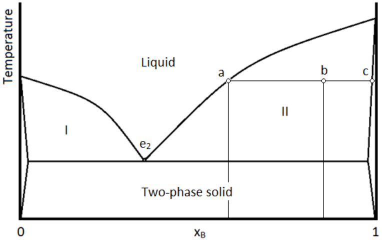
Liquid-solid phase diagram

- A eutectic system is a homogeneous mixture of substances that melts or solidifies at a single temperature that is lower than the melting point of either of the constituents.
- Eutectics: eutectic solid crystallizes out in a nearly homogeneous mixture of microcrystals.

Figure: Solid liquid binary phase diagram, taken from `chem.libretexts.org/`



Liquid-solid phase diagram

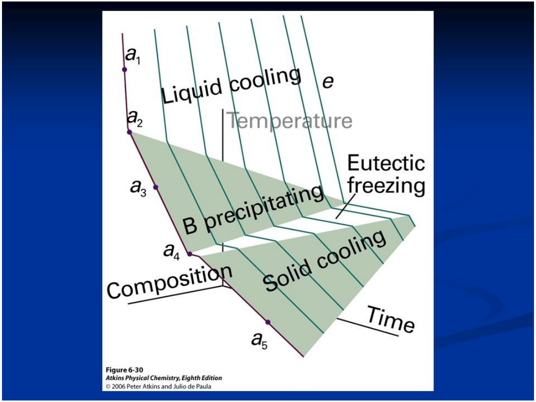
- Thermal analysis leading to a eutectic halt.
- 

Figure 6-30
Atkins Physical Chemistry, Eighth Edition
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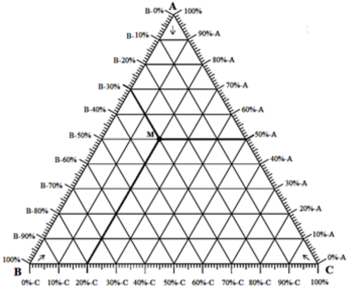
- Reacting systems
- Incongruent melting
- Ultrapurity and controlled impurity

Three component systems

- A ternary plot, ternary graph, triangle plot, simplex plot, Gibbs triangle or de Finetti diagram is a barycentric plot on three variables which sum to a constant.
- It graphically depicts the ratios of the three variables as positions in an equilateral triangle.
- It is used in physical chemistry, petrology, mineralogy, metallurgy, and other physical sciences to show the compositions of systems composed of three species.
- Triangular phase diagram, $x_A + x_B + x_C = 1$
- Determining the mixture composition for a point on the graph, using a grid, perpendicular distance to each side and finally the inverse-lever-arm-rule.

Three component systems

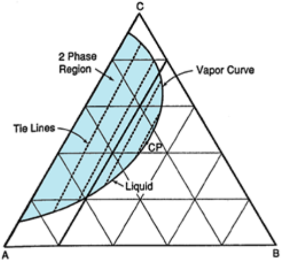
Figure: A ternary phase diagram
`perminc.com/resources/`



Component	Weight mixtur
A	50
B	30
C	20

- Partially miscible liquids

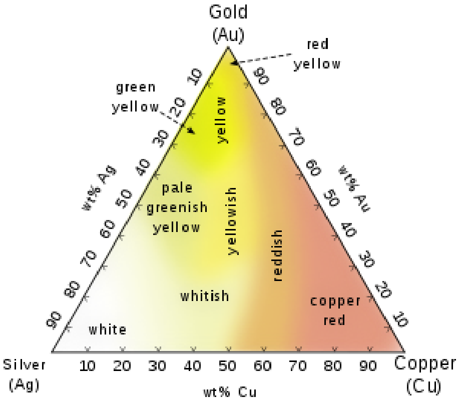
Figure: A ternary phase diagram
`perminc.com/resources/`

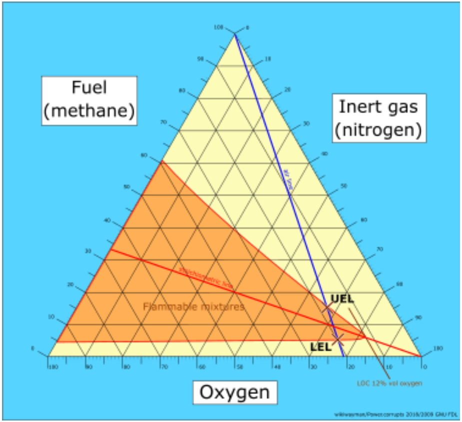


#1
1.0 lbm
85% A
5% B
10% C

#2
1.0 lb
60% A
30% B
10% C

Three component systems





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Chemical reactions

- The Gibbs function minimum
- The extent of reaction, $\frac{dn_r}{\nu_r} = -d\xi \quad \frac{dn_p}{\nu_p} = d\xi$
- $dG = \mu_p \nu_p d\xi - \mu_r \nu_r d\xi$
- The reaction Gibbs function, $(\frac{\partial G}{\partial \xi})_{p,T} = \Delta G_r$
- Exergonic reactions, $\Delta G_r < 0$
- Endergonic reactions, $\Delta G_r > 0$
- The composition of reactions at equilibrium
- Perfect gas equilibrium
- $\Delta G_r = \Delta G^0 + RT \ln Q_p$
- At equilibrium $K_p = (Q_p)_{equilibrium} = (\frac{P_p^{\nu_p}}{P_r^{\nu_r}})_{eq}$
- $RT \ln K_p = -\Delta G^0$
- $\sum_j \nu_j S_j = 0$
- $\Delta G_r = \sum_j \nu_j \mu_j$

Chemical reactions

- $\mu_j = \mu_j^0 + RT \ln a_j$
- $\Delta G_r = \Delta G^0 + RT \ln Q$ where $Q = \Pi_j a_j^{\nu_j}$
- Thermodynamic equilibrium constant $K = \Pi_J a_J^{\nu_J}$
- $\Delta G^0 = \sum_J \nu_J \Delta G_f^0(J)$
- For a gas phase reaction $K = \Pi_J(\frac{f_J}{p^0})^{\nu_J}$
- Thermodynamic vs. practical equilibrium constants, $K = \Pi_J a_J^{\nu_J} = \Pi_J \gamma_J^{\nu_J} \Pi_k m_k^{\nu_k} = K_\gamma K_m \approx K_m$
- Response of equilibrium to pressure $(\frac{\partial \ln K}{\partial p})_T = \frac{-1}{RT}(\frac{\partial \Delta G^0}{\partial p})_T = \frac{-\Delta V^0}{RT} \approx 0$, where equality holds for a gas phase reaction.
- Le Chatelier's principle: A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance.

