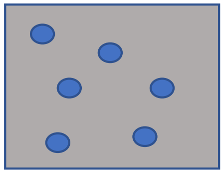
Phase Diagrams



Gibbs Phase Rule

$F + Ph = C + 2$

2 is T and P; for isobaric
$F + Ph = C + 1$

FCC a_{Ag} = 4.1 Å
FCC a_{Cu} = 3.6 Å

Eutectic Phase Diagram Ag + Cu
Univariant Equilibrium
  Liquidus
  Solidus
Invariant Equilibrium
  Eutectic

$\text{liquid} \rightarrow \text{Cu(ss)} + \text{Ag(ss)}$

Lever Rule
Tieline (conode)

$$\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \ldots \quad \text{for } i = 1, 2, \ldots, C$$

$$\mu_A^{\alpha}(x_A^{\alpha}) = \mu_A^{\beta}(x_A^{\beta}) \quad \text{and} \quad \mu_B^{\alpha}(x_A^{\alpha}) = \mu_B^{\beta}(x_A^{\beta})$$

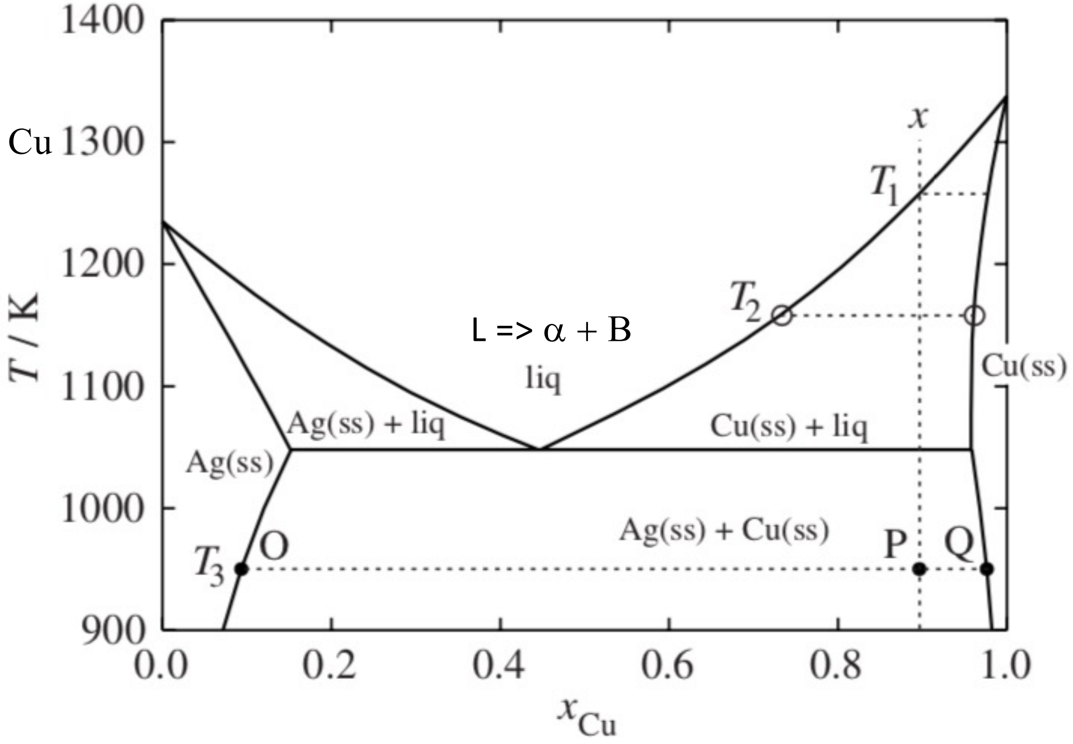
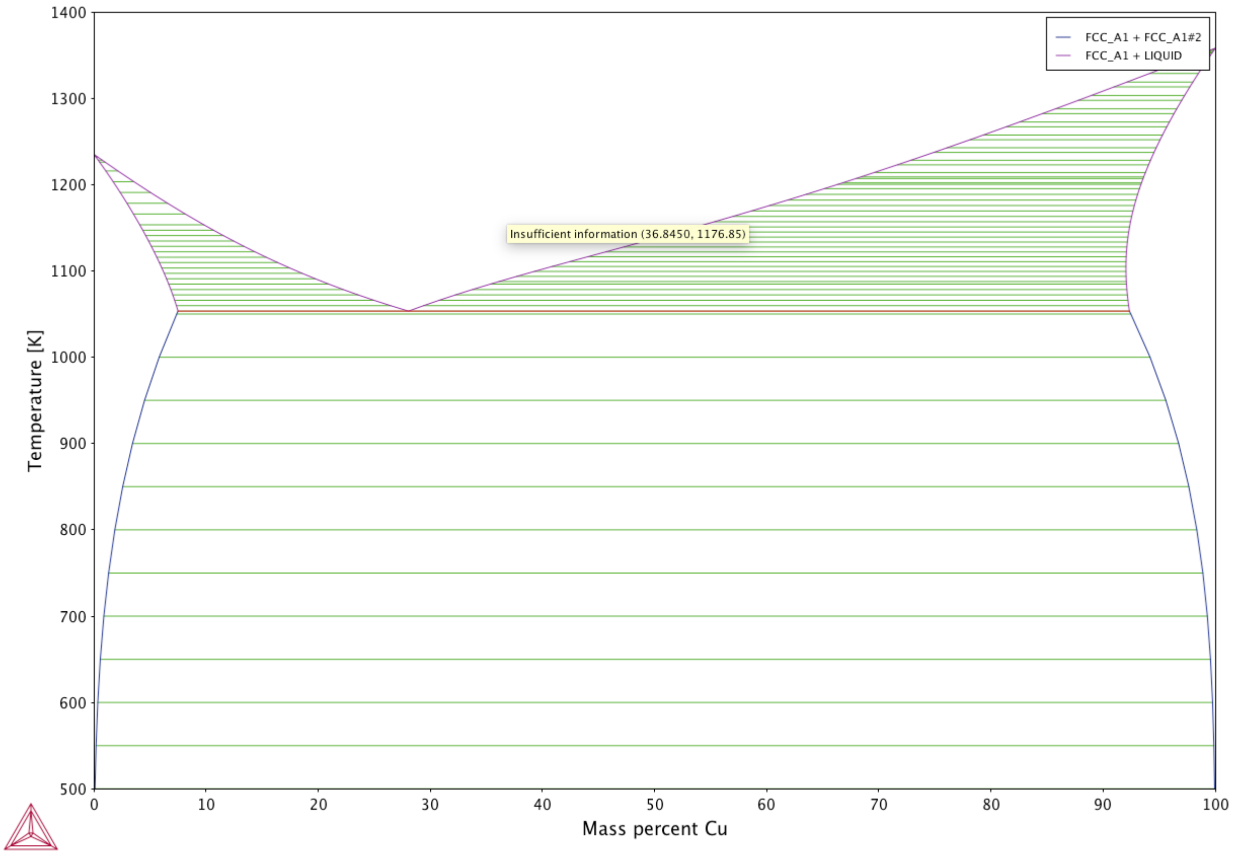


Figure 4.1 Phase diagram of the system Ag–Cu at 1 bar [1].

Silver acts like a solvent to copper and copper acts like a solvent to silver with limited solubility that is a function of temperature with a solubility limit at the eutectic point (3 phases in equilibrium)

From Thermo-Calc Program (Solder Demo)

CALPHAD is another program for phase diagrams



Phase Diagrams

Gibbs Phase Rule

$F + Ph = C + 2$

Eutectic Phase Diagram Ag + Cu

Univariant Equilibrium

- Liquidus
- Solidus

Invariant Equilibrium

- Eutectic

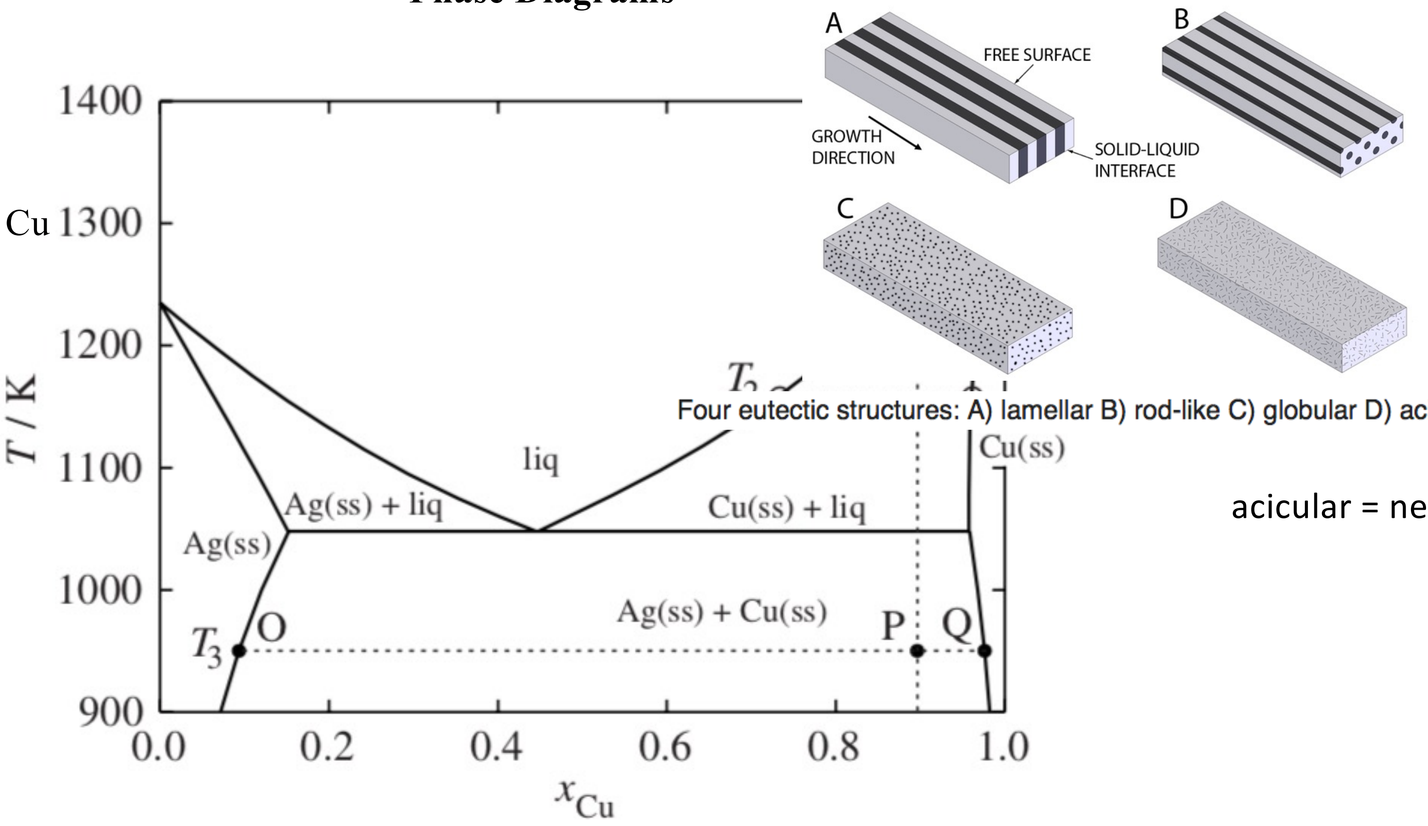
$\text{liquid} \rightarrow \text{Cu(ss)} + \text{Ag(ss)}$

Lever Rule

Tieline (conode)

$\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \dots \quad \text{for } i = 1, 2, \dots, C$

$\mu_A^{\alpha}(x_A^{\alpha}) = \mu_A^{\beta}(x_A^{\beta})$ and $\mu_B^{\alpha}(x_A^{\alpha}) = \mu_B^{\beta}(x_A^{\beta})$

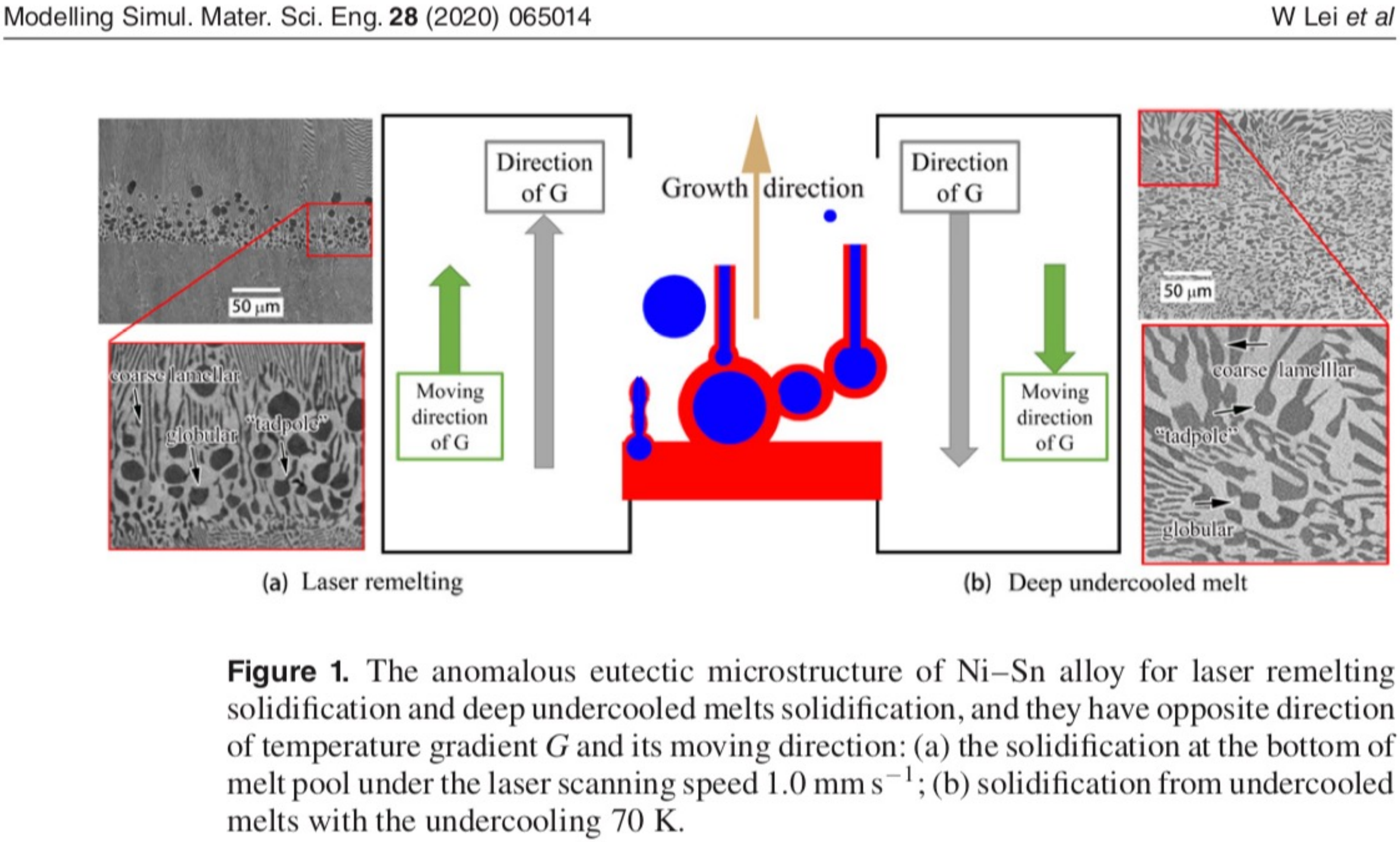


Four eutectic structures: A) lamellar B) rod-like C) globular D) acicular.

acicular = needle

Figure 4.1 Phase diagram of the system Ag–Cu at 1 bar [1].

Phase Diagrams



Modelling Simul. Mater. Sci. Eng. **28** (2020) 065014 W Lei *et al*

(a) Laser remelting

(b) Deep undercooled melt

Figure 1. The anomalous eutectic microstructure of Ni–Sn alloy for laser remelting solidification and deep undercooled melts solidification, and they have opposite direction of temperature gradient *G* and its moving direction: (a) the solidification at the bottom of melt pool under the laser scanning speed 1.0 mm s^{-1}; (b) solidification from undercooled melts with the undercooling 70 K.

Phase Diagrams

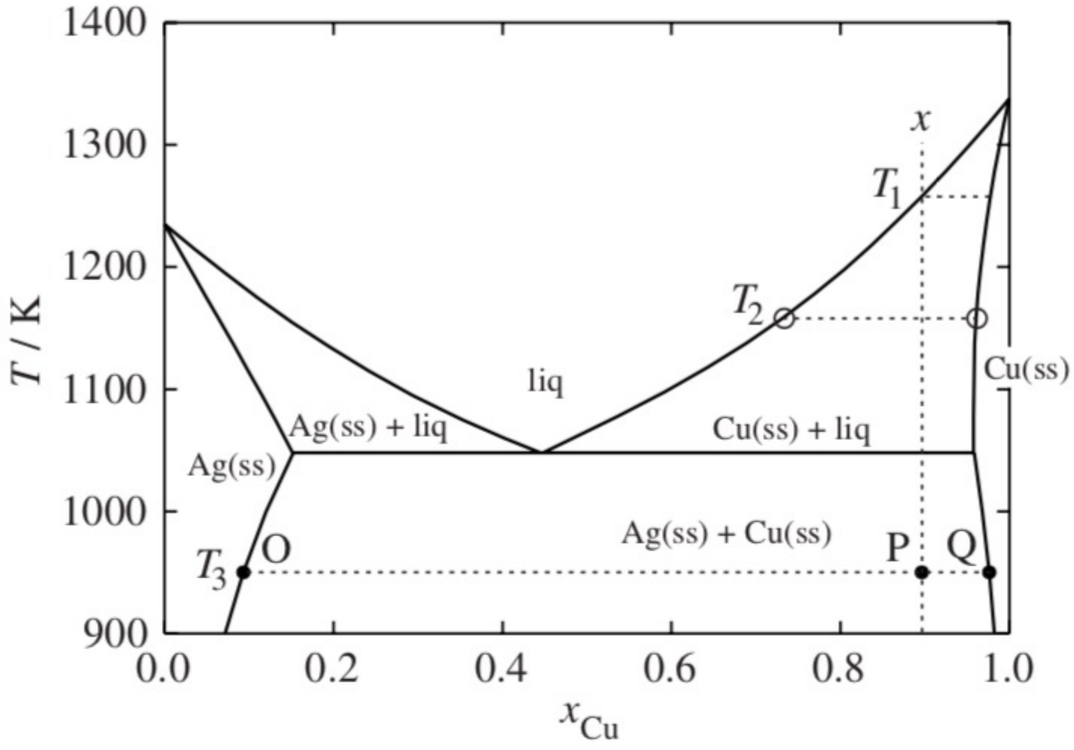


Figure 4.1 Phase diagram of the system Ag–Cu at 1 bar [1].

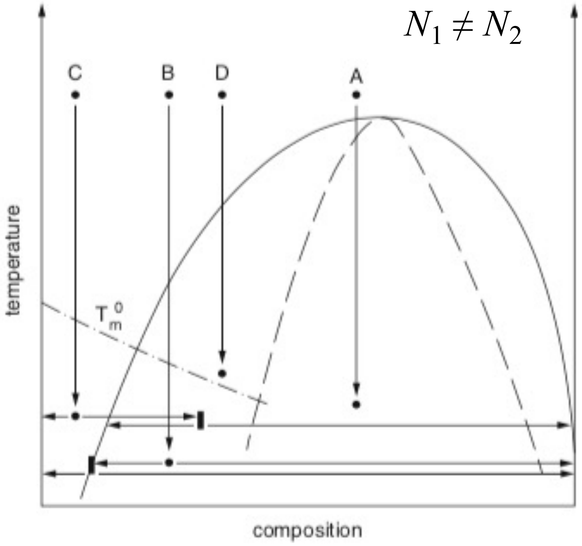
Slow Cool Morphology

Consider the morphology in a slow cool from T1 (liquid) to T3 (solid). Just below T1 domains of Cu/Ag at about 98% Cu form in the liquid matrix. The fraction Cu/Ag solid increases as temperature drops, probably growing on the seeds formed at T1. By T2 the matrix is solid with domains of liquid. The composition of the matrix is richer in Ag at the outside, close to 95% Cu. At the eutectic domains of Cu/Ag with 15% Cu become immersed in a matrix of about 95% Cu/Ag. The entire system is solid so diffusion essentially stops and the structure is locked.