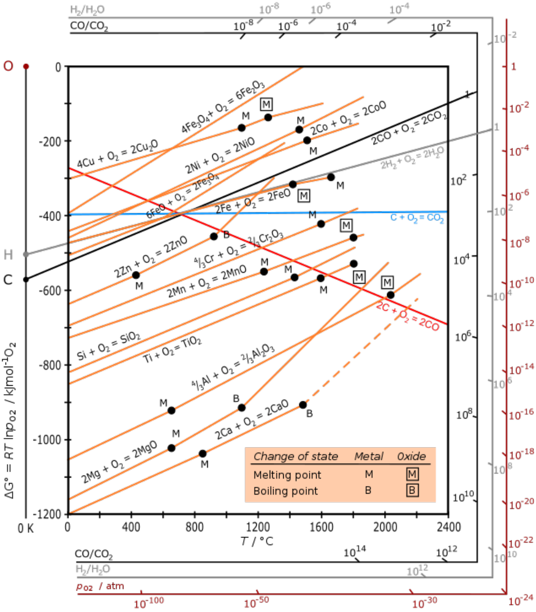
Chemical reactions

- Variance of composition with pressure: A$\rightleftharpoons$ 2B, $x_A = \frac{(1-\alpha)n}{(1-\alpha)n+2\alpha n} = \frac{1-\alpha}{1+\alpha} \quad x_B = \frac{2\alpha}{1+\alpha}$
- Equilibrium constant is $K_p = \frac{(p_B/p^0)^2}{(p_A/p^0)} = \frac{(x_B p/p^0)^2}{(x_A p/p^0)} = \frac{4\alpha^2}{1-\alpha^2}\frac{p}{p^0}$
- $\alpha = (\frac{K_p}{K_p+4p/p^0})^{1/2}$
- In general $K_p = K_x(p/p^0)^{\nu} \quad \nu = \sum_J \nu_J$
- K_p is independent of pressure, thus $K_x \propto p^{-\nu}$
- The response of equilibrium to temperature
- $\ln K = -\frac{\Delta G^0}{RT} \rightarrow \frac{d\ln K}{dT} = -\frac{1}{R}\frac{d}{dT}(\frac{\Delta G^0}{T})$
- Gibbs-Helmholtz equation: $\frac{d}{dT}(\frac{\Delta G^0}{T}) = \frac{-\Delta H^0}{T^2}$
- The van't Hoff equation $\frac{d\ln K}{dT} = \frac{\Delta H^0}{RT^2}$ or $\frac{d\ln K}{d(1/T)} = -\frac{\Delta H^0}{R}$
- $\ln K_2 - \ln K_1 = \frac{-\Delta H^0}{R}(\frac{1}{T_2} - \frac{1}{T_1})$
- Giauque functions: Functions related to G, designed to vary slowly with T allow accurate interpolation at different temperatures.
- $\Phi_0 = \frac{G_m^0(T)-H_m(0)}{T} = \frac{H_m^0(T)-H_m(0)}{T} - S_m^0(T)$
- $\Phi_T = \Phi_0 - \frac{H_m^0(\bar{T})-H_m^0(0)}{T}$

Applications of reaction thermodynamics

- Extraction of metals from oxides
- $\mathrm{MO(s)+C(s)\rightleftharpoons M(s)+CO(g)}$
- $MO(s)+\frac{1}{2}C(s)\rightleftharpoons M(s)+\frac{1}{2}CO_2(g)$
- I) $M(s)+\frac{1}{2}O_2(g)\rightleftharpoons MO(s)$
- II) $\frac{1}{2}C(s)+\frac{1}{2}O_2(g)\rightleftharpoons \frac{1}{2}CO_2(g)$
- III) $C(s)+\frac{1}{2}O_2(g)\rightleftharpoons CO(g)$
- IV) $CO(g)+\frac{1}{2}O_2(g)\rightleftharpoons CO_2(g)$
- An Ellingham diagram is a graph showing the temperature dependence of the stability for compounds.
- usually used to evaluate the ease of reduction of metal oxides and sulfides.
- Ellingham diagram is used to predict the equilibrium temperature between a metal, its oxide, and oxygen and by extension, reactions of a metal with sulfur, nitrogen, and other non-metals.

Applications of reaction thermodynamics



Applications of reaction thermodynamics

- Deduce carbons ability to reduce a metal oxide as a function of the temperature.
- Bronsted-Lowry acid base definition.
- $AH(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq) \quad K = \frac{a(H_3O^+)a(A^-)}{a(HA)a(H_2O)}$
- Acid base conjugate pair
- Acidity constant, $K_a = \frac{a(H_3O^+)a(Base)}{a(Acid)}$
- $\Delta G^0 = -RT \ln K_a = 2.303 RT pK_a$
- Water is amphiprotic
- Autoprotolysis equilibrium: a proton transfer equilibrium involving a single substance.
- $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad K_w = a(H_3O^+)a(OH^-) \quad pK_w = -\log K_w$
- $K_a K_b = a(H_3O^+)a(OH^-) = K_w$

Applications of reaction thermodynamics

- $a \approx m/m^0 \approx [X]/M$ thus $K_a \approx \frac{[H_3O^+][Base]}{[Acid]}$
- pH calculations
- Strong and weak acids
- Polyprotic acids
- Acid base titrations
- Equivalence point: the stage when a stoichiometrically equivalent amount of acid has been added to a base.
-

Acid	pK_{a1}	pK_{a2}	pK_{a3}
CH_3COOH	4.75		
NH_4^+	9.25		
H_2CO_3	6.37	10.25	
H_3PO_4	2.12	7.21	12.67

Applications of reaction thermodynamics

- pH curve:
- $[M^+] + [H_3O^+] = [A^-] + [OH^-]$
- $[HA] + [A^-] = A \qquad A = \frac{A_0 V_A}{V_A + V_B}$
- $[M^+] = \frac{B V_B}{V_A + V_B} \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$
- $\frac{[H_3O^+][A^-]}{K_a} + [A^-] = A \qquad [A^-] = \frac{A K_a}{K_a + [H_3O^+]}$
- Then write the electric neutrality condition and derive an expression for the volume of added base for a value of $[H_3O^+]$.
- $\alpha = \frac{V_B}{V_A} = \frac{A_0 K_a [H_3O^+] + K_w (K_a + [H_3O^+]) - [H_3O^+](K_a + [H_3O^+])}{(K_a + [H_3O^+])[(B + [H_3O^+])[H_3O^+] - K_w]}$
- Approximating the pH curve:
- Initial pH: 0.01 M HOCl, ($pK_a = 7.43$); 0.01 M NH_3, ($pK_a = 9.25$);
- Henderson-Hasselbalch equation: $pH = pK_a - \log \frac{A'}{S}$
- pH at the equivalent point: E.g., 25 mL 0.1 M HOCl(aq)+0.1 M NaOH(aq); 25 mL 0.2 M NH_3(aq)+0.3 M HCl(aq)
- pH after the equivalence point

Applications of reaction thermodynamics

- Buffers: 0.1 M $NH_3(aq)+0.2$ M $NH_4Cl(aq)$
- 0.2 M $KH_2PO_4(aq)+0.1$ M $K_2HPO_4(aq)$, $pK_{a2} = 7.21$
- Acid - Base indicators (also known as pH indicators) are substances which change colour with pH. They are usually weak acids or bases.
- Indicators: Generally large organic molecules, solvable in water, where acid (HIn) and base (In^-) forms have different colors.
- $HIn(aq)+H_2O(l) \rightleftharpoons In^-(aq)+H_3O^+(aq)$, $\quad K_{In} = \frac{a(In^-)a(H_3O^+)}{a(H_2O)a(HIn)}$
- pH in the middle of the color change range of indicator is called the end point of titration.
- In the best indicator the end point pH matches the equivalence point of the titration.
- Phenolphthalein is a colorless, weak acid which dissociates in water forming pink anions.
- The pH of the solution at its turning point is pKIn and is the pH at which half of the indicator is in its acid form and the other half in the form of its conjugate base.

Applications of reaction thermodynamics

- An indicator is most effective if the color change is distinct and over a low pH range. For most indicators the range is within ±1 of the pKIn value
-

Indicator	Acid Color	Base Color	pKIn	pH range
Thymol Blue–1st change	red	yellow	1.5	1.2-2.8
Methyl Orange	red	yellow	3.7	3.2-4.4
Bromocresol Green	yellow	blue	4.7	3.8-5.4
Methyl Red	yellow	red	5.1	4.8-6.0
Bromothymol Blue	yellow	blue	7.0	6.0-7.6
Phenol Red	yellow	red	7.9	6.8-8.4
Thymol Blue–2nd chan	yellow	blue	8.9	8.0 - 9.6
Phenolphthalein	colorless	pink	9.4	8.2 - 10.0

- A Universal Indicator is a mixture of indicators which give a gradual change in colour over a wide pH range - the pH of a solution can be approximately identified when a few drops of universal indicator are mixed with the solution.

Biological activity: Thermodynamics of ATP

- Adenosine triphosphate (ATP) is a complex organic chemical that provides energy to drive many processes in living cells, e.g. muscle contraction, nerve impulse propagation, and chemical synthesis.
-

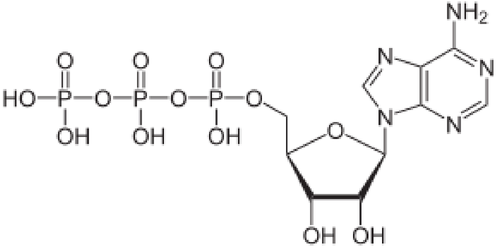


Figure: Adenosin triphosphate (ATP) taken from `https://en.wikipedia.org`

- ATP(aq)+H_2O(l) $\rightleftharpoons ADP(aq) + P_i^-$(aq)+$H^+$(aq) ΔG°= -72 kJ mol^{-1}.
- Standard state of hydrogen ions is unit activity, pH=0.

Biological activity: Thermodynamics of ATP

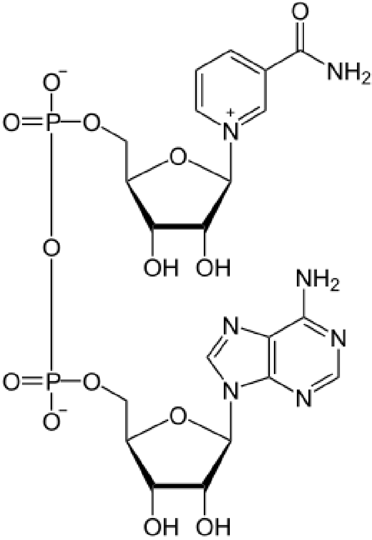


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Figure: Nicotinamide adenine dinucleotide (NAD) taken from https://en.wikipedia.org

Biological activity: Thermodynamics of ATP

- Biological standard state is an activity of 10^{-7}, pH=7. Corresponding standard thermodynamic functions are G°', H°' and S°'.
- Calculate ΔG°' for the reaction:
  $NADH(aq)+H^+(aq) \rightarrow NAD^+(aq)+H_2(g)$ $\Delta G^\circ =$ -21.8 kJ mol^{-1}
- If there are no H^+ or OH^- biological standard is the same as the normal standard.
- Find ΔG°' for ATP hydrolysis at 310 K?
- For ATP hydrolysis at 310K, ΔH°' = -20 kJ mol^{-1}, ΔG°' = -30 kJ mol^{-1}, ΔS°' = 34 J mol^{-1} K^{-1},
- ΔG°(Glucose) = -2880 kJ mol^{-1}

Equilibrium electrochemistry

- Thermodynamic properties of ions in solution
- Thermodynamic functions of formation
- Ag(s)+$\frac{1}{2}Cl_2(g) \rightarrow Ag^+(aq) + Cl^-(aq)$ ΔH°= -61.58 kJ mol^{-1}
- Enthalpies of formation of ions, $\Delta H_f{}^\circ$(H$^+$,aq)=0 at all temperatures.
-

Ion	$\Delta H_f{}^\circ$/(kJ mol^{-1})	S°/(J mol^{-1} K^{-1})	$\Delta G_f{}^\circ$/(kJ mol^{-1})
Cl$^-$	-167.2	56.5	-131.2
Cu^{2+}	64.8	-99.6	+65.5
H$^+$	0	0	0
K$^+$	-252.4	+102.5	-283.3
Na$^+$	-240.1	59.0	-261.9
PO_4^{3-}	-1277	-221.8	-1019

- Calculate the solubility of silver chloride in water at 25 C, $\Delta G_f{}^\circ$(AgCl,s)=-109.79 kJ mol^{-1}.