Rapid Quench Morphology

For a rapid quench to T3, domains of 10% Cu form in a matrix of 97% Cu.

Fig. 3.41 Phase diagram of a binary polymer blend with miscibility gap (UCST) and intersecting crystal/melt coexistence curve. The T_m° curve is extrapolated into the miscibility gap. Quenching routes *A* to *D* are explained in the text. For routes *B* and *C*, the quenching-induced phase separation and crystallization are indicated. —— binodal, ——— spinodal, and —. crystal/melt coexistence curve (Li et al. 1991)



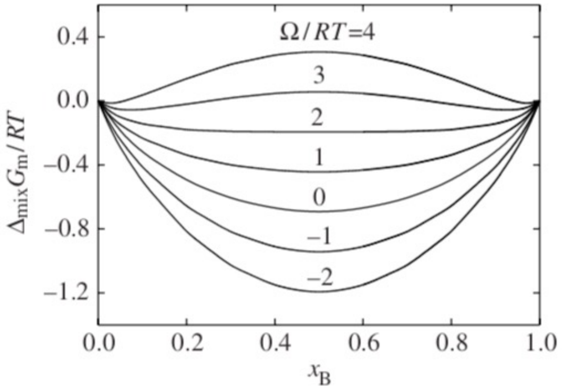
$N_1 \neq N_2$

A. Simultaneous spinodal decomposition and crystallization
   The blend is quenched into the unstable region of the miscibility gap and to a temperature below the crystallization/melt coexistence curve.
B. Simultaneous binodal decomposition and crystallization
   This type is similar to spinodal decomposition, but a composition is quenched into the metastable region of the miscibility gap.
C. Crystallization induced decomposition
   The blend is quenched outside the miscibility gap to a temperature below the crystallization/melt coexistence curve. The concentration of the noncrystallizable component increases with crystallization until the miscibility gap is reached inducing demixing.
D. Decomposition-induced crystallization
   The blend is quenched into the miscibility gap to a temperature that lies above the crystallization/melt coexistence curve for the actual composition but lies below the crystallization curve for the binodal composition. When the blend is quenched, demixing occurs resulting in two coexisting phases of which one is able to crystallize. The demixing can result in spinodally as well as in binodally decomposed material.

Only few experimental studies have been performed on polymer blends

Y. Li, M. Stein, B.-J. Jungnickel, Colloid Polym. Sci. 269, 772 (1991); and 'Mitteilungen aus dem Deutschen Kunststoff-Institut', Nr. 53, April, Darmstadt, 1991

$$\frac{\Delta_{\mathrm{mix}}G}{k_{\mathrm{B}}TV} = \frac{1}{\nu^*}\left(\frac{\varphi_1}{N_1}\ln\varphi_1 + \frac{\varphi_2}{N_2}\ln\varphi_2 + \varphi_1\varphi_2\chi\right)$$



$N_1 = N_2$

Figure 3.10 The molar Gibbs energy of mixing of a regular solution A–B for different values of Ω/RT.

Solid Solutions

Does $dG/dx_i = dG/dn_i = \mu_i$?

Not exactly

$dG/dn_i = dG/dx_i \; dx_i/dn_i$

$dx_i/dn_i = d(n_i/(n_i+n_j))/dn_i = 1/(n_i+n_j) - n_i/(n_i+n_j)^2$

Common Tangent Construction

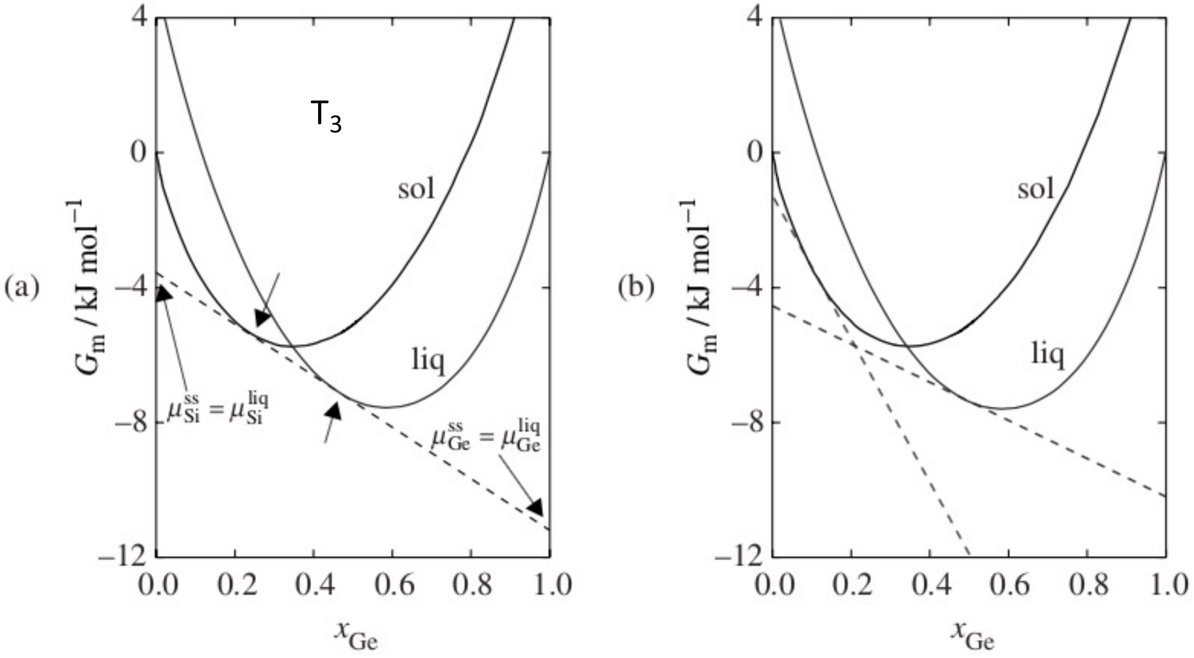
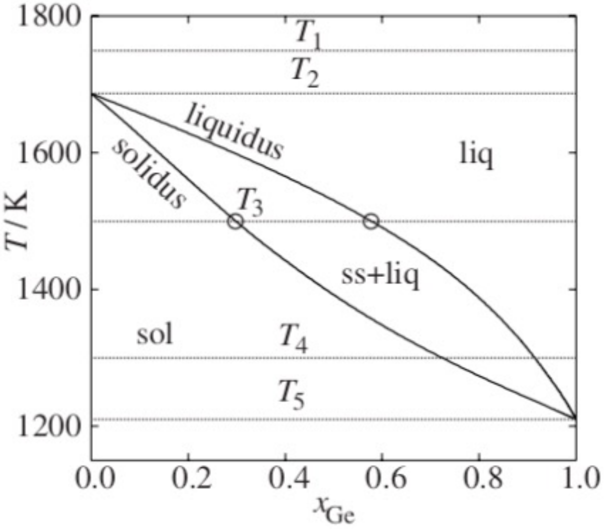
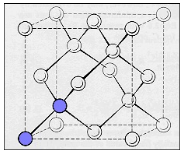


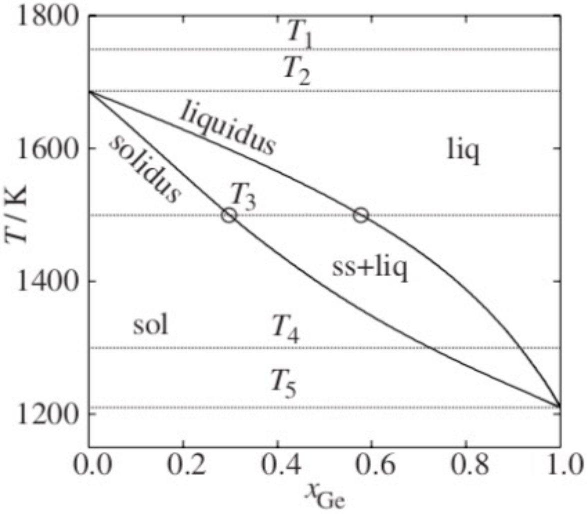
Figure 4.2 Gibbs energy curves for the liquid and solid solution in the binary system Si–Ge at 1500 K. (a) A common tangent construction showing the compositions of the two phases in equilibrium. (b) Tangents at compositions that do not give two phases in equilibrium. Thermodynamic data are taken from reference [2].



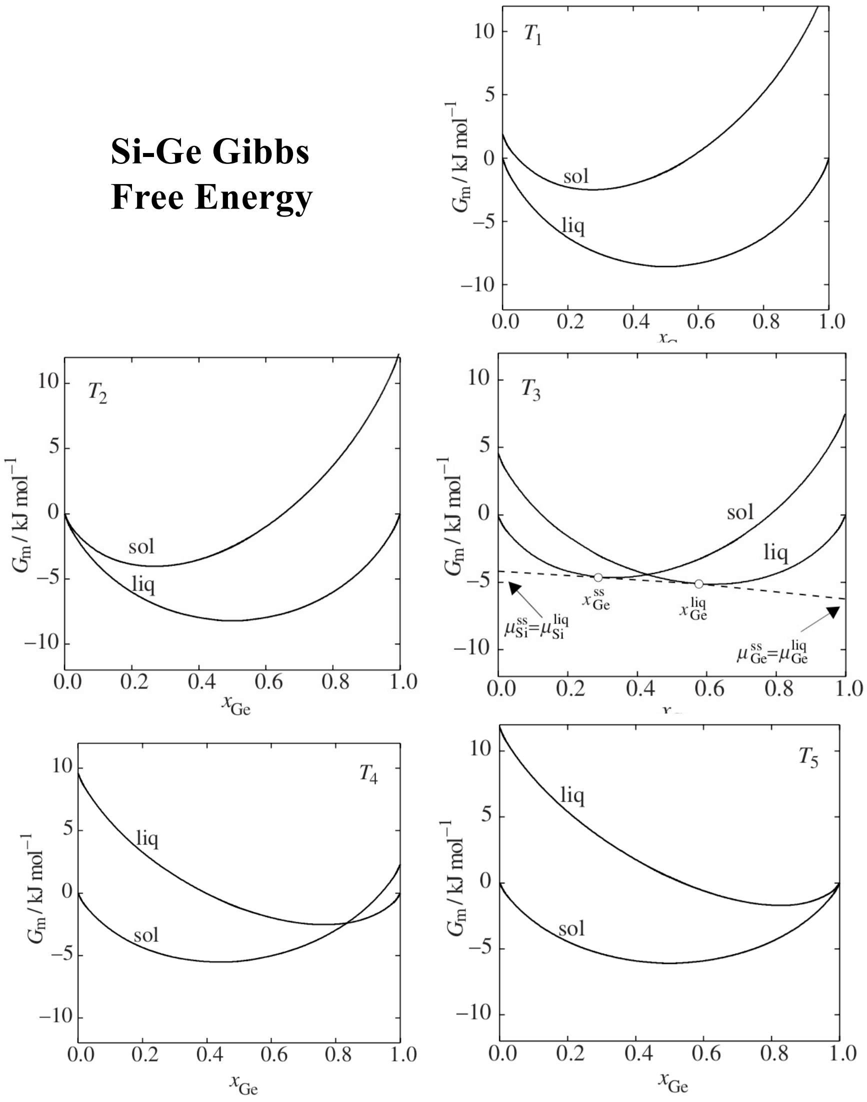
Both have diamond cubic structure



Si-Ge phase diagram



Si-Ge Gibbs Free Energy



Single crossing of solid/liquid free energy curves

Pressure Expression: Mix two ideal gasses, A and B

-S U V
H A
-p G T

$p = p_A + p_B$ p_A is the partial pressure $p_A = x_A p$

For single component molar $G = \mu$
μ_0 is at $p_{0,A} = 1$ bar
At pressure p_A for a pure component isothermal ideal gas
$\mu_A = \mu_{0,A} + RT \ln(p/p_{0,A}) = \mu_{0,A} + RT \ln(p)$

dG=SdT+Vdp
Isothermal and Ideal Gas
dG = RTdp/p

For a mixture of A and B with a total pressure $p_{tot} = p_{0,A} = 1$ bar and $p_A = x_A p_{tot}$

For component A in an ideal binary mixture

$\mu_A(x_A) = \mu_{0.A} + RT \ln (x_A p_{tot}/p_{0,A}) = \mu_{0.A} + RT \ln (x_A)$

$$\mu_A = \mu_A^* + RT \ln a_A$$

Isothermal and Real Gas

$\mu_A^* = \mu_{0.A}$ if $p = 1$

Calculate the Phase Diagram for a Solid Solution

$$\mu_{\mathrm{A}}^{\mathrm{ss}} = \mu_{\mathrm{A}}^{\mathrm{s,o}} + RT \ln a_{\mathrm{A}}^{\mathrm{ss}}$$

$$\mu_{\mathrm{A}}^{\mathrm{liq}} = \mu_{\mathrm{A}}^{\mathrm{l,o}} + RT \ln a_{\mathrm{A}}^{\mathrm{liq}}$$

$$\mu_{\mathrm{A}}^{\mathrm{ss}} = \mu_{\mathrm{A}}^{\mathrm{liq}} \qquad \mu_{\mathrm{A}}^{\mathrm{s,o}} + RT \ln a_{\mathrm{A}}^{\mathrm{ss}} = \mu_{\mathrm{A}}^{\mathrm{l,o}} + RT \ln a_{\mathrm{A}}^{\mathrm{liq}}$$

$$\mu_{\mathrm{B}}^{\mathrm{ss}} = \mu_{\mathrm{B}}^{\mathrm{liq}} \qquad \mu_{\mathrm{B}}^{\mathrm{s,o}} + RT \ln a_{\mathrm{B}}^{\mathrm{ss}} = \mu_{\mathrm{B}}^{\mathrm{l,o}} + RT \ln a_{\mathrm{B}}^{\mathrm{liq}}$$

$$\ln\left(\frac{a_{\mathrm{A}}^{\mathrm{liq}}}{a_{\mathrm{A}}^{\mathrm{ss}}}\right) = -\frac{\Delta\mu_{\mathrm{A}}^{\mathrm{o}(s\to \mathrm{l})}}{RT} \qquad \ln\left(\frac{a_{\mathrm{B}}^{\mathrm{liq}}}{a_{\mathrm{B}}^{\mathrm{ss}}}\right) = -\frac{\Delta\mu_{\mathrm{B}}^{\mathrm{o}(s\to \mathrm{l})}}{RT}$$

$$\Delta\mu_i^{\mathrm{o}(s\to \mathrm{l})} = \mu_i^{\mathrm{l,o}} - \mu_i^{\mathrm{s,o}} = \Delta_{\mathrm{fus}} G_i^{\mathrm{o}} = \Delta_{\mathrm{fus}} H_i^{\mathrm{o}} - T\Delta_{\mathrm{fus}} S_i^{\mathrm{o}}$$

$$\Delta_{\mathrm{fus}} G_i^{\mathrm{o}} = 0 \qquad \Delta_{\mathrm{fus}} S_i^{\mathrm{o}} = \Delta_{\mathrm{fus}} H_i^{\mathrm{o}} / T_{\mathrm{fus},i}$$

$$\Delta\mu_i^{\mathrm{o}(s\to \mathrm{l})} = \Delta_{\mathrm{fus}} H_i^{\mathrm{o}} - T\Delta_{\mathrm{fus}} S_i^{\mathrm{o}} = \Delta_{\mathrm{fus}} H_i^{\mathrm{o}}\left(1 - \frac{T}{T_{\mathrm{fus},i}}\right)$$

$C_p(T)$ is constant

$$\ln\left(\frac{a_{\mathrm{A}}^{\mathrm{liq}}}{a_{\mathrm{A}}^{\mathrm{ss}}}\right) = -\frac{\Delta\mu_{A}^{\mathrm{o}(s\to \mathrm{l})}}{RT} = -\frac{\Delta_{\mathrm{fus}} H_{\mathrm{A}}^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus,A}}}\right) \qquad \ln\left(\frac{a_{\mathrm{B}}^{\mathrm{liq}}}{a_{\mathrm{B}}^{\mathrm{ss}}}\right) = -\frac{\Delta\mu_{B}^{\mathrm{o}(s\to \mathrm{l})}}{RT} = -\frac{\Delta_{\mathrm{fus}} H_{\mathrm{B}}^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus,B}}}\right)$$

$$x_{\mathrm{A}}^{\mathrm{liq}} = x_{\mathrm{A}}^{\mathrm{ss}} \exp\left[-\frac{\Delta_{\mathrm{fus}} H_{\mathrm{A}}^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus,A}}}\right)\right] \qquad x_{\mathrm{B}}^{\mathrm{liq}} = x_{\mathrm{B}}^{\mathrm{ss}} \exp\left[-\frac{\Delta_{\mathrm{fus}} H_{\mathrm{B}}^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus,B}}}\right)\right]$$

Ideal

$x_A + x_B = 1$

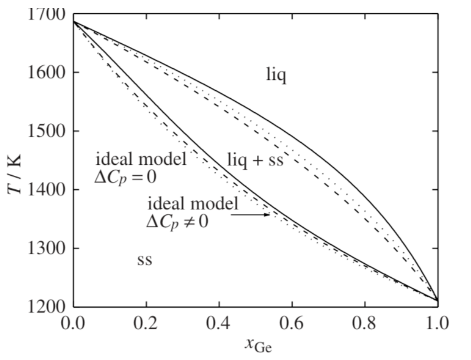


Figure 4.4 Phase diagram for the system Si–Ge at 1 bar. The solid lines represent experimental observations [2] while the dotted and dashed lines represent calculations assuming that the solid and liquid solutions are ideal with $\Delta C_p \neq 0$ and $\Delta C_p = 0$, respectively.

Solve for x_B^{SS} x_B^{liq} since $x_A + x_B = 1$

$$x_{\mathrm{A}}^{\mathrm{ss}} \exp\left[-\frac{\Delta_{\mathrm{fus}} H_{\mathrm{A}}^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus,A}}}\right)\right] + x_{\mathrm{B}}^{\mathrm{ss}} \exp\left[-\frac{\Delta_{\mathrm{fus}} H_{\mathrm{B}}^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus,B}}}\right)\right] = 1$$

$$x_{\mathrm{A}}^{\mathrm{liq}} \exp\left[\frac{\Delta_{\mathrm{fus}} H_{\mathrm{A}}^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus,A}}}\right)\right] + x_{\mathrm{B}}^{\mathrm{liq}} \exp\left[\frac{\Delta_{\mathrm{fus}} H_{\mathrm{B}}^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus,B}}}\right)\right] = 1$$

For *Ideal* you can solve the phase diagram knowing the melting points and heats of fusion.

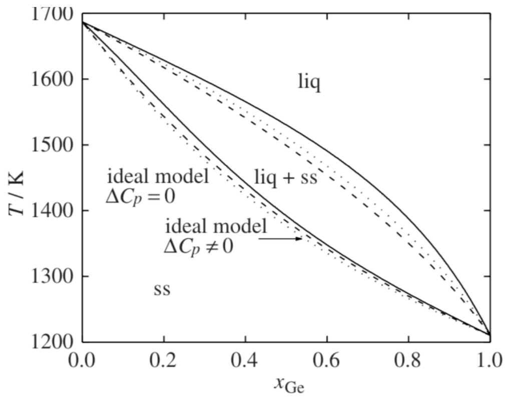


Figure 4.4 Phase diagram for the system Si–Ge at 1 bar. The solid lines represent experimental observations [2] while the dotted and dashed lines represent calculations assuming that the solid and liquid solutions are ideal with $\Delta C_p \neq 0$ and $\Delta C_p = 0$, respectively.