Equilibrium electrochemistry

- Ag(s)+$\frac{1}{2}Cl_2(g) \rightarrow Ag^+(aq) + Cl^-(aq)$ ΔG°= -54.12 kJ mol
- Gibbs functions of formation of ions, $\Delta G_f{}^\circ$(H$^+$,aq)=0 at all temperatures.
- Contributions to the Gibbs function of formation
- Break down the formation of an species into steps and add Gibbs functions for each step.
- E.g., the difference in $\Delta G_f{}^\circ$(Cl$^-$,aq) and $\Delta G_f{}^\circ$(Br$^-$,aq) is due to their Gibbs function of solvation.
-

	$\Delta G^0/(kJ\ mol^{-1})$ X = Cl	 X = Br
$\frac{1}{2}H_2(g) \rightarrow H(g)$	203	203
$H(g) \rightarrow H^+(g) + e^-$	1318	1318
$H^+(g) \rightarrow H^+(aq)$	x	x
$\frac{1}{2}X_2(g) \rightarrow X(g)$	106	82
$X(g) + e^- \rightarrow X^-(g)$	-355	-331
$X^-(g) \rightarrow X^-(aq)$	y	y'
$\frac{1}{2}H_2(g) + \frac{1}{2}X_2(g) \rightarrow H^+(aq) + X^-(aq)$	$\Delta G_f^0(Cl^-)$	$\Delta G_f^0(Br^-)$

Equilibrium electrochemistry

- M$^+$(g)→M$^+$(solution), $\Delta G_s{}^\circ$
- Born identified $\Delta G_s{}^\circ$with the electrical work of transferring an ion from a vacuum into the solvent treated as a continuous dielectric of relative permittivity ϵ_r
- $\Delta G_s^\circ = \frac{-z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i}(1 - \frac{1}{\epsilon_r})$
- $\epsilon_r(H_2O) = 78.54, \epsilon_r(NH_3) = 16.9, \epsilon_r(C_6H_6) = 2.27, \epsilon_r(C_2H_5OH) = 24.3$, $r_{Cl^-} = 181pm$, $r_{Br^-} = 196pm$
- Entropies of ions in solution; S$^\circ$(H$^+$,aq)=0 at all temperatures.
- S$^\circ$(H$^+$,aq) is calculated to be -21 J/mol/K.

Ion activities

- Definition of activity, $\mu = \mu^0 + RT \ln a$
- Standard state is a hypothetical solution of molality m°in which ions are behaving ideally.
- $a = \gamma \frac{m}{m^\circ}$, activity coefficient depend on the composition, concentration and temperature.
- $\gamma \rightarrow 1$ and $a \rightarrow m/m^\circ$ as $m \rightarrow 0$
- $\mu = \mu^0 + RT \ln \frac{m}{m^\circ} + RT \ln \gamma = \mu^\circ + RT \ln \gamma$
- Mean activity coefficients:
- Gibbs function of an ideal solution: $G^\circ = \mu_+^\circ + \mu_-^\circ$
- For real solutions $G = \mu_+ + \mu_- = \mu_+^\circ + \mu_-^\circ + RT \ln \gamma_+ + RT \ln \gamma_- = G^\circ + RT \ln \gamma_+\gamma_-$
- For a 1,1-electrolyte $\gamma_\pm = (\gamma_+\gamma_-)^{1/2}$
- $\mu_+ = \mu_+^\circ + \ln \gamma_\pm \qquad \mu_- = \mu_-^\circ + \ln \gamma_\pm$
- For M_pX_q, $G = p\mu_+ + q\mu_- = G^\circ + pRT \ln \gamma_+ + qRT \ln \gamma_-$

Debye-Huckel limiting law

- Mean activity coefficient $\gamma_\pm = (\gamma_+^p \gamma_-^q)^{1/s}$ where s=p+q.
- $\mu_i = \mu_i^\circ + RT \ln \gamma_\pm \qquad G = p\mu_+ + q\mu_-$
- Coulombic interactions between ions dominate the non-ideality in ionic solutions.
- Near any given ion there is an excess of counter ions, which constitute its ionic atmosphere.
- Interaction with ionic atmosphere lowers energy and chemical potential.
- This reduction is identified with $RT \ln \gamma_\pm$
- Debye-Huckel limiting law: $\lg \gamma_\pm = -|z_+ z_-| A I^{1/2}$ where A depends on relative permittivity and temperature, for an aqueous solution at 25 °C, A=0.509/(mol kg^{-1})$^{1/2}$
- Ionic strength, $I = \frac{1}{2} \sum_i z_i^2 m_i$
- Calculate the ionic strength and average activity coefficient for a 0.001 mol kg^{-1} $CaCl_2$(aq).

Equilibrium electrochemistry

- Limiting Debye-Huckel law is satisfactory at very low concentrations.
- At moderate concentrations, extended Debye-Huckel law is used: $log \gamma_{\pm} = -\frac{A|z_+z_-|I^{1/2}}{1+BI^{1/2}}$
- B is interpreted as the closest distance between two ions but treated as a parameter.
- Electrochemical cells contain two electrodes.
- An electrode is a conductor immersed in an electrolyte.
- An electrolyte is an ionic conductor. An electrode together with electrolyte constitute an electrode compartment.
- Electrode compartments might be connected by a salt bridge.
- In a galvanic cell an spontaneous reaction occurs and electricity is produced.
- In an electrolytic cell electric energy is used to drive a non-spontaneous reaction.
- A redox reaction occurs when electrons are transferred.

Equilibrium electrochemistry

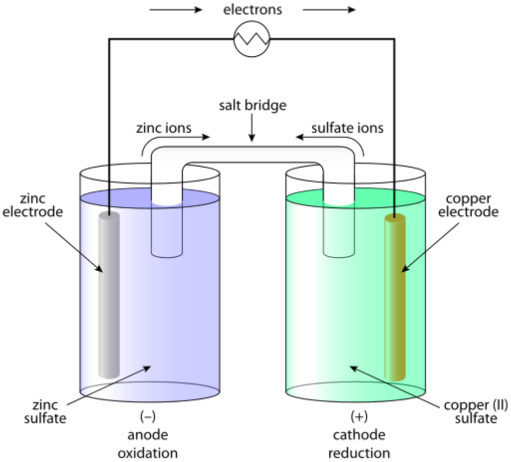
- 

  Figure: A galvanic cell, specifically Daniel cell, taken from `https://en.wikipedia.org`

- Reducing agent or reductant gives and oxidizing agent or oxidant receives electrons, resulting in changes in oxidation numbers.

Equilibrium electrochemistry

- Every redox reaction constitutes two half reactions.
- A galvanic cell or voltaic cell, named after Luigi Galvani or Alessandro Volta, respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell.
- It generally consists of two different metals immersed in an electrolyte, or of individual half-cells with different metals and their ions in solution connected by a salt bridge or separated by a porous membrane.
- Faraday correctly identified the source of emf as the chemical reactions at the two electrode-electrolyte interfaces.
- a half-cell consists of a solid metal (called an electrode) that is submerged in a solution; the solution contains cations of the electrode metal and anions to balance the charge of the cations.
- The full cell consists of two half-cells, usually connected by a semi-permeable membrane or by a salt bridge that prevents the ions of the more noble metal from plating out at the other electrode.

Equilibrium electrochemistry

- RedOx pairs: Ox/Red; Ox$+\nu e^-$ $\rightarrow$Red
- $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad Q = \frac{1}{a(Cu^{2+})}$
- $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad Q = \frac{1}{a(Zn^{2+})}$
- Most reactions can be written as the difference of two redox reactions, e.g., $2H^+(aq) + 2e^- \rightarrow H_2(g, p_f) \qquad 2H^+(aq) + 2e^- \rightarrow H_2(g, p_i)$
- $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \qquad Ag^+(aq) + e^- \rightarrow Ag(s)$
- Write the formation of water as difference of two reduction half reactions.
- Redox reaction in two separate compartments
- The anode is the electrode where oxidation (loss of electrons) takes place (metal-A electrode); in a galvanic cell, it is the negative electrode
- The cathode is the electrode where reduction (gain of electrons) takes place (metal-B electrode); in a galvanic cell, it is the positive electrode
- In anode: $Red_1 \rightarrow Ox_1 + \nu e^-$
- In cathode: $Ox_2 + \nu e^- \rightarrow Red_2$

Equilibrium electrochemistry

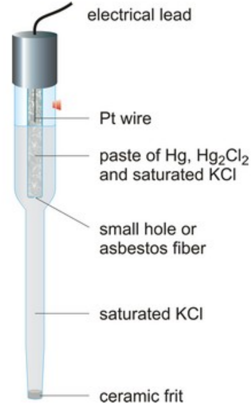
- In a galvanic cell cathode has a higher potential compared to anode.
- In an electrolytic cell anode has a higher potential compared to cathode.
- Gas electrode: Gas and ionic forms of an element or compound reach equilibrium in the presence of an inert metal (e.g., Pt).
- In an hydrogen electrode, hydrogen gas is blown into a solution of hydrogen ions: $Pt|H_2(g)|H^+(aq)$, vertical bar denotes an interface between phases.
- Electrodes are depicted as Red/Ox which is the opposite of redox pair depiction.
- $2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad Q = \frac{f(H_2)/p^0}{a(H^+)^2}$
- $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \qquad Q = \frac{a(H_2O)^2 p^0}{a(H^+)^4 f(O_2)} \approx \frac{p^0}{a(H^+)^4 p(O_2)}$
- Insoluble salt electrode: includes metal core, M, covered with a layer of insoluble salt MX and immersed in a solution of X$^-$,

Electrode types

- $M|MX|X^-$, $MX(s) + e^- \rightarrow M(s) + X^-(aq) \qquad Q = a(X^-)$
- $Ag|AgCl|Cl^- \qquad AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \qquad Q = a(Cl^-)$
- $Pb|PbSO_4(s)|SO_4^{2-}(aq) \qquad PbSO_4(s) + 2e^- \rightarrow$ $Pb(s) + SO_4^{2-}(aq) \qquad Q = a(SO_4^{2-})$
- In the lead-acid battery: Negative plate reaction $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$
- Positive plate reaction: $PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$ taking advantage of the metallic conductivity of PbO_2.
- The total reaction can be written as: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow$ $2PbSO_4(s) + 2H_2O(l) \quad E^\circ_{cell} = 2.05$ V

Electrode types

- Calomel electrode is a type of half cell in which the electrode is mercury coated with calomel (Hg_2Cl_2) and the electrolyte is a solution of potassium chloride and saturated calomel.
- Calomel electrode:
  $Hg(l)|Hg_2Cl_2(s)|Cl^-(aq) \qquad Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-$



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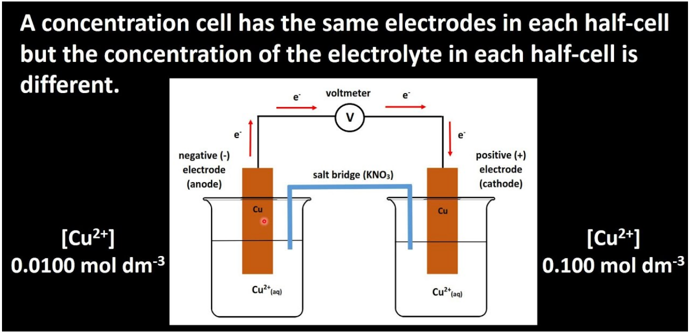
Electrode types

- Oxidation-reduction electrode: both oxidized and reduced forms are in the solution.
- $M|Red, Ox \qquad Ox + \nu e^- \rightarrow Red \qquad Q = \frac{a(Red)}{a(Ox)}$, M is an inert metal providing electric contact with the solution.
- $Pt|Fe^{2+}(aq), Fe^{3+}(aq) \qquad Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad Q = \frac{a(Fe^{2+})}{a(Fe^{3+})}$
- 

A concentration cell has the same electrodes in each half-cell but the concentration of the electrolyte in each half-cell is different.

$[Cu^{2+}]$ $0.0100\ mol\ dm^{-3}$

$[Cu^{2+}]$ $0.100\ mol\ dm^{-3}$

Cell types

- Cell types: Daniel cell, electrolyte concentration cell, electrode concentration cell.
- Liquid junction potential result from difference in mobility of the ions at connection between two electrolytes.
- Use of a salt bridge generally reduces the Liquid junction potential.
- In depicting an electrochemical cell phase boundary is depicted by vertical bars while salt bridge is depicted by a dotted vertical bar.
- In depicting an electrochemical cell, anode is written on the left while cathode is written on the right
- $Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag$
- $Zn(s)|ZnSO_4(aq)\vdots CuSO_4(aq)|Cu(s)$
- Double vertical bars depict a phase interface without junction potential.
- E.g., $Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$
- $Pt|H_2(g)|HCl(aq, m_L)||HCl(aq, m_R)|H_2(g)|Pt$

Nernst equation

- At constant temperature and pressure $w_{e,max} = \Delta G$, which can be achieved only by a cell reaction occurring reversibly.
- Electromotive force (emf) of a cell is its potential at zero current.
- emf of the cell is the difference of the half-cell potentials, a measure of the relative ease of dissolution of the two electrodes into the electrolyte. The emf depends on both the electrodes and on the electrolyte, an indication that the emf is chemical in nature.
- $dG = \sum_j \nu_j \mu_j d\xi = \Delta G_r d\xi \qquad \Delta G_r = (\frac{\partial G}{\partial \xi})_{p,T} = \sum_j \nu_j \mu_j$
- The current produced by a cell is a measure of its reversibility.
- At constant temperature and pressure, the maximum work is $dw_e = \Delta G_r d\xi$
- $dw_e = -\nu N_A e d\xi \times E = -\nu F d\xi \times E \qquad F = N_A e = 96485 C/mol$
- $\Delta G_r d\xi = -\nu F d\xi E \qquad \Delta G_r = -\nu F E$
- The Nernst equation
- $\Delta G_r = \Delta G^0 + RT \ln Q \qquad Q = \Pi_j a_j^{\nu_j}$
- $E = -\frac{\Delta G^0}{\nu F} - \frac{RT}{\nu F} \ln Q$
- Standard cell potential: $-\nu F E^0 = \Delta G^0$