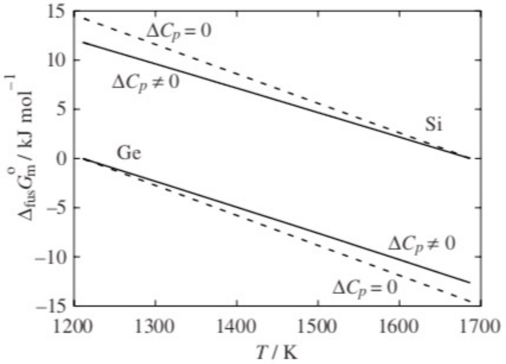


Figure 4.6 Gibbs energy of fusion of Ge and Si. The solid lines represent experimental data [4] while the broken lines are calculated neglecting the heat capacity difference between liquid and solid.

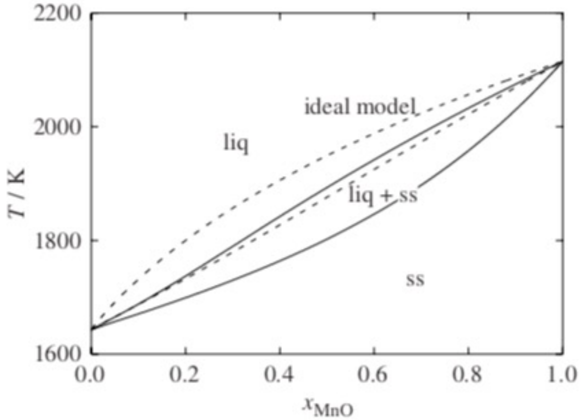
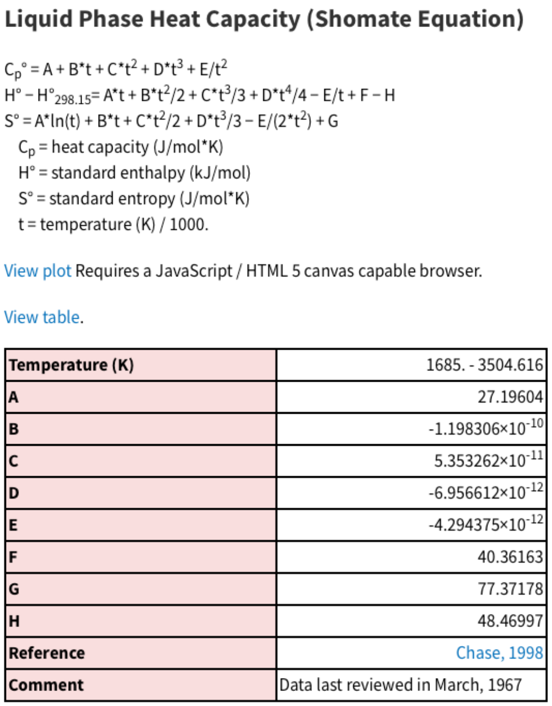


Figure 4.5 Phase diagram of FeO–MnO at 1 bar. The solid lines represent experimental observations [3]. The activity of iron is kept constant and equal to 1 by equilibration with liquid Fe. Dashed lines represent calculations assuming that the solid and liquid solutions are ideal.

$$\Delta\mu_i^{\mathrm{o}(s\to \mathrm{l})} = \mu_i^{\mathrm{l,o}} - \mu_i^{\mathrm{s,o}} = \Delta_{\mathrm{fus}} G_i^{\mathrm{o}} = \Delta_{\mathrm{fus}} H_i^{\mathrm{o}} - T\Delta_{\mathrm{fus}} S_i^{\mathrm{o}}$$

$$\Delta\mu_i^{\mathrm{o}(s\to \mathrm{l})} = \Delta_{\mathrm{fus}} H_i^{\mathrm{o}} + \int_{T_{\mathrm{fus,i}}}^{T} \Delta C_{p,i}^{\mathrm{o}}\,\mathrm{d}T - T\left(\Delta_{\mathrm{fus}} S_i^{\mathrm{o}} + \int_{T_{\mathrm{fus,i}}}^{T} \frac{\Delta C_{p,i}^{\mathrm{o}}}{T}\,\mathrm{d}T\right) \qquad \Delta C_p^{\mathrm{o}} = C_p^{\mathrm{l,o}} - C_p^{\mathrm{s,o}}$$

https://webbook.nist.gov/chemistry/name-ser/



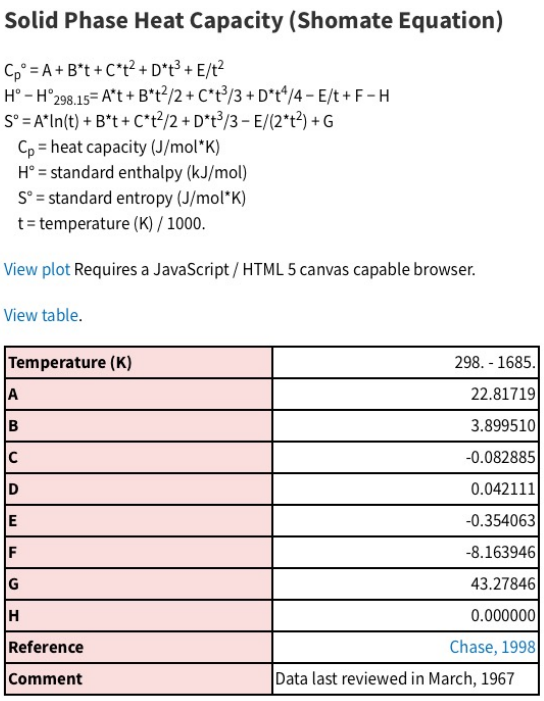
Liquid Phase Heat Capacity (Shomate Equation)

$C_p° = A + B*t + C*t^2 + D*t^3 + E/t^2$
$H° − H°_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 − E/t + F − H$
$S° = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 − E/(2*t^2) + G$
C_p = heat capacity (J/mol*K)
H° = standard enthalpy (kJ/mol)
S° = standard entropy (J/mol*K)
t = temperature (K) / 1000.

View plot Requires a JavaScript / HTML 5 canvas capable browser.

View table.

Temperature (K)	1685. - 3504.616
A	27.19604
B	-1.198306×10^{-10}
C	5.353262×10^{-11}
D	-6.956612×10^{-12}
E	-4.294375×10^{-12}
F	40.36163
G	77.37178
H	48.46997
Reference	Chase, 1998
Comment	Data last reviewed in March, 1967



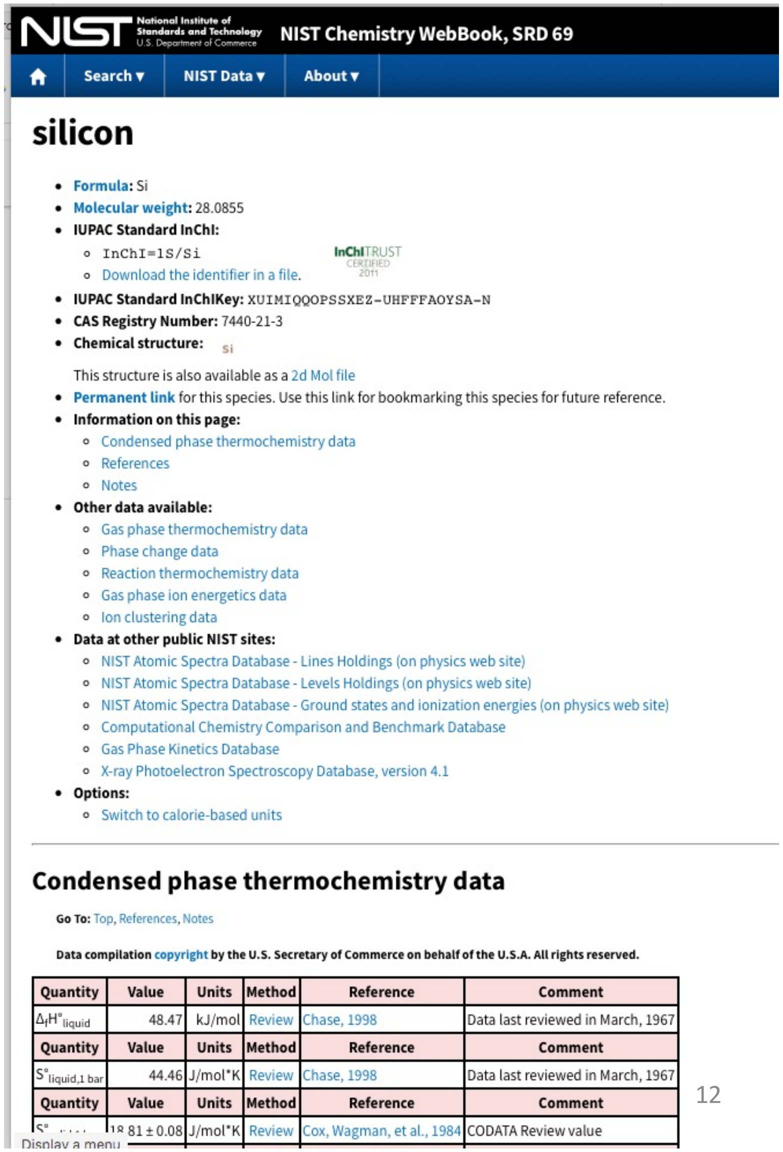
Solid Phase Heat Capacity (Shomate Equation)

$C_p° = A + B*t + C*t^2 + D*t^3 + E/t^2$
$H° − H°_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 − E/t + F − H$
$S° = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 − E/(2*t^2) + G$
C_p = heat capacity (J/mol*K)
H° = standard enthalpy (kJ/mol)
S° = standard entropy (J/mol*K)
t = temperature (K) / 1000.

View plot Requires a JavaScript / HTML 5 canvas capable browser.

View table.

Temperature (K)	298. - 1685.
A	22.81719
B	3.899510
C	-0.082885
D	0.042111
E	-0.354063
F	-8.163946
G	43.27846
H	0.000000
Reference	Chase, 1998
Comment	Data last reviewed in March, 1967



silicon

- **Formula:** Si
- **Molecular weight:** 28.0855
- **IUPAC Standard InChI:**
    - `InChI=1S/Si`
    - Download the identifier in a file.
- **IUPAC Standard InChIKey:** `XUIMIQQOPSSXEZ-UHFFFAOYSA-N`
- **CAS Registry Number:** 7440-21-3
- **Chemical structure:** Si

  This structure is also available as a 2d Mol file
- **Permanent link** for this species. Use this link for bookmarking this species for future reference.
- **Information on this page:**
    - Condensed phase thermochemistry data
    - References
    - Notes
- **Other data available:**
    - Gas phase thermochemistry data
    - Phase change data
    - Reaction thermochemistry data
    - Gas phase ion energetics data
    - Ion clustering data
- **Data at other public NIST sites:**
    - NIST Atomic Spectra Database - Lines Holdings (on physics web site)
    - NIST Atomic Spectra Database - Levels Holdings (on physics web site)
    - NIST Atomic Spectra Database - Ground states and ionization energies (on physics web site)
    - Computational Chemistry Comparison and Benchmark Database
    - Gas Phase Kinetics Database
    - X-ray Photoelectron Spectroscopy Database, version 4.1
- **Options:**
    - Switch to calorie-based units

Condensed phase thermochemistry data

Go To: Top, References, Notes

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Quantity	Value	Units	Method	Reference	Comment
$\Delta_f H°_{\mathrm{liquid}}$	48.47	kJ/mol	Review	Chase, 1998	Data last reviewed in March, 1967
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
$S°_{\mathrm{liquid,1\,bar}}$	44.46	J/mol*K	Review	Chase, 1998	Data last reviewed in March, 1967
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
S°	18.81 ± 0.08	J/mol*K	Review	Cox, Wagman, et al., 1984	CODATA Review value

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Congruent Melting

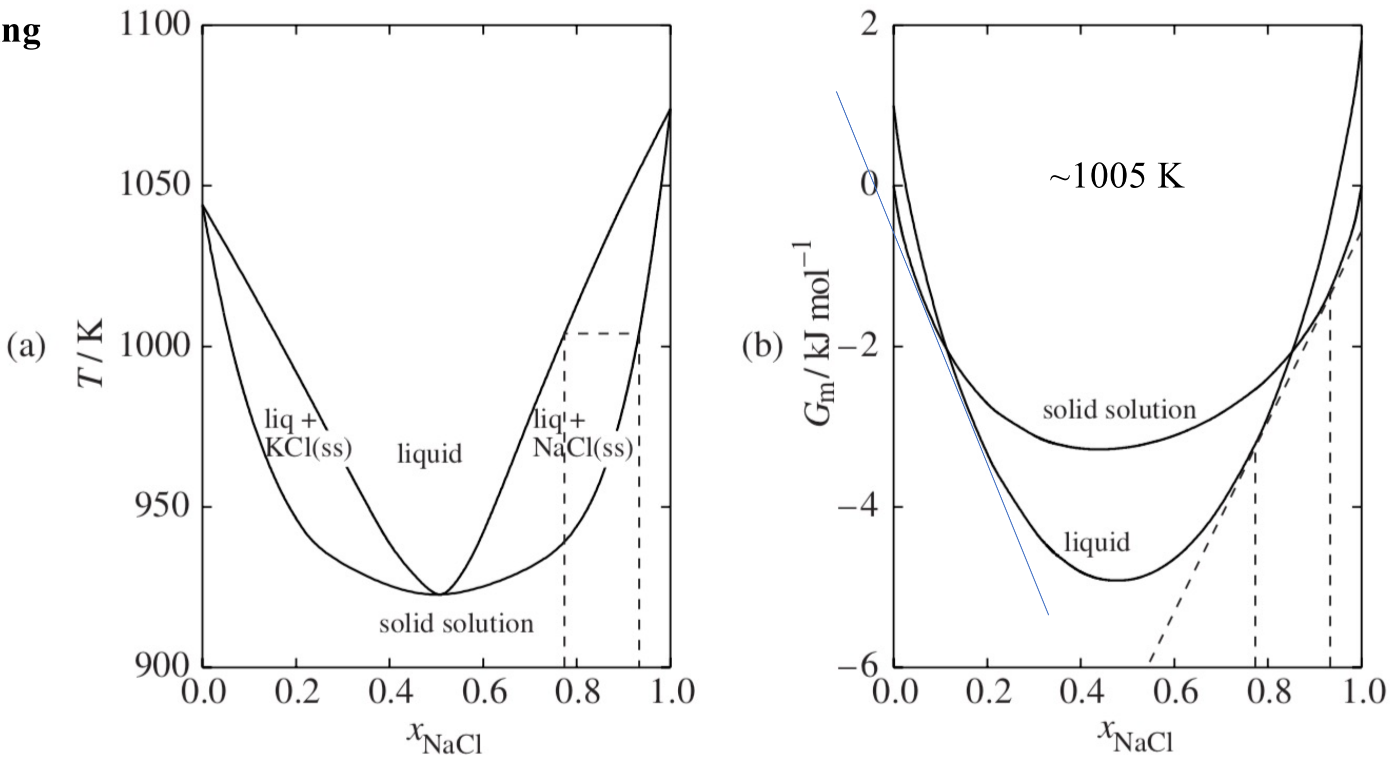
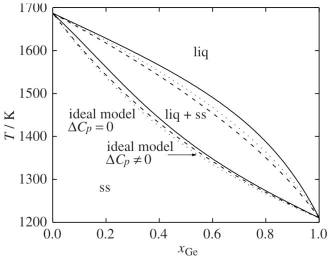


Figure 4.7 (a) Phase diagram of the system KCl–NaCl. (b) Gibbs energy curves for the solid and liquid solutions KCl–NaCl at 1002 K. Thermodynamic data are taken from reference [5].

Double crossing of solid/liquid free energy curves

Solid solution is flatter than ideal (Pos. deviation or destabilized)
Liquid is deeper than ideal (Neg. Deviation or stabilized)
Deviations are associated with minima in phase diagram



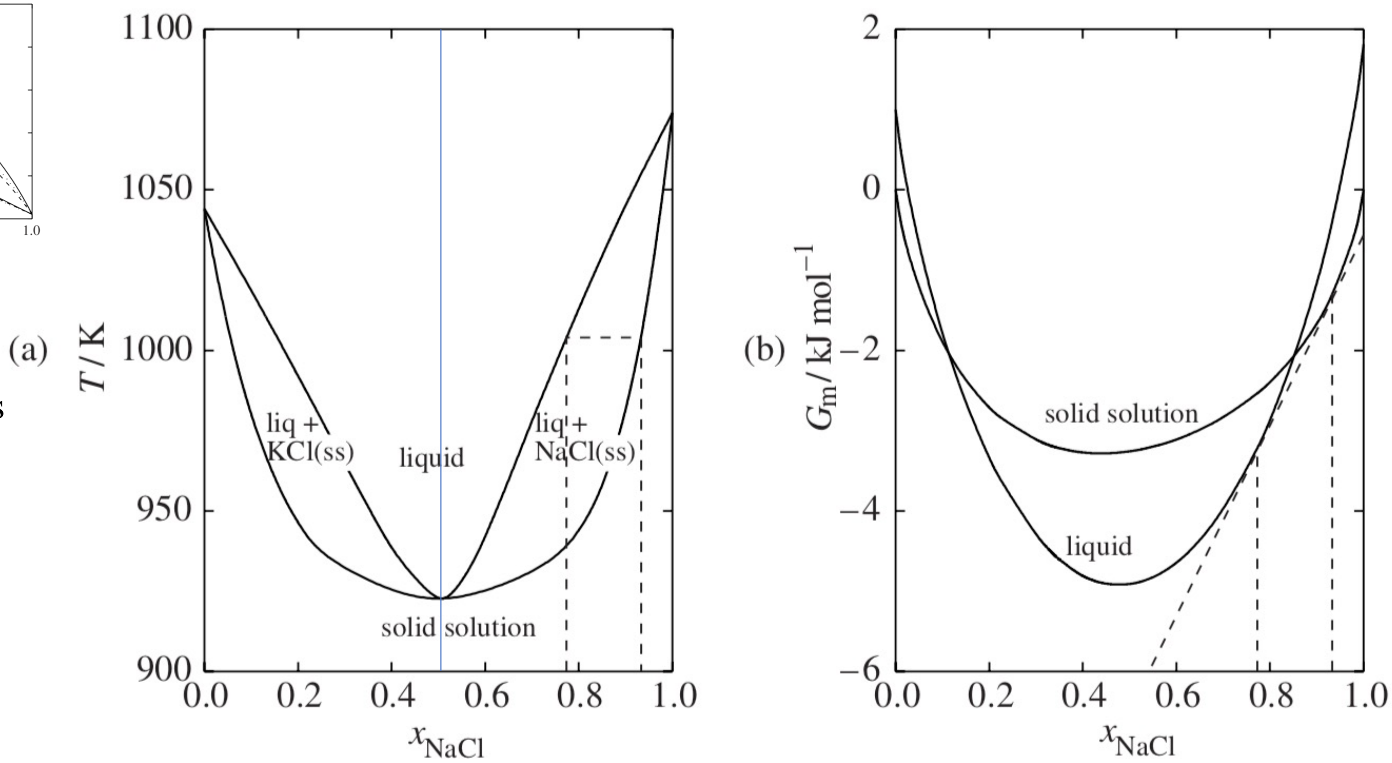
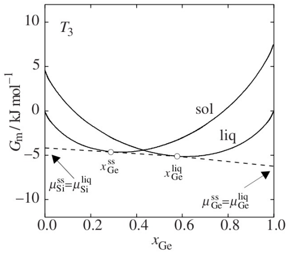


Figure 4.7 (a) Phase diagram of the system KCl–NaCl. (b) Gibbs energy curves for the solid and liquid solutions KCl–NaCl at 1002 K. Thermodynamic data are taken from reference [5].