Nernst equation

- Nernst equation for the zero-current cell potential: $E = E^0 - \frac{RT}{\nu F} \ln Q$
- At 25°C, $E = E^0 - \frac{25.7mV}{\nu} \ln Q$
- Calculate the zero current cell potential of a Daniel cell with $CuSO_4$ 1.0 mmol kg^{-1} and $ZnSO_4$ 3.0 mmol kg^{-1}.
- $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq) \qquad Q = \frac{a(Zn^{2+})}{a(Cu^{2+})} \qquad \nu = 2$
- $log\gamma_{\pm} = -0.509 \times 4 \times (4m)^{1/2} \qquad Q = \frac{0.60\times 0.003}{0.74\times 0.001} = 2.43$
- $\Delta G^0 = \Delta G_f^0(Zn^{2+}) - \Delta G_f^0(Cu^{2+}) = -147.1 - 65.6 = -212.7$ kJ mol^{-1}
- In the Daniell cell, most of the electrical energy of $\Delta_r G_o$ = -213 kJ/mol can be attributed to the -207 kJ/mol difference between Zn and Cu lattice cohesive energies.
- $E^0 = 1.102$ V, $E = 1.102V - 0.0257V \ln 2.43 = 1.08$ V
- Zero current cell potential for $Pt|H_2(g, 2bar)|HCl(aq, 0.1 \text{ mol kg}^{-1})|Hg_2Cl_2(s)|Hg(l)$
- $\Delta G_f^0(HCl(aq)) = -131.23 \qquad \Delta G_f^0(Hg_2Cl_2(s)) = -210.75$
- An electrochemical cell in equilibrium: $\ln K = \frac{\nu F E^0}{RT}$

Nernst equation

- Find the equilibrium constant for the Daniel cell?
- Concentration cell: $M|M^+(aq,L)||M^+(aq,R)|M$ $\quad M^+(aq,R) \to M^+(aq,L)$ $\quad Q = \frac{a_L}{a_R}$ $\quad \nu = 1$ $\quad E = \frac{-RT}{F} \ln \frac{a_L}{a_R} \approx \frac{-RT}{F} \ln \frac{m_L}{m_R}$
- Calculate the potential difference between two sides of a cell membrane, given that K$^+$ concentration is 20 times greater inside the cell.
- In order to attribute portions of the potential difference to each electrode, we attribute 0 to Standard Hydrogen electrode (SHE), $Pt|H_2(g)|H^+(aq)$

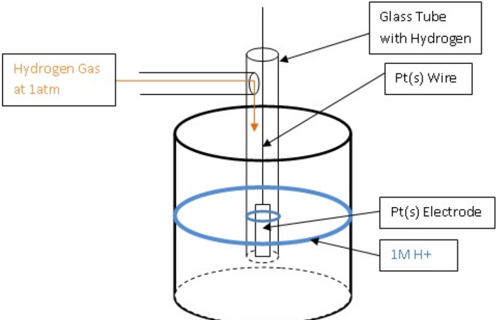


Figure: Standard hydrogen electrode representation courtesy of `chem.libretexts.org`

Nernst equation

- $Pt|H_2(g)|H^+(aq)||Ag^+(aq)|Ag(s) \qquad E^0 = E^0(Ag^+/Ag) = 0.80V$
- $Pt|H_2(g)|H^+(aq)||Cl^-(aq)|AgCl(s)|Ag(s) \qquad E^0 = E^0(AgCl/Ag, Cl^-) = 0.22V$
- $Ag(s)|Ag^+(aq)||Cl^-(aq)|AgCl(s)|Ag(s)$ is equivalent to connected cells $Ag(s)|Ag^+(aq)||H^+(aq)|H_2(g)|Pt---$ $Pt|H_2(g)|H^+(aq)||Cl^-(aq)|AgCl(s)|Ag(s)$, $E^0 = E^0(AgCl/Ag, Cl^-) - E^0(Ag^+/Ag) = -0.58V$
- The standard oxidation potential is much like the standard reduction potential. It is the tendency for a species to be oxidized at standard conditions.
- $E^o_{cell} =$ $E^o_{reduction}$ of reaction at cathode $+$ $E^o_{oxidation}$ of reaction at anode
- $E^o_{cell} =$ $E^o_{reduction}$ of reaction at cathode $-$ $E^o_{reduction}$ of reaction at anode
- Thus a reduction potential table suffice us.

Equilibrium electrochemistry

- Calculate the equilibrium constant of the corrosion reaction $Fe(s) + 2H^+(aq) + \frac{1}{2}O_2(g) \rightarrow Fe^{2+}(aq) + H_2O(l)$
- Calculate the equilibrium constant for $2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$
- $Cu^+(aq) + e^- \rightarrow Cu(s) \qquad E^0 = 0.52V$
- $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq) \qquad E^0 = 0.16V$
- Calculate the equilibrium constant for $Sn^{2+}(aq) + Pb(s) \rightarrow Sn(s) + Pb^{2+}(aq)$
- *Dependence of the reduction potential on composition*
- By placing SHE on the left of a cell with any reduction potential on the right, one drives the Nernst equation for a half cell.
- E.g., $Pt|H_2(g)|H^+(aq)||Ag^+(aq)|Ag(s) \qquad H_2(g) + 2Ag^+(aq) \rightarrow 2H^+(aq) + 2Ag(s) \qquad Q = \frac{a(H^+)^2 p^0}{f(H_2)a(Ag^+)^2}$
- $E = E^0 - \frac{RT}{2F}\ln Q = E^0(Ag^+/Ag) - \frac{RT}{2F}\ln\frac{a(H^+)^2 p^0}{f(H_2)a(Ag^+)^2}$

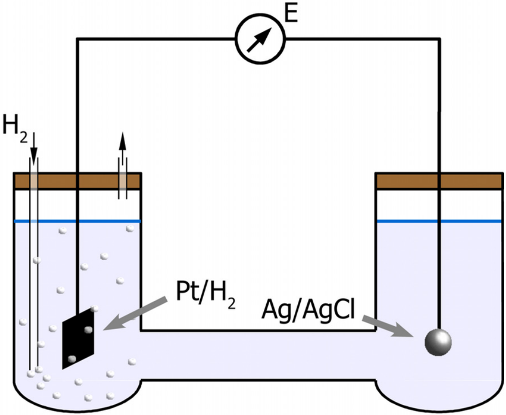
Equilibrium electrochemistry

- With hydrogen electrode at standard condition, $E(Ag^+/Ag) = E^0(Ag^+/Ag) - \frac{RT}{2F}\ln\frac{1}{a(Ag^+)^2} = E^0(Ag^+/Ag) - \frac{RT}{F}\ln\frac{1}{a(Ag^+)}$
- For the right electrode $Ag^+(aq) + e^- \rightarrow Ag(s) \qquad Q = \frac{1}{a(Ag^+)} \qquad E(Ag^+/Ag) = E^0(Ag^+/Ag) - \frac{RT}{F}\ln Q$
- Similarly for the cell $Pt|H_2(g)|H^+(aq)||Cl^-(aq)|AgCl(s)|Ag(s) \qquad H_2(g) + 2AgCl(s) \rightarrow 2HCl(aq) + 2Ag(s) \qquad Q = \frac{a(H^+)^2 a(Cl^-)^2}{f(H_2)/p^0}$
- With hydrogen electrode at standard composition $E(AgCl/Ag, Cl^-) = E^0(AgCl/Ag, Cl^-) - \frac{RT}{2F}\ln a(Cl^-)^2 = E^0(AgCl/Ag, Cl^-) - \frac{RT}{F}\ln a(Cl^-)$
- Same as writing Nernst equation for $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \qquad Q = a(Cl^-)$
- In the Silver/Silver Chloride electrode what is the change in emf if enough KCl is added to have 0.01 mol Kg^{-1} KCl as electrolyte. a(Cl^{-1}) in saturated AgCl solution is 1.3×10^{-5}.

Equilibrium electrochemistry

- $\Delta E = -\frac{RT}{F} \ln \frac{\gamma_{\pm,f} m_f}{\gamma_{\pm,i} m_i} = -\frac{8.314 \times 298}{96487} \frac{0.906 \times 0.01}{1.3 \times 10^{-5}} = -0.17V.$
- Calculate ΔE for Calomel electrode $(a(Cl^-) = 8.7 \times 10^{-7})$ when electrolyte is turned to 0.05 mol Kg^{-1} KCl(aq)
- *The hydrogen electrode and pH*
- $E(H^+/H_2) = E^0(H^+/H_2) - \frac{RT}{2F} \ln Q = \frac{RT}{F} \ln \frac{a(H^+)p^{0\,1/2}}{f(H_2)^{1/2}}$
- At 298K, $E(H^+/H_2) = -59.16mV \times pH$
- Calculate the change in electrode potential when chlorine pressure bubbling over a platinum electrode increases from 1 to 2 atm.
- Find the potential expression for $G_2(g) + 4e^- \rightarrow 2G^{2-}(aq)$
- Electric control of solution composition $E(Fe^{3+}/Fe^{2+}) = E^0(Fe^{3+}/Fe^{2+}) - \frac{RT}{F} \ln \frac{a(Fe^{2+})}{a(Fe^{3+})}$

Standard reduction potential measurement

- Platinum, Hydrogen — Silver, silver chloride cell (so-called Harned cell) for primary pH measurements
  $Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag(s)$ $\frac{1}{2}H_2(g) + AgCl(s) \rightarrow HCl(aq) + Ag(s)$
- $E = E^0(AgCl/Ag, Cl^-) - \frac{RT}{F} \ln \frac{a(H^+)a(Cl^-)}{(f/p^0)^{1/2}}$
- 

Standard reduction potential table

Reduction Half-Reaction	Standard Reduction Potential (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$	+2.01
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.09
$Ag^+(aq) + e^- \rightarrow \mathrm{Ag(s)}$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$I_2(l) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$S(s) + 2H^+(aq) + 2e^- \rightarrow H_2S(g)$	+0.14
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$	-0.26
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	-1.18
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

Standard reduction potential measurement

- $E + \frac{2RT}{F}\ln(\frac{m}{m^0}) = E^0(AgCl/Ag, Cl^-) - \frac{2RT}{F}\ln\gamma_\pm$
- For a one-one electrolyte, $\ln\gamma_\pm = -Am^{1/2}$
- $E + \frac{2RT}{F}\ln(\frac{m}{m^0}) = E^0(AgCl/Ag, Cl^-) + \frac{2.34RT}{F}(\frac{m}{m^0})^{1/2}$
- Thus a graph of $E + \frac{2RT}{F}\ln(\frac{m}{m^0})$ vs. $(\frac{m}{m^0})^{1/2}$ is extrapolated to m=0.
- *Measuring activity coefficient*
- $\ln\gamma_\pm = \frac{F}{2RT}[E^0(AgCl/Ag, Cl^-) - E] - \ln\frac{m}{m^0}$
- *Electrochemical series*
- Redox potential is a measure of the tendency of a chemical species to acquire electrons from or lose electrons to an electrode and thereby be reduced or oxidized
- Each species has its own intrinsic redox potential
- redox potential is a measure of the tendency of the solution to either gain or lose electrons when it is subjected to change by introduction of a new species.

Equilibrium electrochemistry

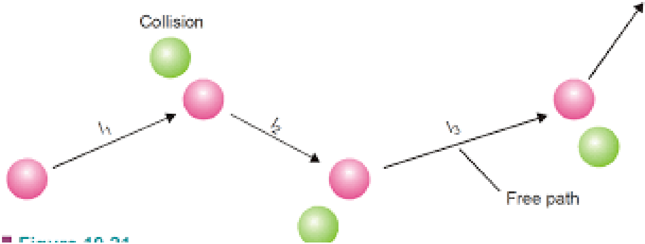
- Reduction potentials of aqueous solutions are determined by measuring the potential difference between an inert sensing electrode in contact with the solution and a stable reference electrode connected to the solution by a salt bridge.
- Redox potential represents how easily electrons are transferred to or from species in solution. Redox potential characterizes the ability under the specific condition of a chemical species to lose or gain electrons instead of the amount of electrons available for oxidation or reduction.
- It is possible to define pe, the negative logarithm of electron concentration (-log[e]) in a solution, which will be directly proportional to the redox potential.
- The standard reduction potential (E_0) is measured under standard conditions: 25°C, a 1 activity for each ion participating in the reaction, a partial pressure of 1 bar for each gas that is part of the reaction, and metals in their pure state.