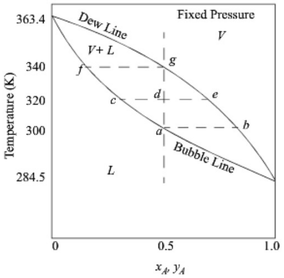


Phase diagram is split into two solid solutions by the **congruent melting point**

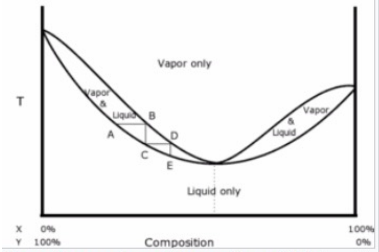
Solid solution is flatter than ideal (Pos. deviation or destabilized)
Liquid is deeper than ideal (Neg. Deviation or stabilized)
Deviations are associated with minima in phase diagram

Liquid/Vapor Equilibria

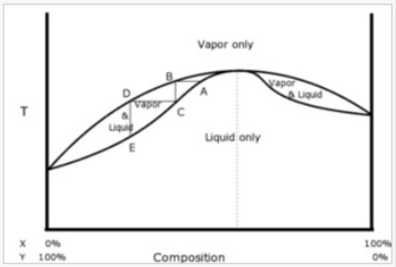
Ideal



Azeotrope

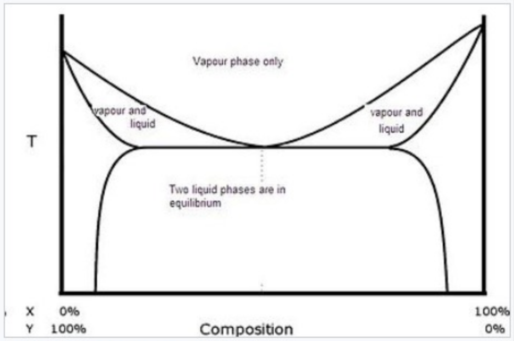


Phase diagram of a positive azeotrope. Vertical axis is temperature, horizontal axis is composition.



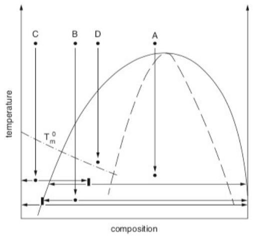
Phase diagram of a negative azeotrope. Vertical axis is temperature, horizontal axis is composition.

Heteroazeotrope



Phase diagram of a heteroazeotrope.

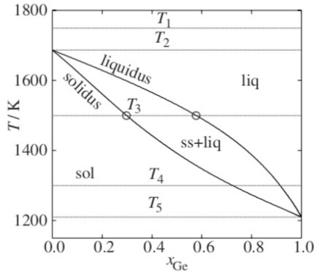
Liquid/Liquid Equilibria



Phase diagram is split into two phase diagrams with a special composition that acts as a pure component

Solid/Liquid Equilibria

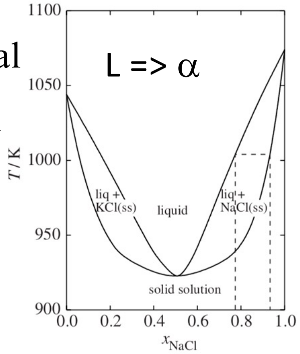
Ideal



L => α + L

Non-Ideal

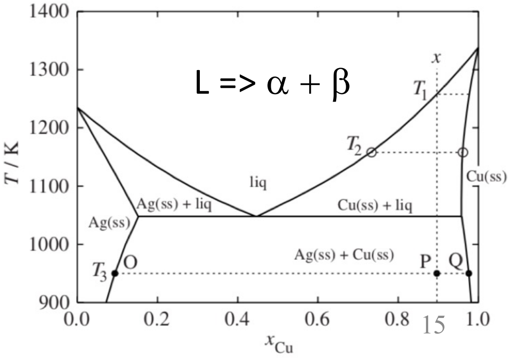
Congruent melting solid solution



L => α

Same crystallographic structure in solid solution phase

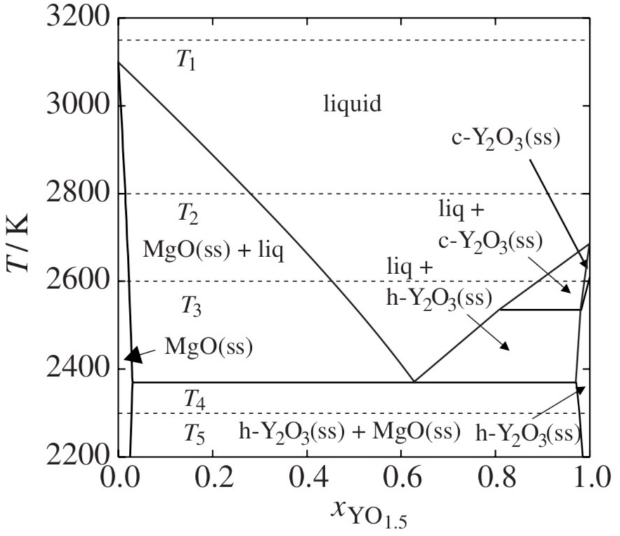
Eutectic

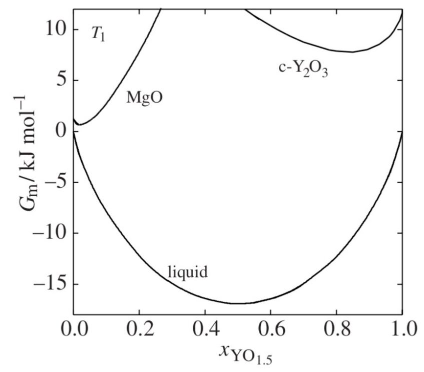


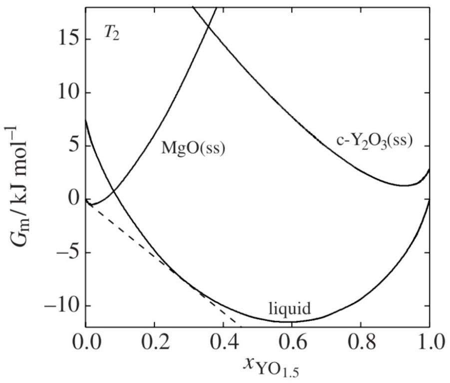
L => α + β

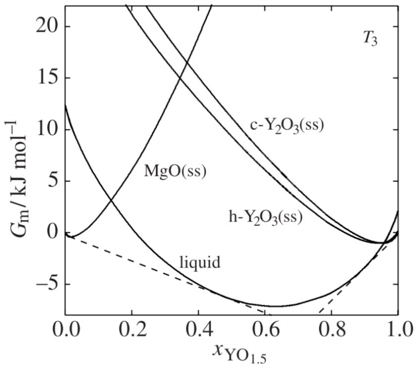
Different crystallographic structures in solid solution phases

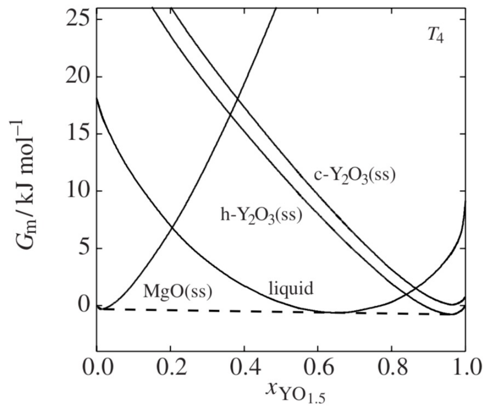
Eutectic Phase Diagram with Three Crystallographic Phases, Two Cubic and One Hexagonal

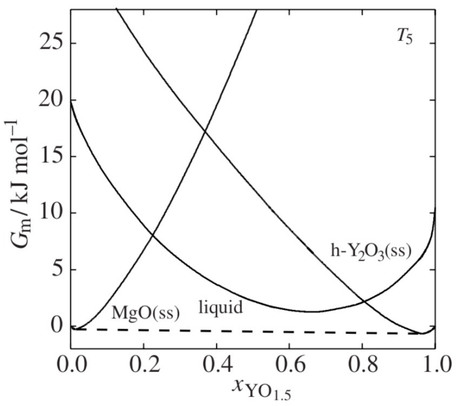












Regular Solution Modeling for Phase Diagrams

$$\ln\left(\frac{a_A^{liq}}{a_A^{ss}}\right) = \ln\left(\frac{x_A^{liq}\gamma_A^{liq}}{x_A^{ss}\gamma_A^{ss}}\right) = -\frac{\Delta\mu_A^{o(s\to l)}}{RT} \qquad \ln\left(\frac{a_B^{liq}}{a_B^{ss}}\right) = \ln\left(\frac{x_B^{liq}\gamma_B^{liq}}{x_B^{ss}\gamma_B^{ss}}\right) = -\frac{\Delta\mu_B^{o(s\to l)}}{RT}$$

$G^E/RT = x_A \ln \gamma_A + x_B \ln \gamma_B$ **Generic expression using activity coefficient**

$G^E/RT = \Omega\, x_A x_B$ **Hildebrand Regular Solution expression**

Two unknowns & Two equations:

We found that a solution of $\mathbf{RT \ln \gamma_A = \Omega x_B^2}$ and $\mathbf{RT \ln \gamma_B = \Omega x_A^2}$ worked

$$\ln(1-x_B^{liq}) + \frac{\Omega^{liq}}{RT}(x_B^{liq})^2 - \ln(1-x_B^{ss}) - \frac{\Omega^{ss}}{RT}(x_B^{ss})^2 = -\frac{\Delta\mu_A^{o(s\to l)}}{RT}$$

$$\ln x_B^{liq} + \frac{\Omega^{liq}}{RT}(1-x_B^{liq})^2 - \ln x_B^{ss} - \frac{\Omega^{ss}}{RT}(1-x_B^{ss})^2 = -\frac{\Delta\mu_B^{o(s\to l)}}{RT}$$

Two unknowns, x_B^{SS}, x_B^{liq} & Two equations

Solve numerically

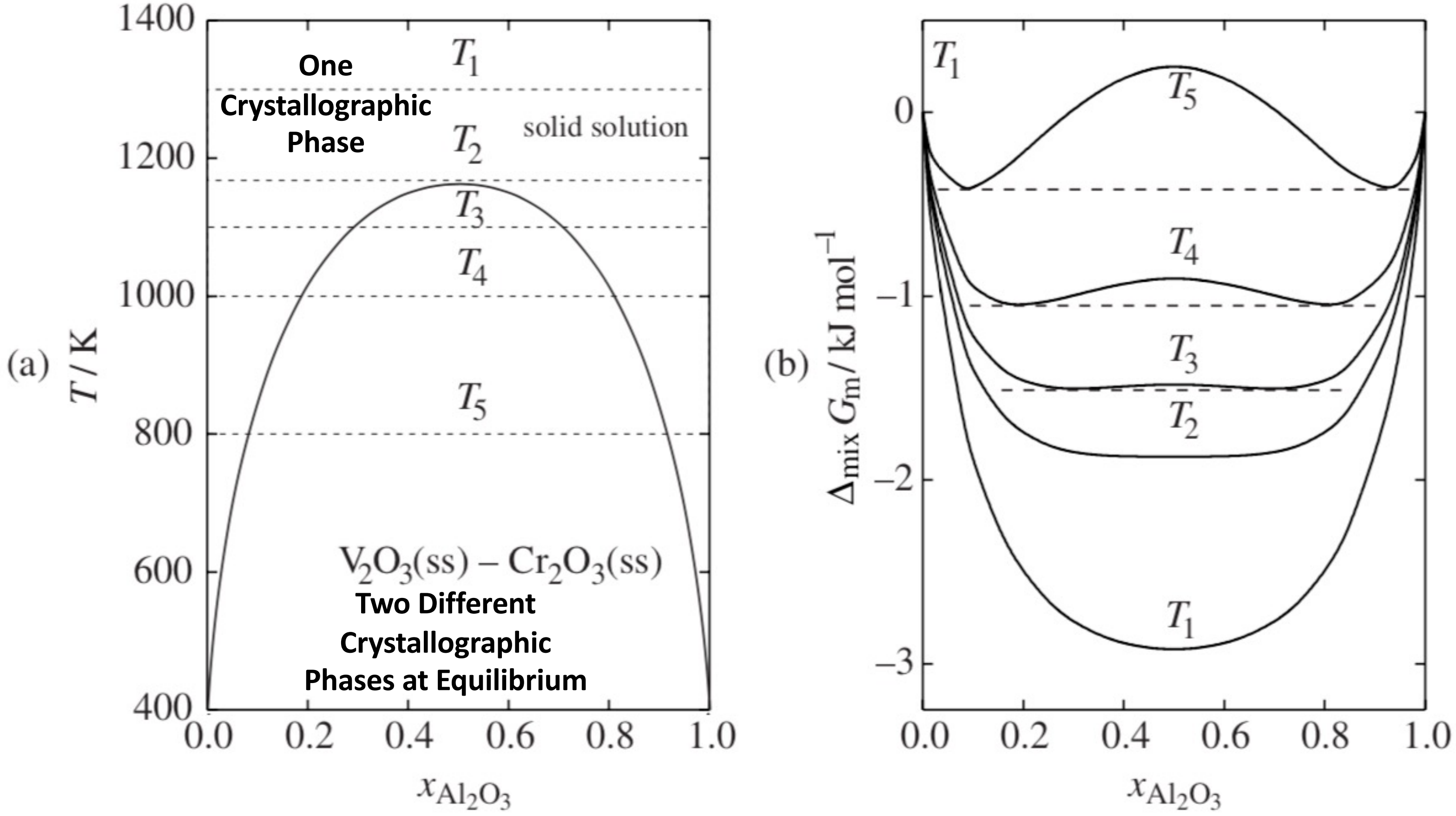
Generate Phase diagram since Δμ is a function of T

$$\Delta\mu_i^{o(s\to l)} = \Delta_{fus}H_i^o - T\Delta_{fus}S_i^o = \Delta_{fus}H_i^o\left(1-\frac{T}{T_{fus,i}}\right)$$

Positive Ω is necessary for phase separation

$$\Delta G_m = RT(x_A \ln(x_A) + x_B \ln(x_B)) + \Omega\, x_A x_B$$

Knowing 2 omegas and the temperatures and heats of fusion you can predict the phase diagram

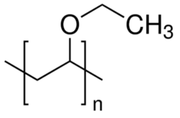


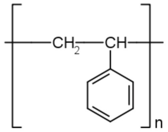
One Crystallographic Phase

Two Different Crystallographic Phases at Equilibrium

$\gamma \Rightarrow \alpha + \beta$

Figure 4.9 (a) Immiscibility gap of the binary solid solution V_2O_3–Cr_2O_3 as described by the regular solution model. (b) Gibbs energy of mixing curve of the solid solution at the temperatures marked in the phase diagram. Thermodynamic data are taken from reference [7].





Polyvinylmethyl Ether/Polystyrene (LCST Phase behavior)

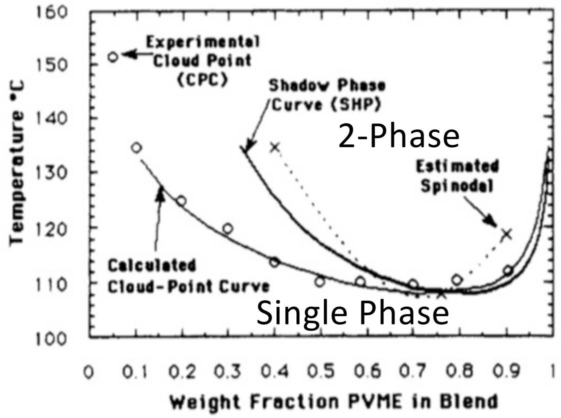


Figure 4. Flory–Huggins–Staverman fit to the CPC of the i89/120 blend.

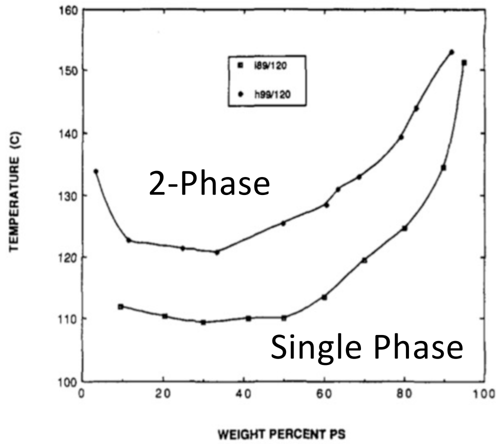


Figure 7. Cloud-point curves for i89/120 and h99/120 blends.

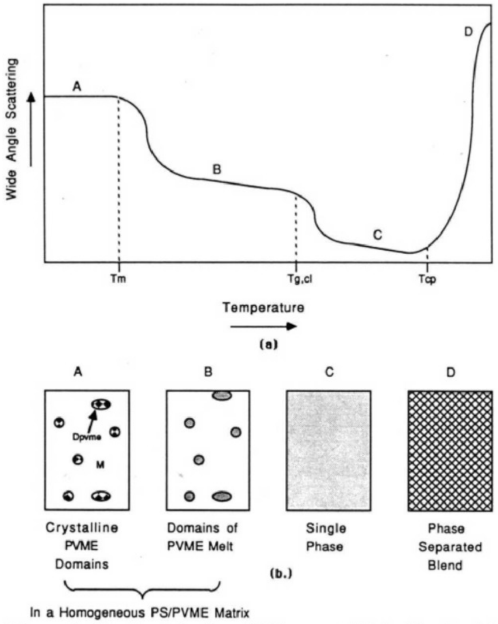


Figure 4. Clearing behavior of higher crystallinity blends. (a) Wide-angle scattering versus temperature. (b) Schematic of phase behavior.

$$\frac{\Delta G}{NRT} = \frac{\phi_1}{m_1}\ln\phi_1 + \sum\left(\frac{\phi_{2i}}{m_{2i}}\ln\phi_{2i}\right) + g\phi_1\phi_2$$

$$g = a + \frac{(b_0 + b_1/T)}{(1 - c\phi_2)}$$

$\Delta G_m = RT(x_A \ln(x_A) + x_B \ln(x_B)) + \Omega\, x_A x_B$

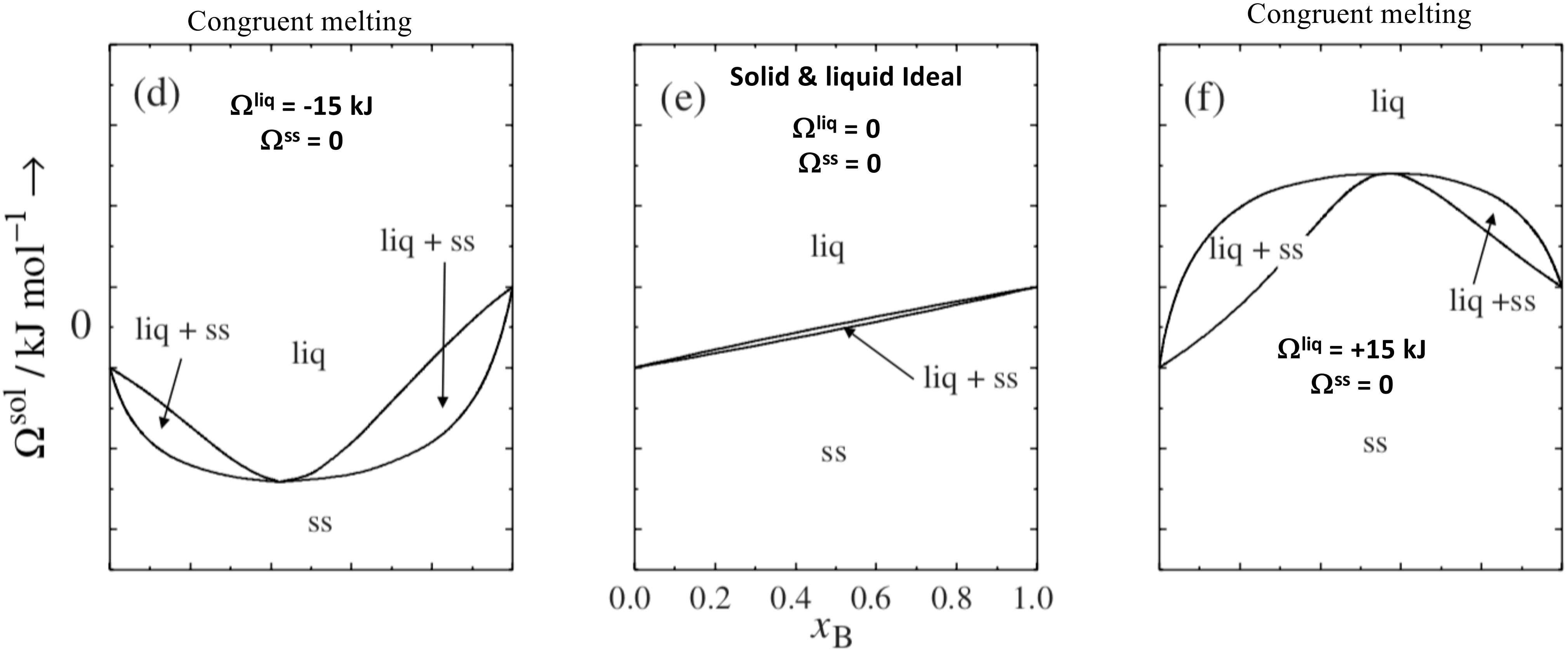
Ω must have a temperature dependence for UCST