Kinetic theory: Energy distribution among gaseous molecules

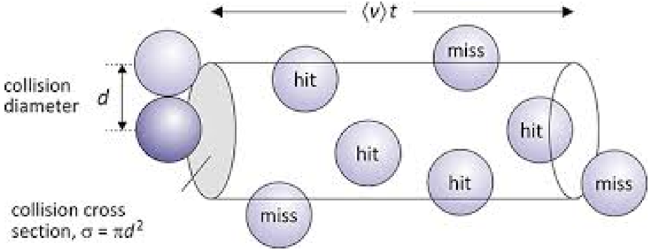
- The principle of equal a priori probabilities.
- For a gas system, assume n_i molecules to each have energy ϵ_i
- The number of possible ways each distribution happens is $W(\{n_i\}) = \frac{N!}{\Pi_i n_i!}$
- The number of microstates are so vast that average values may be substituted by most probable values.
- To find the most probable distribution, $\{n_i^*\}$, we maximize $W(\{n_i\})$ subject to $\sum_i n_i = N$ and $\sum_i n_i \epsilon_i = E$.
- Thus $\frac{n_i}{N} \propto e^{-\epsilon_i/kT}$.

Kinetic theory of gases.

- $P = \frac{F}{A} = \frac{1}{A}\frac{d(mc)}{dt} = \frac{Nm}{3l^3}\bar{c^2}$
- $\bar{c^2} = \int_0^\infty c^2 4\pi(\frac{m}{2\pi kT})^{3/2} e^{-\frac{mc^2}{2kT}} c^2 dc = 4\pi(\frac{m}{2\pi kT})^{3/2} \int_0^\infty c^4 e^{-\frac{mc^2}{2kT}} dc = 4\pi(\frac{m}{2\pi kT})^{3/2} 3\frac{kT}{m} \int_0^\infty c^2 e^{-\frac{mc^2}{2kT}} dc = 4\pi(\frac{m}{2\pi kT})^{3/2} 3\frac{kT}{m}\frac{kT}{m}\frac{1}{2}\sqrt{\frac{2\pi kT}{m}} = 3\frac{kT}{m}$
- $PV = NkT$
- Average number of collisions per unit time = volume of collision cylinder× molecules/unit volume $= \pi\rho^2\bar{c}n$.



Molecular diffusion

- 

- Mean free path of a molecule? $\lambda = \frac{\bar{c}}{\pi\rho^2\bar{c}n} = \frac{1}{\pi\rho^2 n}$. Assuming $\rho = \sigma \approx 3 \times 10^{-8}$ cm, $\lambda \approx 10^{-5}$ cm explains poor diffusion and thermal conduction in gases.
- Diffusion is the movement of a substance from a region of high concentration to a region of low concentration without bulk motion.

Molecular diffusion

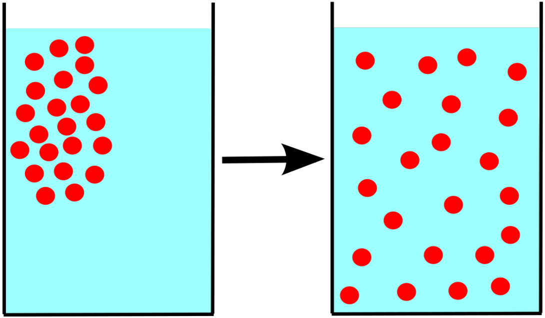


Figure: Molecular diffusion taken from `https://en.wikipedia.org`

- Fick's first law: the diffusion flux is proportional to the negative of the concentration gradient: $\mathbf{J} = -D\,\nabla n\;,\quad J_i = -D\frac{\partial n}{\partial x_i}$.
- transfer of a physical quantity N through a small area ΔS with normal ν per time Δt, $\quad \Delta N = (\mathbf{J}, \nu)\,\Delta S\,\Delta t$.
- Dimensional analysis: $D(\frac{cm^2}{s}) \propto \lambda\bar{c}(\frac{cm^2}{s})$

Viscosity coefficient

- The rate at which molecules cross a unit area in one direction is $n\bar{c}/6$.
- Number of molecules crossing from above $\frac{\bar{c}}{6}[n_i(0) + \lambda\frac{\Delta n_i}{\Delta d}]$. Number of molecules crossing from below $\frac{\bar{c}}{6}[n_i(0) - \lambda\frac{\Delta n_i}{\Delta d}]$.
- Net flux $= -\frac{1}{3}\lambda\bar{c}\frac{\Delta n_i}{\Delta d} = -D\frac{\Delta n_i}{\Delta d}$. Thus $D = \frac{1}{3}\lambda\bar{c}$.
- Dimensional analysis for viscosity coefficient: force/area $= -\eta\frac{\Delta u}{\Delta d}$. Thus η (gr/s cm). Achieved by writing $\eta \propto nm\bar{c}\lambda$
- Average values of transported momentum one mean free path above and below the reference plane is, respectively, $m(u + \lambda\frac{\Delta u}{\Delta d})$ and $m(u - \lambda\frac{\Delta u}{\Delta d})$.
- Multiplying by $n\bar{c}/6$ one finds momentum transport in each direction.

Conductivity

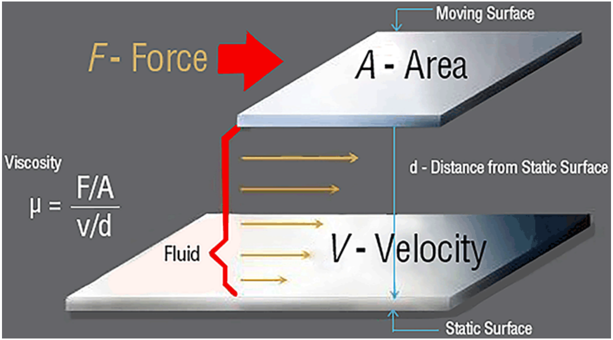
- 

Figure: Schematic for measuring viscosity courtesy of Hydraulic Institute `http://pumps.org`

- momentum transport rate per unit area $= -\frac{1}{3} nm\bar{c}\lambda \frac{\Delta u}{\Delta d}$
- $\eta = \frac{1}{3} nm\bar{c}\lambda$
- To determine thermal conductivity we consider a reference plane perpendicular to the temperature gradient. At this plane average molecular energy is $c_v T$.

Conductivity

- Average energies λ above and below the the reference plane is respectively $c_v(T + \lambda\frac{\Delta T}{\Delta d})$ and $c_v(T - \lambda\frac{\Delta T}{\Delta d})$
- rate of energy transport per unit area $= -\frac{1}{3}n\bar{c}c_v\lambda\frac{\Delta T}{\Delta d} = -\kappa\frac{\Delta T}{\Delta d}$
- $\kappa = \frac{1}{3}n\bar{c}c_v\lambda$