$\Omega = A + B/T$ so that it gets smaller with increasing temperature this is a non-combinatorial entropy i.e. ordering on mixing

$$\ln(1-x_{\mathrm{B}}^{\mathrm{liq}}) + \frac{\Omega^{\mathrm{liq}}}{RT}(x_{\mathrm{B}}^{\mathrm{liq}})^2 - \ln(1-x_{\mathrm{B}}^{\mathrm{ss}}) - \frac{\Omega^{\mathrm{ss}}}{RT}(x_{\mathrm{B}}^{\mathrm{ss}})^2 = -\frac{\Delta\mu_{\mathrm{A}}^{\mathrm{o}(s\to \mathrm{l})}}{RT}$$

$$\ln x_{\mathrm{B}}^{\mathrm{liq}} + \frac{\Omega^{\mathrm{liq}}}{RT}(1-x_{\mathrm{B}}^{\mathrm{liq}})^2 - \ln x_{\mathrm{B}}^{\mathrm{ss}} - \frac{\Omega^{\mathrm{ss}}}{RT}(1-x_{\mathrm{B}}^{\mathrm{ss}})^2 = -\frac{\Delta\mu_{\mathrm{B}}^{\mathrm{o}(s\to \mathrm{l})}}{RT}$$

Pure A and B melt at 800 and 1000 K with the entropy of fusion of both compounds set to 10 J K^{-1} mol^{-1} typical for metals. The interaction coefficients of the two solutions have been varied systematically in order to generate nine different phase diagrams.



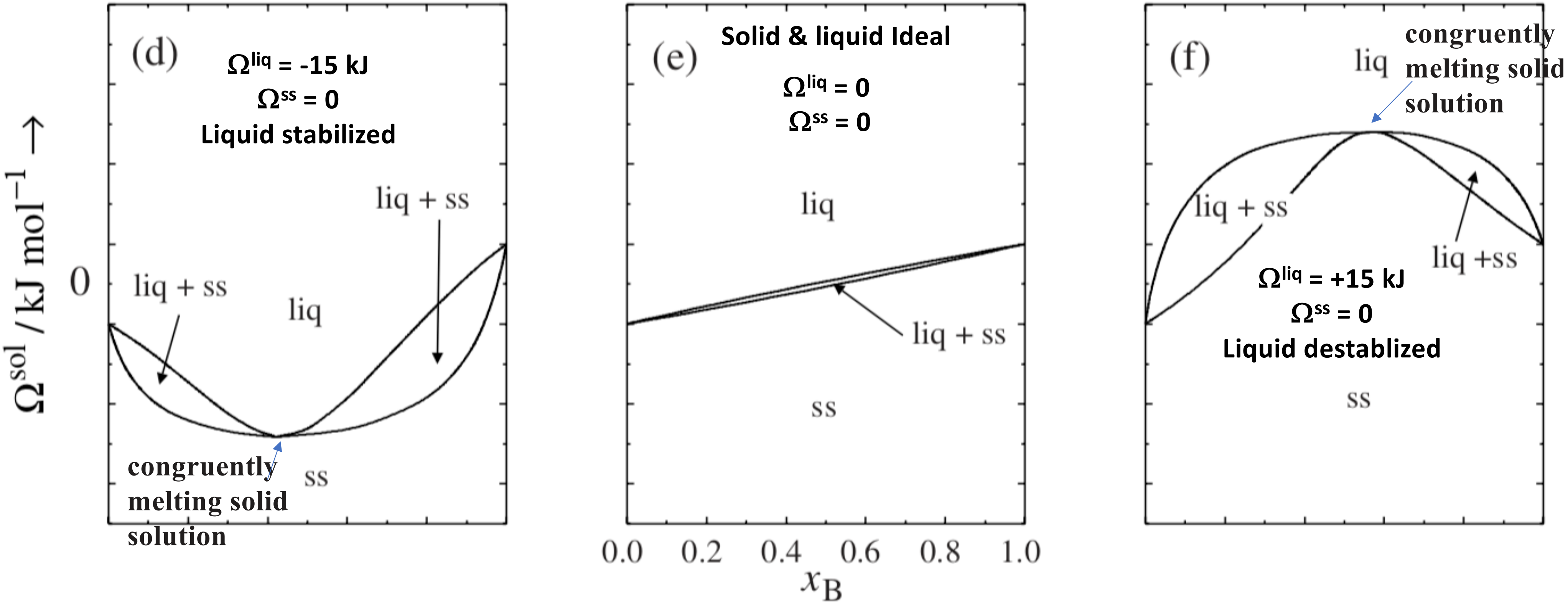
Congruent melting

Congruent melting

$$\ln(1-x_{\mathrm{B}}^{\mathrm{liq}}) + \frac{\Omega^{\mathrm{liq}}}{RT}(x_{\mathrm{B}}^{\mathrm{liq}})^2 - \ln(1-x_{\mathrm{B}}^{\mathrm{ss}}) - \frac{\Omega^{\mathrm{ss}}}{RT}(x_{\mathrm{B}}^{\mathrm{ss}})^2 = -\frac{\Delta\mu_{\mathrm{A}}^{\mathrm{o}(s\to \mathrm{l})}}{RT}$$

$$\ln x_{\mathrm{B}}^{\mathrm{liq}} + \frac{\Omega^{\mathrm{liq}}}{RT}(1-x_{\mathrm{B}}^{\mathrm{liq}})^2 - \ln x_{\mathrm{B}}^{\mathrm{ss}} - \frac{\Omega^{\mathrm{ss}}}{RT}(1-x_{\mathrm{B}}^{\mathrm{ss}})^2 = -\frac{\Delta\mu_{\mathrm{B}}^{\mathrm{o}(s\to \mathrm{l})}}{RT}$$

Pure A and B melt at 800 and 1000 K with the entropy of fusion of both compounds set to 10 J K^{-1} mol^{-1} typical for metals. The interaction coefficients of the two solutions have been varied systematically in order to generate nine different phase diagrams.



Ω^{liq} = -15 kJ
Ω^{ss} = 0
Liquid stabilized

congruently melting solid solution

Solid & liquid Ideal

Ω^{liq} = 0
Ω^{ss} = 0

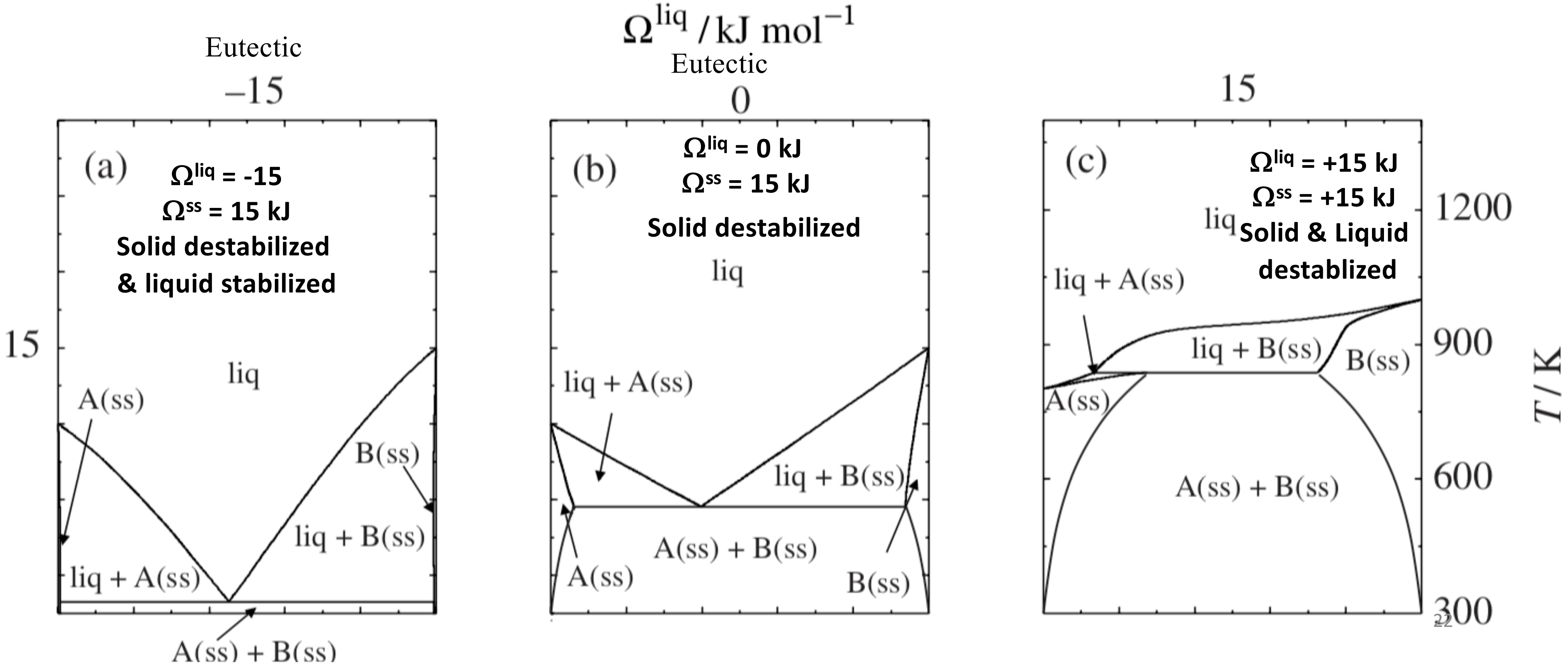
congruently melting solid solution

Ω^{liq} = +15 kJ
Ω^{ss} = 0
Liquid destablized

$$\ln(1-x_{\mathrm{B}}^{\mathrm{liq}}) + \frac{\Omega^{\mathrm{liq}}}{RT}(x_{\mathrm{B}}^{\mathrm{liq}})^2 - \ln(1-x_{\mathrm{B}}^{\mathrm{ss}}) - \frac{\Omega^{\mathrm{ss}}}{RT}(x_{\mathrm{B}}^{\mathrm{ss}})^2 = -\frac{\Delta\mu_{\mathrm{A}}^{\mathrm{o}(s\to\mathrm{l})}}{RT}$$

$$\ln x_{\mathrm{B}}^{\mathrm{liq}} + \frac{\Omega^{\mathrm{liq}}}{RT}(1-x_{\mathrm{B}}^{\mathrm{liq}})^2 - \ln x_{\mathrm{B}}^{\mathrm{ss}} - \frac{\Omega^{\mathrm{ss}}}{RT}(1-x_{\mathrm{B}}^{\mathrm{ss}})^2 = -\frac{\Delta\mu_{\mathrm{B}}^{\mathrm{o}(s\to\mathrm{l})}}{RT}$$

Pure A and B melt at 800 and 1000 K with the entropy of fusion of both compounds set to 10 J K^{-1} mol^{-1} typical for metals. The interaction coefficients of the two solutions have been varied systematically in order to generate nine different phase diagrams.



Ω^{liq} = -15
Ω^{ss} = 15 kJ
Solid destabilized
& liquid stabilized

Ω^{liq} = 0 kJ
Ω^{ss} = 15 kJ
Solid destabilized

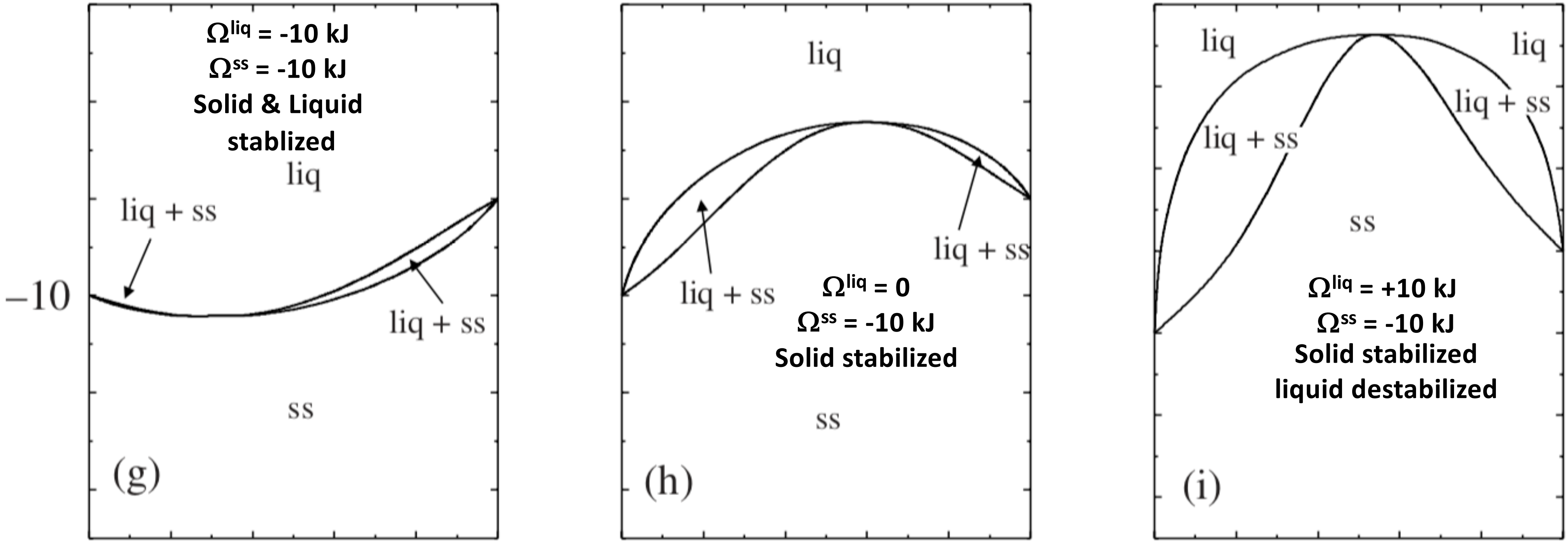
Ω^{liq} = +15 kJ
Ω^{ss} = +15 kJ
Solid & Liquid
destablized

$$\ln(1-x_{\mathrm{B}}^{\mathrm{liq}}) + \frac{\Omega^{\mathrm{liq}}}{RT}(x_{\mathrm{B}}^{\mathrm{liq}})^2 - \ln(1-x_{\mathrm{B}}^{\mathrm{ss}}) - \frac{\Omega^{\mathrm{ss}}}{RT}(x_{\mathrm{B}}^{\mathrm{ss}})^2 = -\frac{\Delta\mu_{\mathrm{A}}^{\mathrm{o}(s\to \mathrm{l})}}{RT}$$

$$\ln x_{\mathrm{B}}^{\mathrm{liq}} + \frac{\Omega^{\mathrm{liq}}}{RT}(1-x_{\mathrm{B}}^{\mathrm{liq}})^2 - \ln x_{\mathrm{B}}^{\mathrm{ss}} - \frac{\Omega^{\mathrm{ss}}}{RT}(1-x_{\mathrm{B}}^{\mathrm{ss}})^2 = -\frac{\Delta\mu_{\mathrm{B}}^{\mathrm{o}(s\to \mathrm{l})}}{RT}$$

Pure A and B melt at 800 and 1000 K with the entropy of fusion of both compounds set to 10 J K^{-1} mol^{-1} typical for metals. The interaction coefficients of the two solutions have been varied systematically in order to generate nine different phase diagrams.

Congruent melting



Ω^{liq} = -10 kJ
Ω^{ss} = -10 kJ
Solid & Liquid stablized

Ω^{liq} = 0
Ω^{ss} = -10 kJ
Solid stabilized

Ω^{liq} = +10 kJ
Ω^{ss} = -10 kJ
Solid stabilized
liquid destabilized

$$\ln(1-x_{\mathrm{B}}^{\mathrm{liq}}) + \frac{\Omega^{\mathrm{liq}}}{RT}(x_{\mathrm{B}}^{\mathrm{liq}})^2 - \ln(1-x_{\mathrm{B}}^{\mathrm{ss}}) - \frac{\Omega^{\mathrm{ss}}}{RT}(x_{\mathrm{B}}^{\mathrm{ss}})^2 = -\frac{\Delta\mu_{\mathrm{A}}^{\mathrm{o}(s\to l)}}{RT}$$

$$\ln x_{\mathrm{B}}^{\mathrm{liq}} + \frac{\Omega^{\mathrm{liq}}}{RT}(1-x_{\mathrm{B}}^{\mathrm{liq}})^2 - \ln x_{\mathrm{B}}^{\mathrm{ss}} - \frac{\Omega^{\mathrm{ss}}}{RT}(1-x_{\mathrm{B}}^{\mathrm{ss}})^2 = -\frac{\Delta\mu_{\mathrm{B}}^{\mathrm{o}(s\to l)}}{RT}$$

If it is assumed that

$$a_{\mathrm{A}}^{\mathrm{ss}} = a_{\mathrm{B}}^{\mathrm{ss}} = 1$$

$$\ln x_{\mathrm{A}}^{\mathrm{liq}} + \frac{\Omega^{\mathrm{liq}}}{RT}(x_{\mathrm{B}}^{\mathrm{liq}})^2 = -\frac{\Delta_{\mathrm{fus}} H_{\mathrm{A}}^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus,A}}}\right)$$

$$\ln x_{\mathrm{B}}^{\mathrm{liq}} + \frac{\Omega^{\mathrm{liq}}}{RT}(x_{\mathrm{A}}^{\mathrm{liq}})^2 = -\frac{\Delta_{\mathrm{fus}} H_{\mathrm{B}}^{\mathrm{o}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus,B}}}\right)$$

Then you need only one Ω
(The solid state doesn't mix)

Regular solution model has only a few parameters

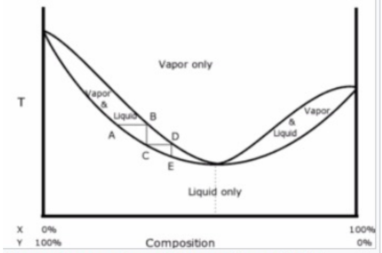
This means that experimentally you need only determine a few points of equilibrium composition to predict the entire phase diagram.

Invariant Phase Equilibria

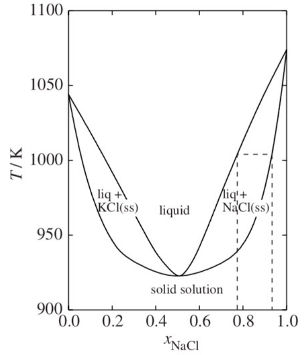
$F = C - P + 2$ for binary $F = 4 - P$
composition diagram holds one DOF constant

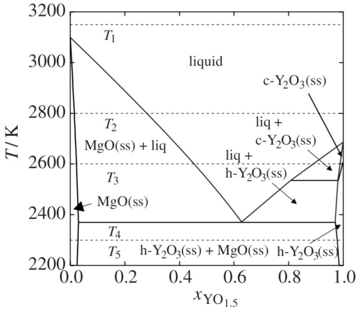
There are three degrees of freedom for a binary system. If three phases meet the conditions are invariant. This means that the phase composition acts like a pure component. An azeotrope or congruent melting point splits the phase diagram into two phase diagrams. There are several types of "**invariant reactions**".

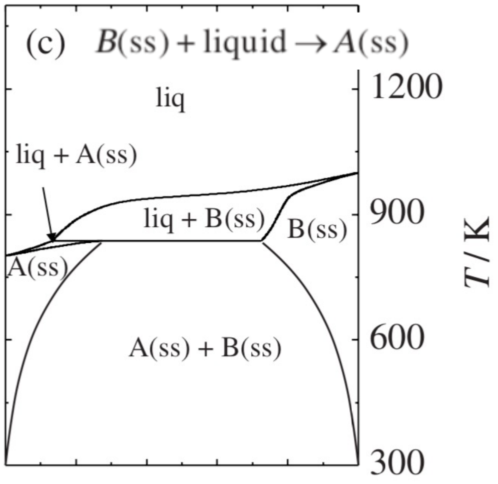
Azeotrope V => L Composition fixed, $x_i = y_i$
Congruent melting point L => S Composition fixed, $x_i^s = x_i^l$
Hex to Cubic Phase transition of Y_2O_3 Comp. fixed
Peritectic Reaction
    Peritectoid = 3 solid phases
Eutectic Reaction
    Eutectoid = liquid & 2 solid phases
Monotectic Reaction $L_1 => S + L_2$
Syntectic Reaction $L_1 + L_2 => S$

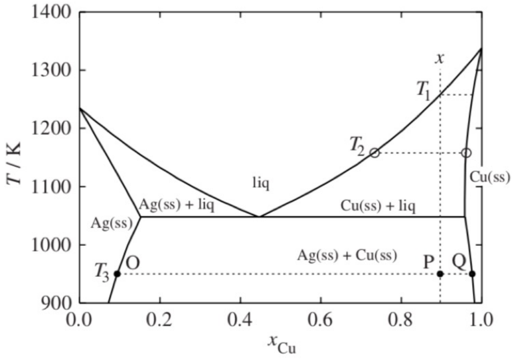


Phase diagram of a positive azeotrope. Vertical axis is temperature, horizontal axis is composition.









Stoichiometric Intermediate Phase, $CaZrO_3$

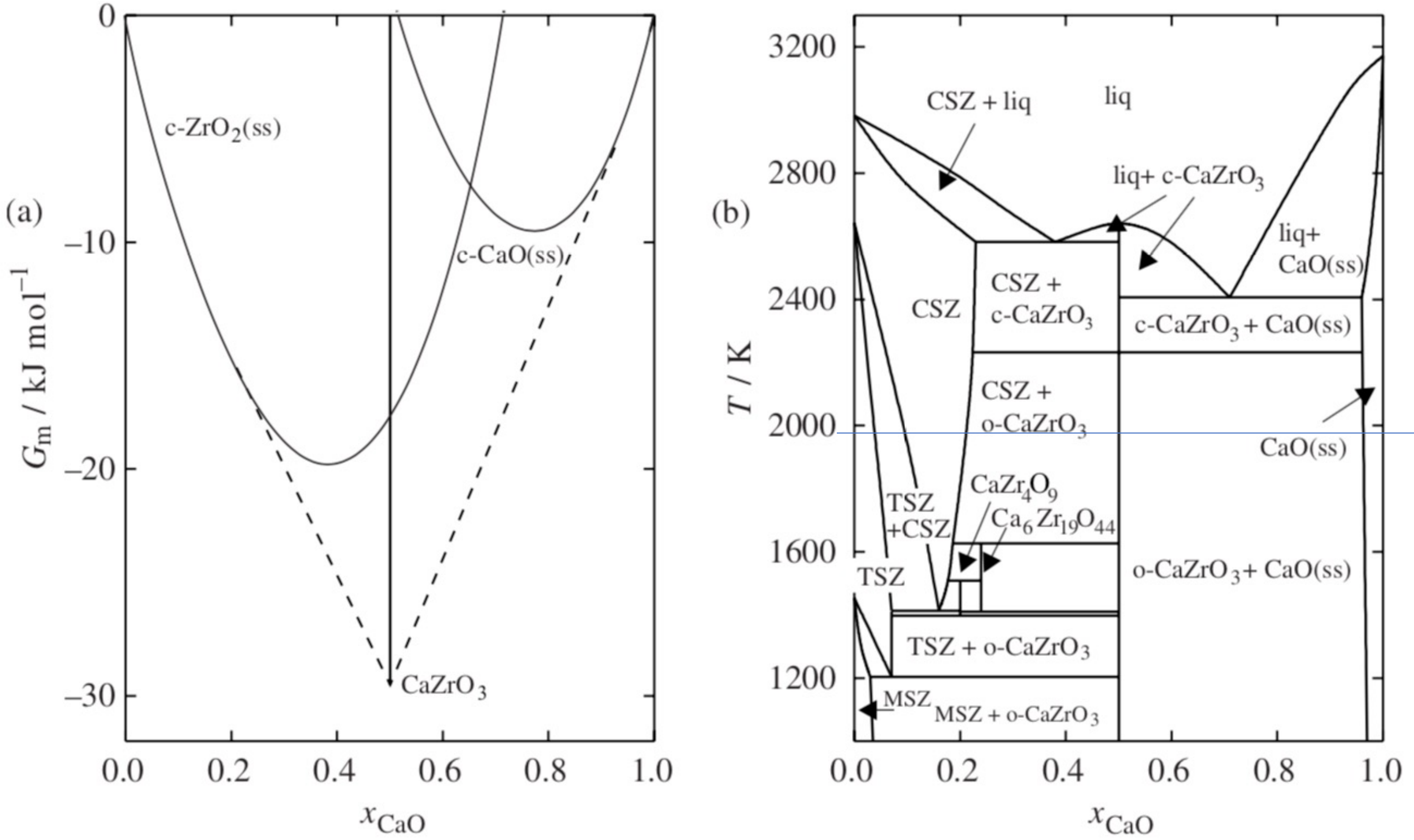
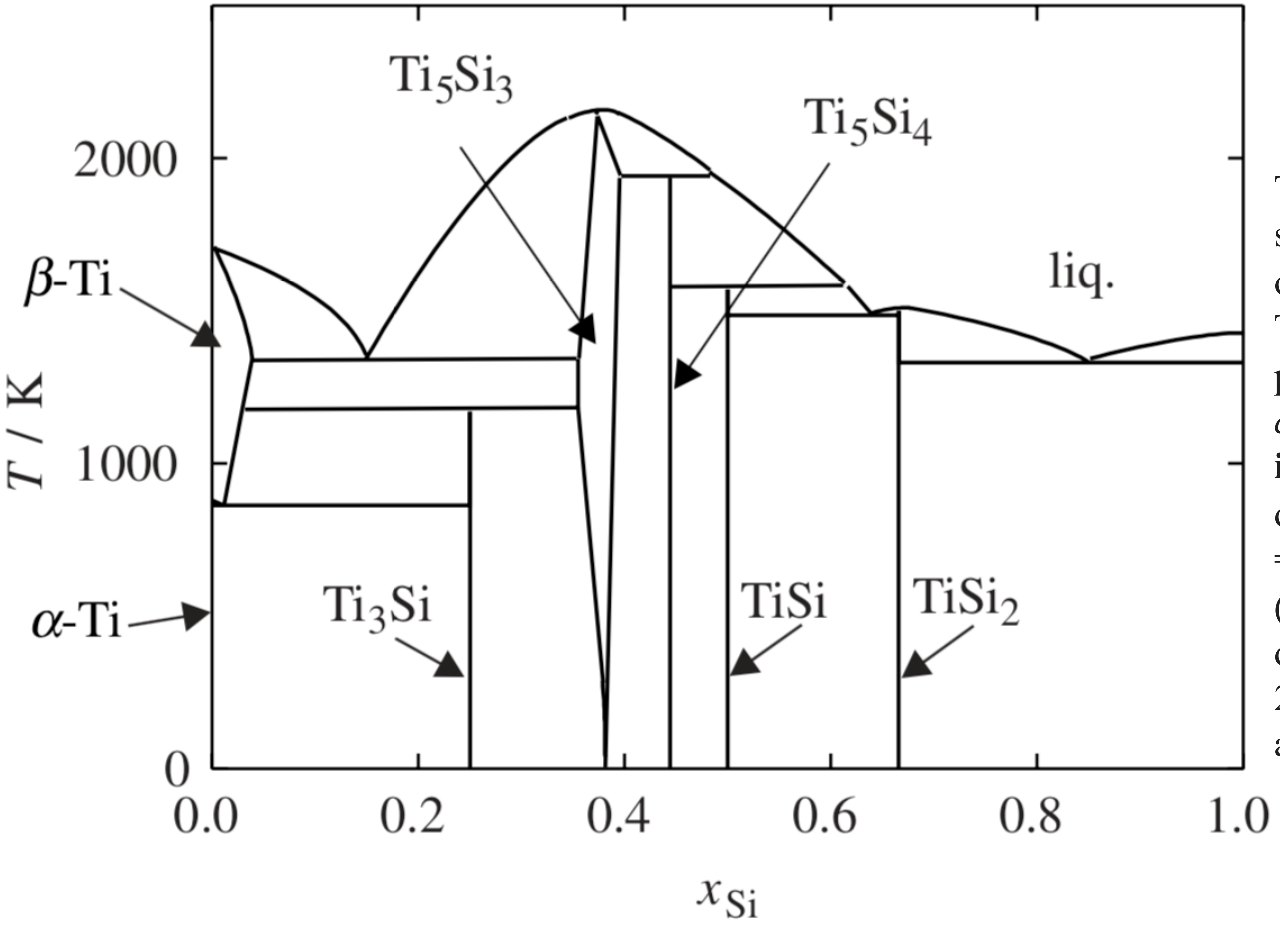


Figure 4.12 (a) Gibbs energy representation of the phases in the system ZrO_2–CaO at 1900 K. $\mu^{o}_{CaO} = \mu^{o}_{ZrO_2} = 0$. TSZ is not included for clarity. (b) Calculated phase diagram of the system ZrO_2–CaO. Thermodynamic data are taken from reference [9].

Stoichiometric Intermediate Phase

Only stable at one exact composition where it has a very low free energy

Intermediate Phases



The intermediate phases in the system Si–Ti display also a variety of other features. While $TiSi_2$ and Ti_5Si_3 are **congruently melting** phases (*melt and crystal have same composition*), Ti_5Si_4 and TiSi **melt incongruently**. Finally, Ti_3Si decomposes to β-Ti and Ti_5Si_3 at $T = 1170$ K, in a **peritectoid reaction** (*3 solid phases*) while β-Ti decomposes **eutectoidally** (L and 2S) on cooling forming α-Ti + Ti_3Si at $T = 862$ K.

Figure 4.13 Phase diagram of the system Si–Ti [10].

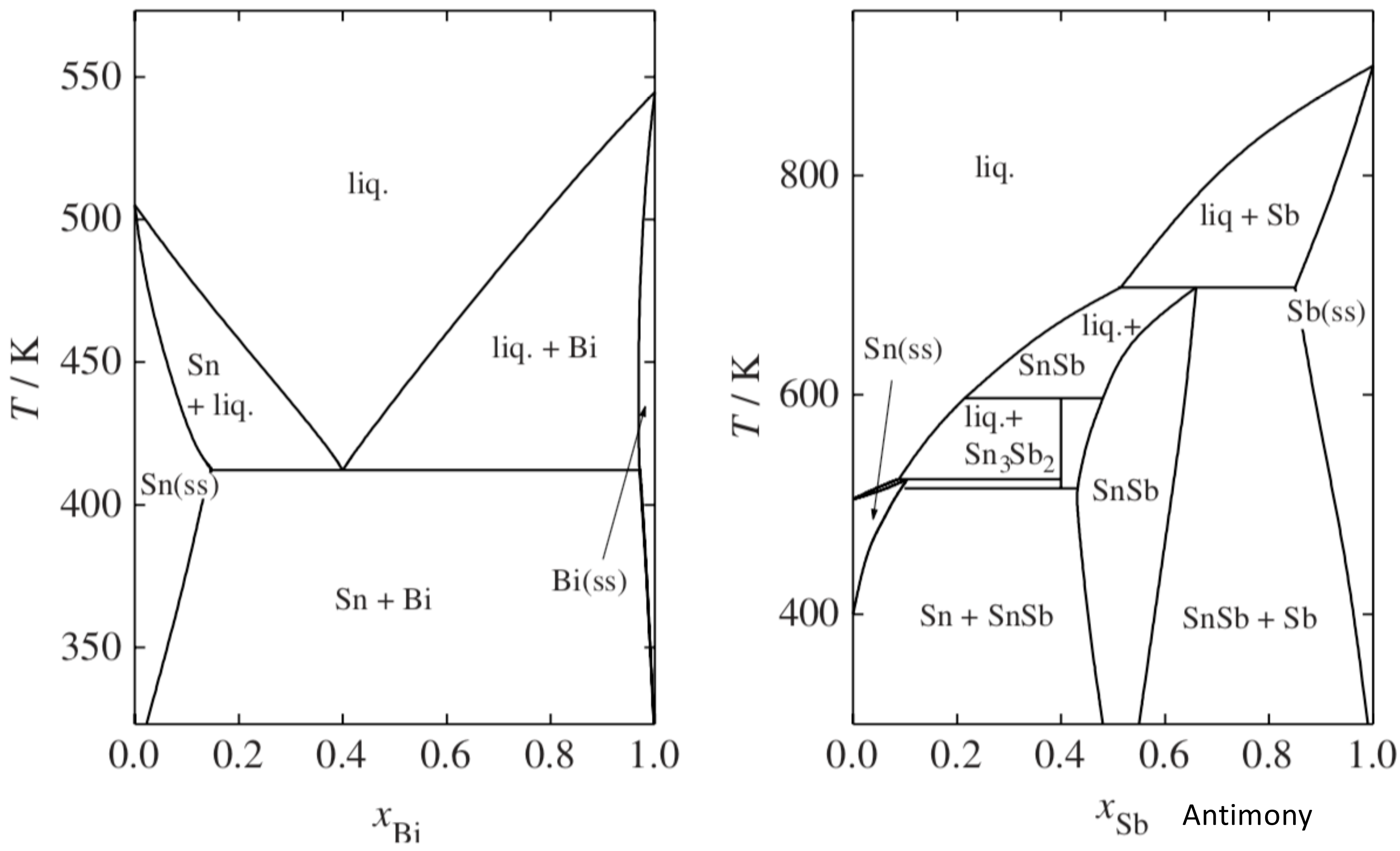
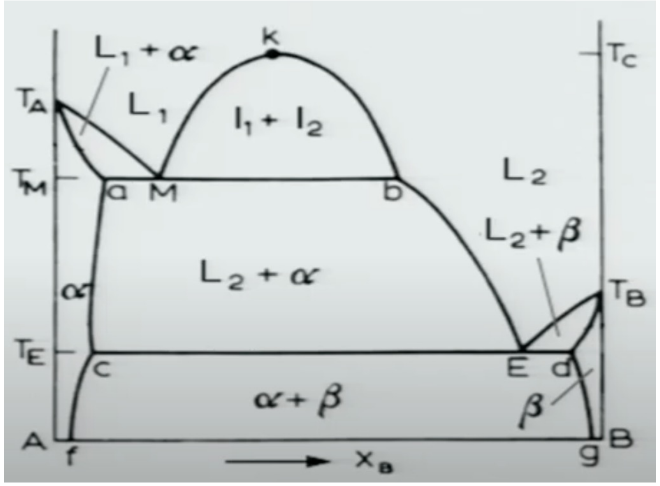
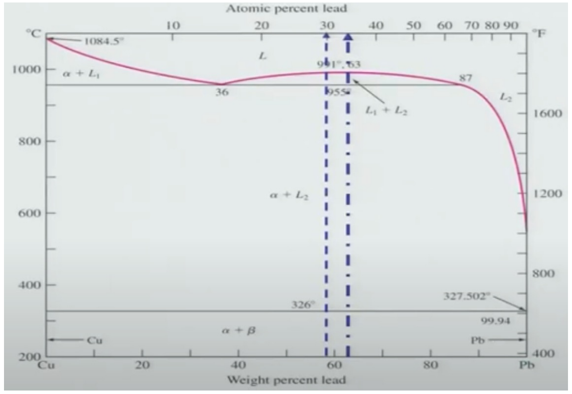


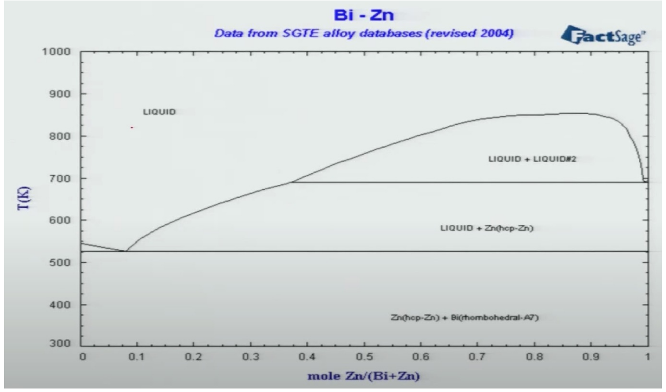
Figure 4.14 Phase diagrams of the systems (a) Sn–Bi [13] and (b) Sn–Sb [14]. Reprinted from [12]. Copyright (1999), with permission from Elsevier.

Monotectic Phase Diagram
$L_1 \Rightarrow L_2 + \alpha$





Self-lubricating bearings



Nano-structure Bi

Freezing Point Depression

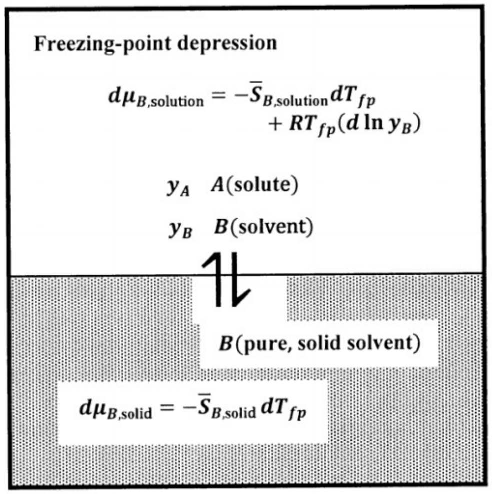


Figure 8. Schematic description of freezing-point depression.

Pure solid in equilibrium with a binary solution following Henry's Law

$d\mu_{B,Solid} = V^m_{B,Solid}\, dP - S^m_{B,Solid}\, dT + RT\, d(\ln a_{B,Solid})$

Isobaric, pure component B so $\ln a_{B,Solid} = 0$

$d\mu_{B,Solid} = - S^m_{B,Solid}\, dT_{fp}$

Binary solution following Henry's Law

$d\mu_{B,Solution} = - S^m_{B,Solultion}\, dT_{fp} + RT_{fp}\, d(\ln y_{B,Solution})_{P,T}$

For small x: $e^{-x} = 1 - x + \ldots$ or $\ln(1-x) = -x$

So, for small $y_{B,Solution}$: $\ln y_{B,Solution} \sim -y_{A,Solution}$

So, if $d\mu_{B,Solid} = d\mu_{B,Solution}$

$S^m_{B,Solid}\, dT_{fp} = S^m_{B,Solution}\, dT_{fp} + RT_{fp}\, dy_{A,Solution}$

$dy_{A,Solution} = (S^m_{B,Solid} - S^m_{B,Solution})/(RT_{fp})\, dT_{fp} \sim -\Delta S^m_B/(RT_{fp})\, dT_{fp} = -\Delta H^m_B/(RT_F)\, (dT_{fp})/T_{fp}$

$y_{A,Solution} = -\Delta H^m_B/(RT_F)\, \ln(T_{fp}/T_F)$ For small x: $\ln(x) = x - 1$

$y_{A,Solution} = -\Delta H^m_B/(RT_F)\, (T_{fp}/T_F - 1) = -\Delta H^m_B/(RT^2_F)\, \Delta T$

$T_{fp} = T_F - y_{A,Solution} RT^2_F/\Delta H^m_B$

-S U V
H A
-p G T

$dG = Vdp - SdT$

$dG = -SdT + Vdp$
Isothermal and Ideal Gas
$dG = RTdp/p$
$G = RT \ln(p/p_0) = RT \ln(a)$
$dG = RT\, d(\ln(a))$
For solution
$dG = RT\, d(\ln(x/x_0)) = RT\, d(\ln(x))$

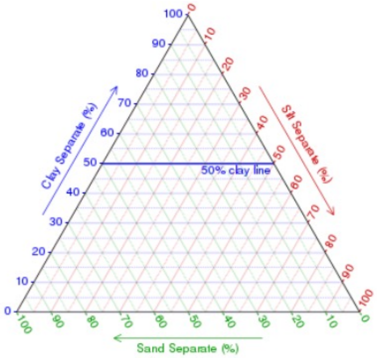
$$\Delta T = -RT^2_F y_{A,Solution} / \Delta H^m_B$$

$$\Delta T = T - T_{\mathrm{fus,A}} = -\frac{x_{\mathrm{B}} R T_{\mathrm{fus,A}}}{\Delta_{\mathrm{fus}} S^{\mathrm{o}}_{\mathrm{A}}} \left[\frac{1}{F - K} \right]$$

F is the fraction of the sample melted at ΔT departure from $T_{\mathrm{fus,A}}$

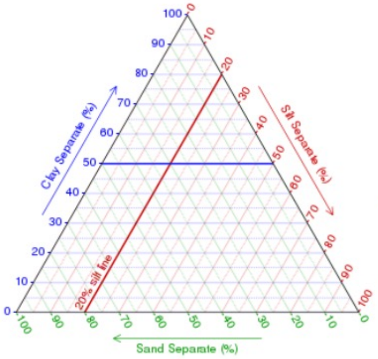
$$K = \frac{\gamma_{\mathrm{B}}^{\infty,\mathrm{liq}}}{\gamma_{\mathrm{B}}^{\infty,\mathrm{liq}} - \gamma_{\mathrm{B}}^{\infty,\mathrm{ss}}}$$

Ternary Phase Diagram, x_A, x_B, x_C

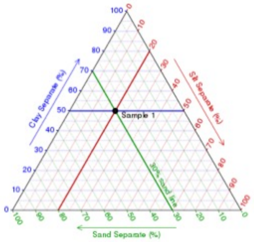


Plotting Sample 1 (1): Find the 50% clay line

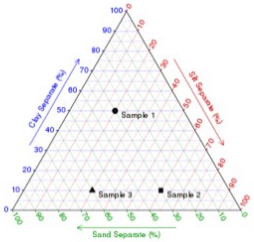
Go clockwise
0 at start 1 at corner
Phase point is where parallel lines meet
Plot is isothermal, isobaric, isochoric
$x_A + x_B + x_C = 1$
This can be read if the plot has a grid



Plotting Sample 1 (2): Find the 20% silt line

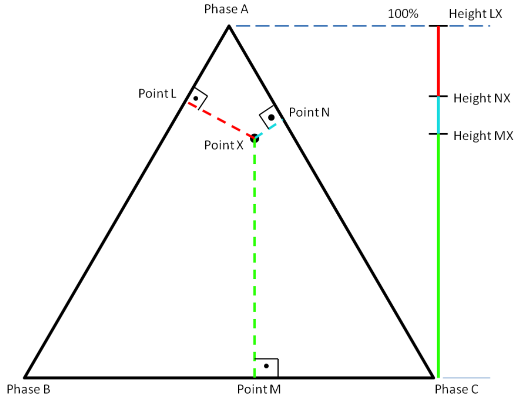


Plotting Sample 1 (3): The intersect coincides with the 30% sand line, as it is mathematically dependent on the first two

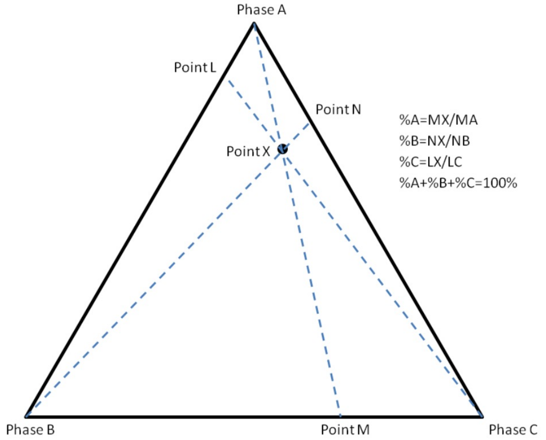


Plotting all the samples

With no grid you can get the composition
From the normals



You can also use intersection lines to get the composition



%A=MX/MA
%B=NX/NB
%C=LX/LC
%A+%B+%C=100%

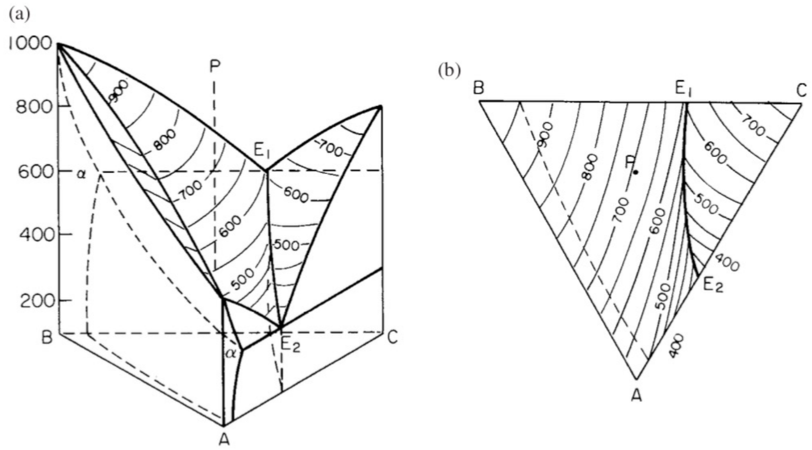


Figure 4.16 (a) Triangular prism phase diagram for a ternary system A–B–C with the equilateral triangular base giving composition. Temperature is given along the vertical axis [17]. (b) Projection of the liquidus surface onto the ternary composition triangle. The bold line is the intersection between the primary crystallization fields of C and the solid solution α. The dashed line represents the extension of the solid solution α. Reprinted with permission of The American Ceramic Society, www.ceramics.org. Copyright [1984]. All rights reserved.

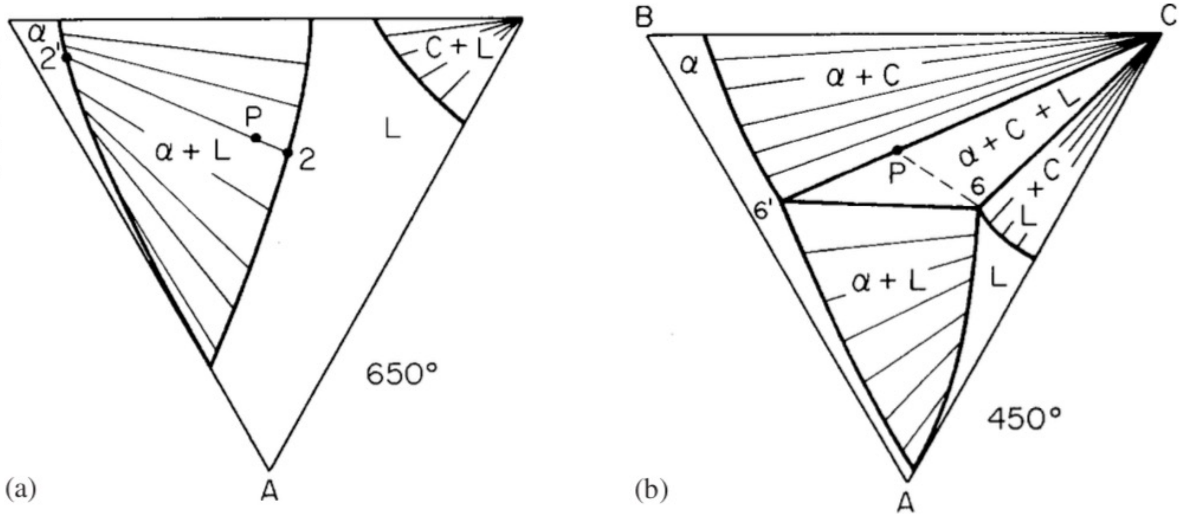
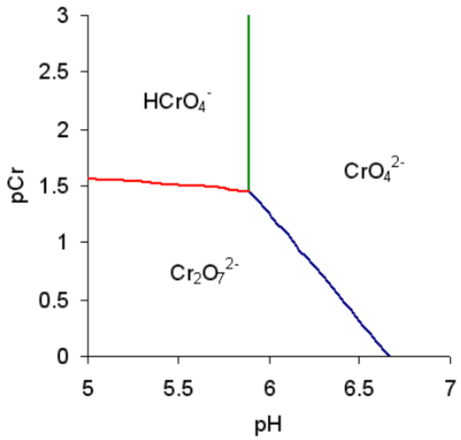


Figure 4.17 Isothermal sections of the ternary phase diagram A–B–C shown in Figure 4.16 at (a) 650 °C and (b) 450 °C [17]. Here L denotes liq. Reprinted with permission of The American Ceramic Society, www.ceramics.org. Copyright [1984]. All rights reserved.

Predominance Diagram (Which species is dominant)

pH = -log [H$^+$]
pCr = -log [Cr]



$$\overbrace{\mathrm{CrO_4^{2-}}}^{chromate} + \mathrm{H^+} \rightleftharpoons \mathrm{HCrO_4^-}; \qquad K_1 = \frac{[\mathrm{HCrO_4^-}]}{[\mathrm{CrO_4^{2-}}][\mathrm{H^+}]} \qquad \textbf{(1)}$$

$$2\,\mathrm{HCrO_4^-} \rightleftharpoons \underbrace{\mathrm{Cr_2O_7^{2-}}}_{dichromate} + \mathrm{H_2O}; \qquad K_D = \frac{[\mathrm{Cr_2O_7^{2-}}]}{[\mathrm{HCrO_4^-}]^2} \qquad \textbf{(2)}$$

$$2\,\mathrm{H^+} + 2\,\mathrm{CrO_4^{2-}} \rightleftharpoons \mathrm{Cr_2O_7^{2-}} + \mathrm{H_2O}; \qquad \beta_2 = \frac{[\mathrm{Cr_2O_7^{2-}}]}{[\mathrm{H^+}]^2[\mathrm{CrO_4^{2-}}]^2}; \qquad \beta_2 = K_1^2 K_\mathrm{D} \qquad \textbf{(3)}$$

Green line

Chromate and hydrogen chromate have equal concentrations. Setting [CrO$_4^{2-}$] equal to [HCrO$_4^-$] in eq. **1**, [H$^+$] = $\frac{1}{K_1}$, or pH = log K_1. This relationship is independent of pCr, so it requires a vertical line to be drawn on the predominance diagram.

Red line

Hydrogen chromate and dichromate have equal concentrations. Setting [HCrO$_4^-$] equal to [Cr$_2$O$_7^{2-}$] in Eq. **2**, [HCrO$_4^-$] = $\frac{1}{K_D}$; from Eq. **1**, then, [CrO$_4^{2-}$] = $\frac{1}{K_1 K_D[\mathrm{H^+}]}$.

Blue line

Chromate and dichromate have equal concentrations. Setting [CrO$_4^{2-}$] equal to [Cr$_2$O$_7^{2-}$] in Eq. **3** gives [CrO$_4^{2-}$] = $\frac{1}{\beta_2[\mathrm{H^+}]^2}$.

Chapter 18 Electrolytes

Strong Electrolyte NaCl in water (strong dielectric, ions completely formed)
Weak Electrolyte Acetic Acid in water (use dissociation constant)

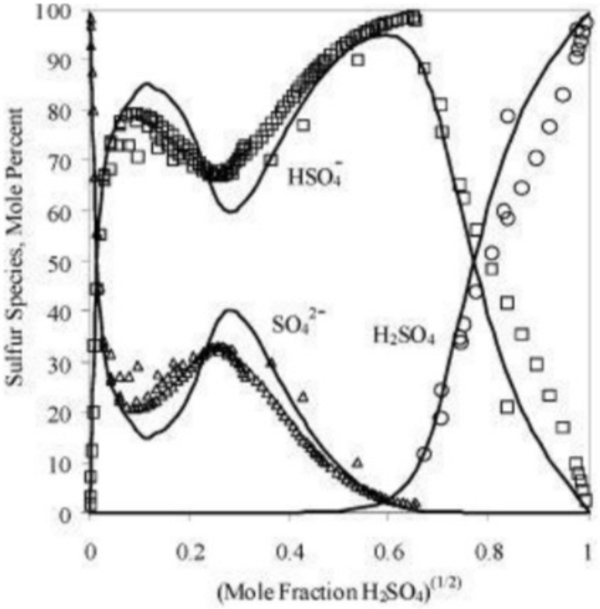
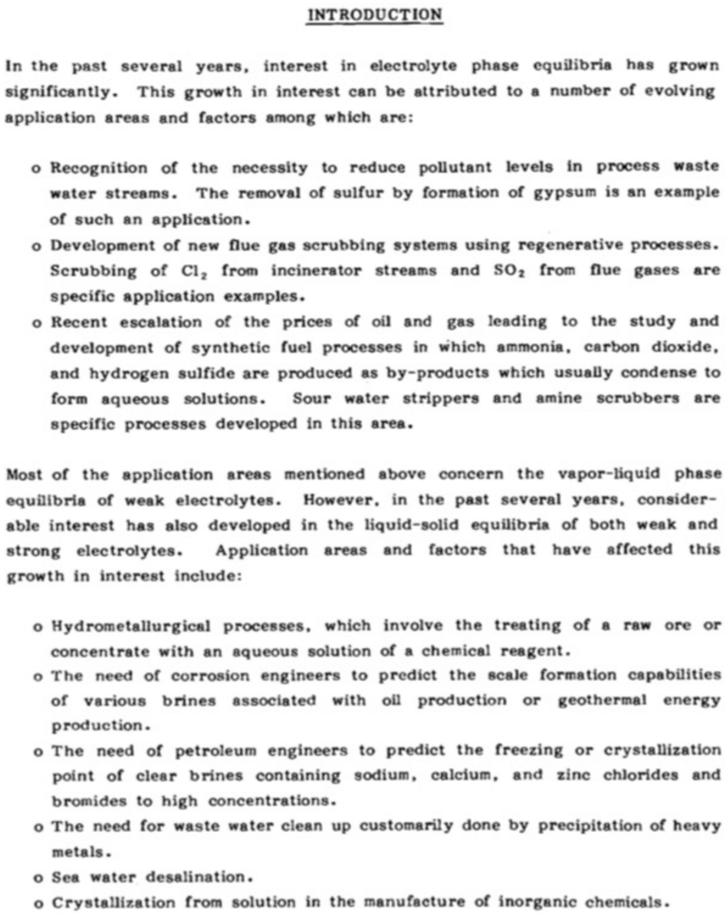


Figure 18.1. Speciation of sulfuric acid in aqueous solutions as measured by experiments[1] and modeled by OLI Systems, Inc.[2] Note the square root scale to emphasize the dilute region.

Chapter 18 Electrolytes



INTRODUCTION

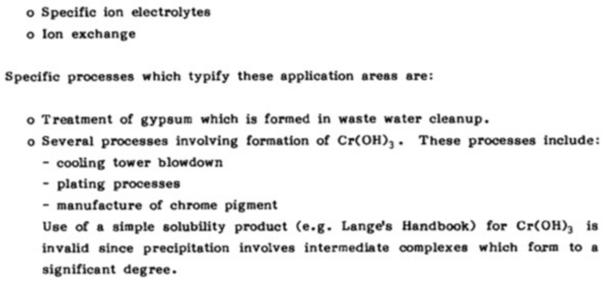
In the past several years, interest in electrolyte phase equilibria has grown significantly. This growth in interest can be attributed to a number of evolving application areas and factors among which are:

- o Recognition of the necessity to reduce pollutant levels in process waste water streams. The removal of sulfur by formation of gypsum is an example of such an application.
- o Development of new flue gas scrubbing systems using regenerative processes. Scrubbing of Cl_2 from incinerator streams and SO_2 from flue gases are specific application examples.
- o Recent escalation of the prices of oil and gas leading to the study and development of synthetic fuel processes in which ammonia, carbon dioxide, and hydrogen sulfide are produced as by-products which usually condense to form aqueous solutions. Sour water strippers and amine scrubbers are specific processes developed in this area.

Most of the application areas mentioned above concern the vapor-liquid phase equilibria of weak electrolytes. However, in the past several years, considerable interest has also developed in the liquid-solid equilibria of both weak and strong electrolytes. Application areas and factors that have affected this growth in interest include:

- o Hydrometallurgical processes, which involve the treating of a raw ore or concentrate with an aqueous solution of a chemical reagent.
- o The need of corrosion engineers to predict the scale formation capabilities of various brines associated with oil production or geothermal energy production.
- o The need of petroleum engineers to predict the freezing or crystallization point of clear brines containing sodium, calcium, and zinc chlorides and bromides to high concentrations.
- o The need for waste water clean up customarily done by precipitation of heavy metals.
- o Sea water desalination.
- o Crystallization from solution in the manufacture of inorganic chemicals.

Handbook of Aqueous Electrolyte Thermodynamics



- o Specific ion electrolytes
- o Ion exchange

Specific processes which typify these application areas are:

- o Treatment of gypsum which is formed in waste water cleanup.
- o Several processes involving formation of $Cr(OH)_3$. These processes include:
  - - cooling tower blowdown
  - - plating processes
  - - manufacture of chrome pigment

  Use of a simple solubility product (e.g. Lange's Handbook) for $Cr(OH)_3$ is invalid since precipitation involves intermediate complexes which form to a significant degree.

Colligative (counting) Properties

$\ln(x_i\gamma_i) = \frac{-\Delta H_i^{fus}}{R}\left(\frac{1}{T}-\frac{1}{T_{m,i}}\right)$ Melting Point Depression

$\Pi = -\frac{RT}{\bar{V}_W}\ln a_W$ Osmotic Pressure $\Pi/RT = (c/M_\mathrm{w})\,(1 + B_2\,c + \ldots)$

$y_{\mathrm{H2O}}\,P = P = x_{\mathrm{H2O}}P_{\mathrm{H20}}^{\mathrm{Sat}}$ Boiling Point Elevation (for non-volatile solute)

Example 18.1. Freezing point depression

Compare NaCl (used on icy roads), ethylene glycol (used in car radiators), and glucose (used by hibernating frogs) as alternatives for freezing point depression. Consider 5 g of each for 0.1 L (5.55 mol) of water and then compare 0.1 mol of each in 0.1 L of water. For the molar basis, compare the masses used and the effectiveness. Assume NaCl totally dissociates, and use an ideal solution approximation.

Solution

The melting point is calculated with Eqn. 14.24. To calculate mole fractions, the molecular weights are NaCl 58.44, ethylene glycol (EG) 62.07, and glucose 180.16. For 5 g of each, the molar amounts are 0.0855 mol, 0.0805 mol, and 0.027 mol, respectively. The mole fractions of water in the solutions (recall that NaCl forms two moles of ions!) are $x_{H_2O} = 5.55/(5.55 + 2\cdot 0.0855) = 0.970$, $x_{H_2O} = 5.55/(5.55 + 0.0805) = 0.986$, $x_{H_2O} = 0.995$, respectively, and

$$\ln(x_{\mathrm{H_2O}}) = -\frac{6009.5}{(8.314)(273.15)}\left(\frac{273.15}{T} - 1\right)$$

$$\Rightarrow T = \frac{273.15}{1-(8.314)(273.15)\ln(x_{\mathrm{H_2O}})/6009.5} \qquad 18.1$$

The freezing points for 5 g of each are 270.0 K, 271.7 K, 272.7 K for depressions of 3.2°C, 1.5°C, and 0.5°C respectively. NaCl is more effective than an equivalent mass of EG. Frogs must generate a very concentrated solution of glucose to keep from freezing while hibernating (though concentrated glucose also forms a metastable subcooled liquid easily). For 0.1 mol of each, the mol fractions are $x_{H_2O} = 0.965$, $x_{H_2O} = 0.982$, $x_{H_2O} = 0.982$, with freezing points of 269.6 K, 271.3 K, 271.3 K for depressions of 3.6°C, 1.9°C, and 1.9°C, respectively. There is no difference between the last two solutes because they do not dissociate. The masses needed for 0.1 mol are 5.8 g, 6.2 g, 18.0 g. On a mass basis, NaCl is more effective than glucose even though only one-third as much is used. For EG and glucose, 0.1 mol of each gives the same melting depression, but the mass of glycol is about one-third because the molecular weight is smaller.

Example 18.2. Example of osmotic pressure

Consider the solutes from Example 18.1 assuming complete dissociation of NaCl and ideal solutions. (a) Compare the osmotic pressure for 0.1 mol of each in 0.1 L of water at 298.15 K. (b) What concentration of NaCl (wt%) is isotonic with human blood?

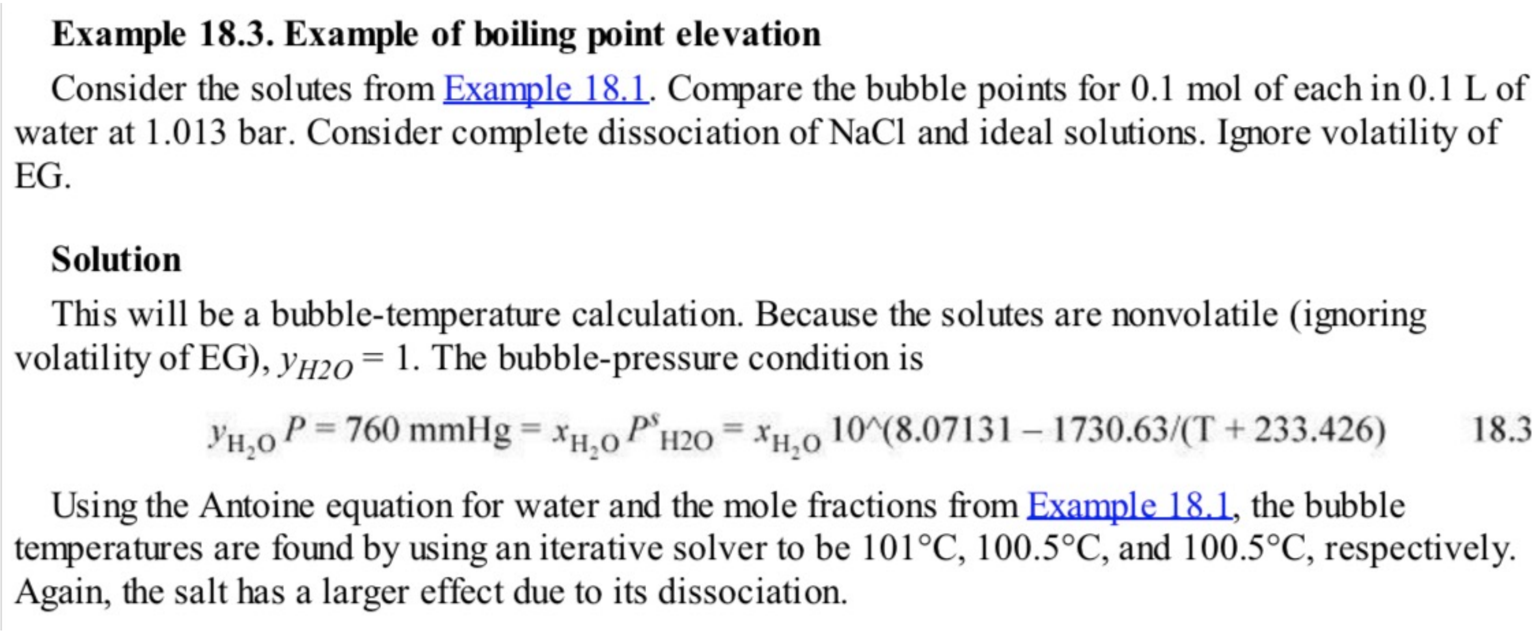
Solution

a. The mole fractions have been calculated in Example 18.1 as 0.965, 0.982, and 0.982. The osmotic pressure is given by Eqn. 11.71. The osmotic pressure for an ideal solution is

$$\Pi = \frac{-RT}{V_W}\ln(x_W) = -\frac{(8.314)(298.15)}{18.07}\ln(x_W) \qquad 18.2$$

Inserting the mole fractions of each, the osmotic pressures are 4.89 MPa, 2.5 MPa, 2.5 MPa. In a reverse osmosis system, a solution of NaCl requires much more pressure to purify than a solution of a nonelectrolyte with the same apparent concentration.

b. Isotonicity with human blood is defined in Section 11.13 on page 449 as having a concentration that is 0.308 mol/L of solute. Since two ions are obtained for each NaCl that dissociates, this corresponds to 0.154 mol/L of NaCl, or 8.99 g/L. Assuming the concentration is sufficiently low, a dilute aqueous solution corresponds to a density of 1000 g/L. Therefore, the weight fraction is 9/1000 = 0.009 or 0.9wt%. This is commonly known as “physiological saline” or just “saline.”



Example 18.3. Example of boiling point elevation

Consider the solutes from Example 18.1. Compare the bubble points for 0.1 mol of each in 0.1 L of water at 1.013 bar. Consider complete dissociation of NaCl and ideal solutions. Ignore volatility of EG.

Solution

This will be a bubble-temperature calculation. Because the solutes are nonvolatile (ignoring volatility of EG), $y_{H2O} = 1$. The bubble-pressure condition is

$$y_{H_2O} P = 760 \text{ mmHg} = x_{H_2O} P^{s}{}_{\text{H2O}} = x_{H_2O}\, 10\text{^}(8.07131 - 1730.63/(T + 233.426) \qquad 18.3$$

Using the Antoine equation for water and the mole fractions from Example 18.1, the bubble temperatures are found by using an iterative solver to be 101°C, 100.5°C, and 100.5°C, respectively. Again, the salt has a larger effect due to its dissociation.

Speciation and dissociation constant $K_{a,298}$, charge balance

$$H_2O_{(l)} \rightleftarrows H^+_{(aq)} + OH^-_{(aq)}$$

$$K_{a,298} = [H^+][OH^-] = 10^{-14}$$

$$K_{a,298} = \exp(-\Delta G^o_{298}/RT) = \frac{a_{H^+}\,a_{OH^-}}{a_{H_2O}}$$

a_{H+} is dimensionless, $[H^+]$ is moles/liter (molarity, M_{H+})
A neutral solution is pure water so $a_{H2O} = 1$
With temperature changes $[H^+]$ changes due to thermal expansion
Molality, number of moles of H^+ per kg of H_2O is used, m_{H+}

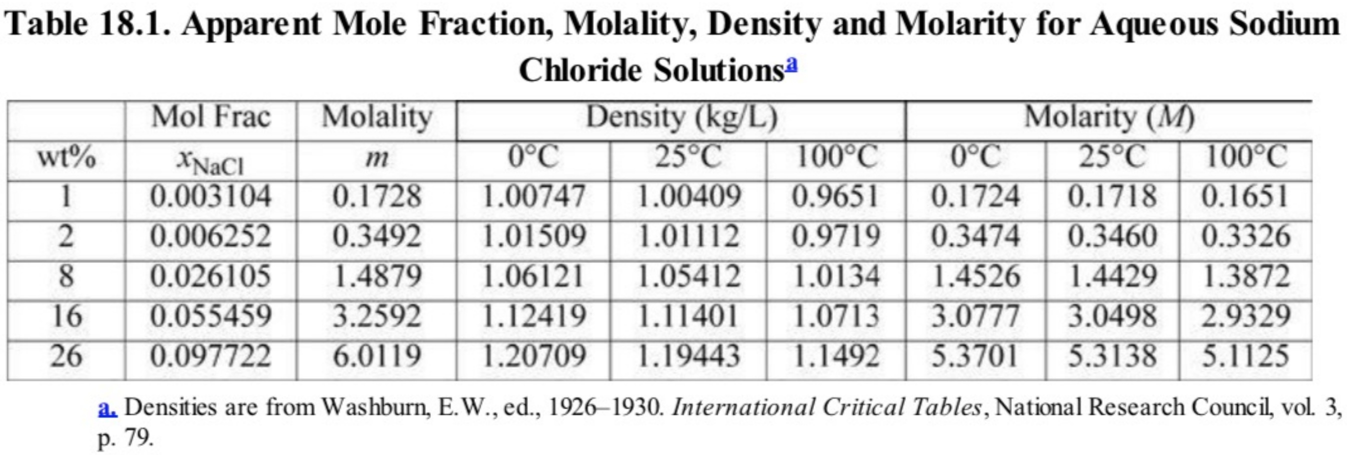


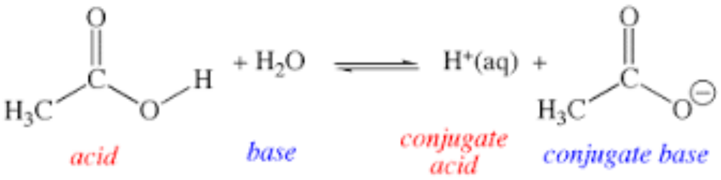
Table 18.1. Apparent Mole Fraction, Molality, Density and Molarity for Aqueous Sodium Chloride Solutions[a]

	Mol Frac	Molality	Density (kg/L)			Molarity (M)		
wt%	x_{NaCl}	m	0°C	25°C	100°C	0°C	25°C	100°C
1	0.003104	0.1728	1.00747	1.00409	0.9651	0.1724	0.1718	0.1651
2	0.006252	0.3492	1.01509	1.01112	0.9719	0.3474	0.3460	0.3326
8	0.026105	1.4879	1.06121	1.05412	1.0134	1.4526	1.4429	1.3872
16	0.055459	3.2592	1.12419	1.11401	1.0713	3.0777	3.0498	2.9329
26	0.097722	6.0119	1.20709	1.19443	1.1492	5.3701	5.3138	5.1125

[a] Densities are from Washburn, E.W., ed., 1926–1930. *International Critical Tables*, National Research Council, vol. 3, p. 79.

Concentration with speciation

Acetic Acid in water



$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = 10^{-4.8}$$

Apparent concentration: g/liter you put in of $C_2H_4O_2$

True concentration has to do with the dissociation species (based on a model)

VLE is based on the true concentration of undissociated species

pH

$pH = -\log_{10}(a_{H+})$

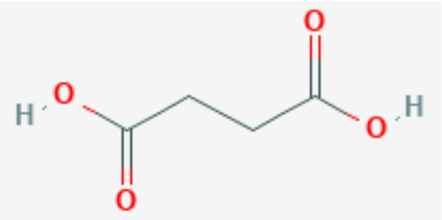
a_{H+} is molal (molar as an approximation)

$$K_{a,w} = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} = 10^{-14}$$

$$-\log(a_{H^+} a_{OH^-}) = -\log(a_{H^+}) = -\log(a_{OH^-}) = -\log K_{a,w}$$

$$pH + pOH = pK_{a,w}$$

Electrolyte Equilibrium Constant



Succinic Acid

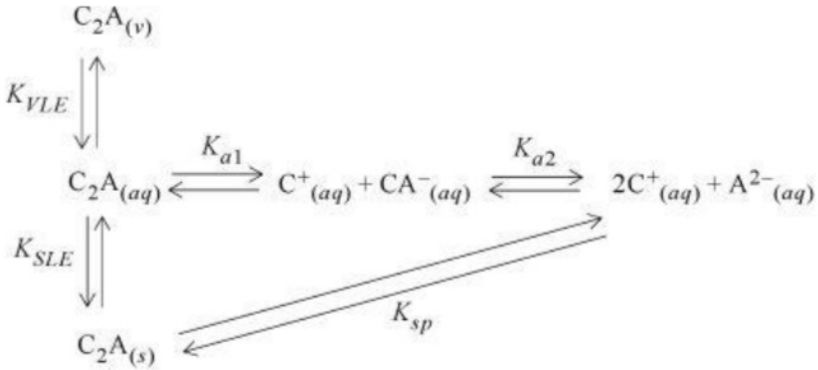


Figure 18.2. Reaction network for an example electrolyte where C is a monovalent cation and A is a divalent cation. The equilibrium constants are related as explained in the text.

$$\mu_i^L = \mu_{i(aq)}$$

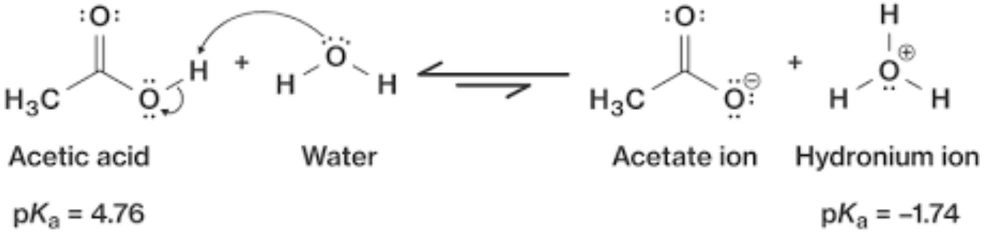
$$C_2A_{(s)} \overset{K_{sp}}{\rightleftarrows} 2C^+{}_{(aq)} + A^{2-}{}_{(aq)}$$

$$K_{sp} = K_{SLE}K_{a1}K_{a2}$$

Water of hydration and hydronium ion
Cations have water of hydration associated with the ion
Degree of hydration changes with concentration
At high concentrations ion pairs with the counter ion form

$$2H_2O_{(l)} \rightleftarrows H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$AcOH_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+{}_{(aq)} + AcO^-{}_{(aq)}$$



Acids and conjugate bases

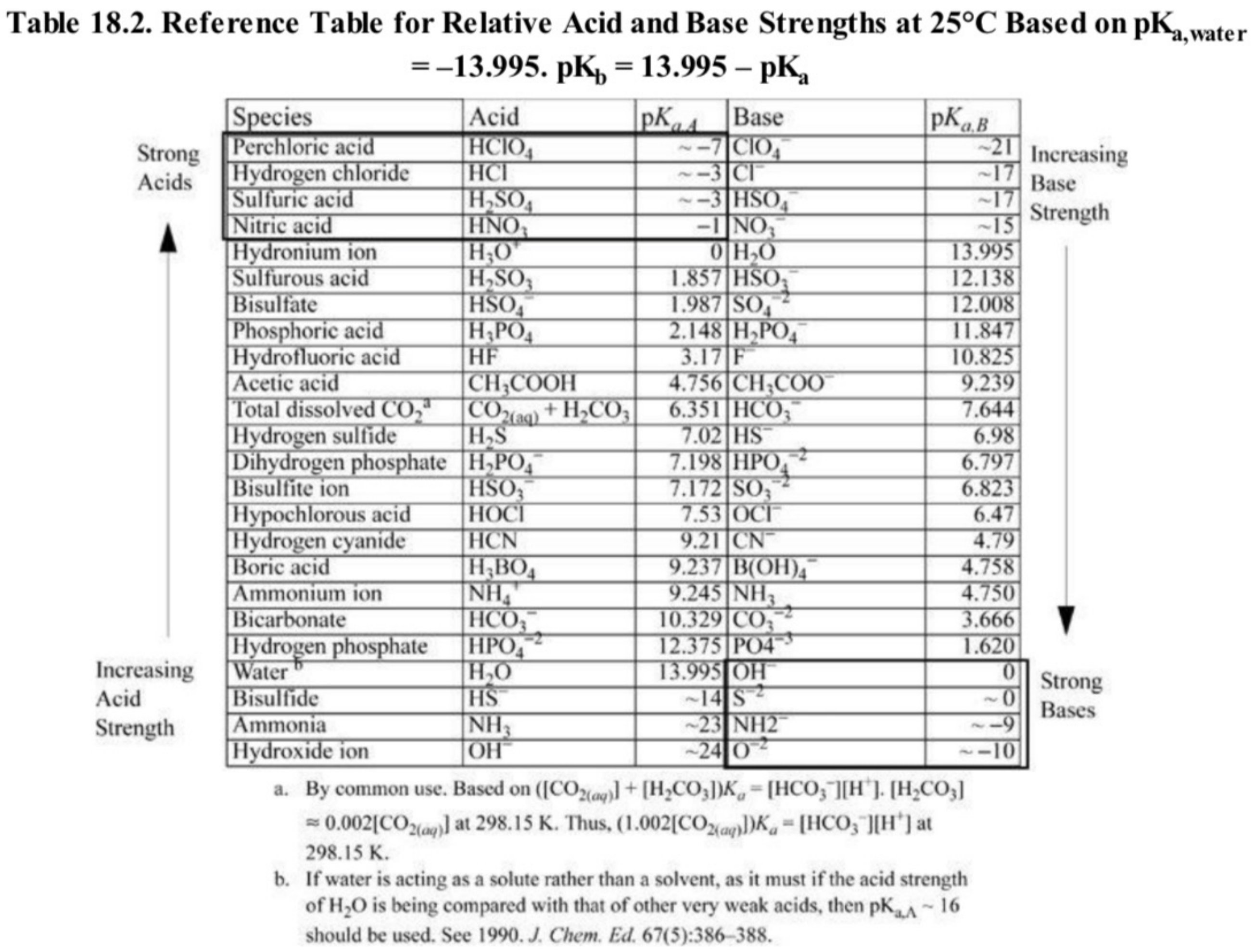


Table 18.2. Reference Table for Relative Acid and Base Strengths at 25°C Based on $pK_{a,water} = -13.995$. $pK_b = 13.995 - pK_a$

Strong Acids

Increasing Base Strength

Species	Acid	$pK_{a,A}$	Base	$pK_{a,B}$
Perchloric acid	$HClO_4$	~ −7	ClO_4^-	~21
Hydrogen chloride	HCl	~ −3	Cl^-	~17
Sulfuric acid	H_2SO_4	~ −3	HSO_4^-	~17
Nitric acid	HNO_3	−1	NO_3^-	~15
Hydronium ion	H_3O^+	0	H_2O	13.995
Sulfurous acid	H_2SO_3	1.857	HSO_3^-	12.138
Bisulfate	HSO_4^-	1.987	SO_4^{-2}	12.008
Phosphoric acid	H_3PO_4	2.148	$H_2PO_4^-$	11.847
Hydrofluoric acid	HF	3.17	F^-	10.825
Acetic acid	CH_3COOH	4.756	CH_3COO^-	9.239
Total dissolved CO_2[a]	$CO_{2(aq)} + H_2CO_3$	6.351	HCO_3^-	7.644
Hydrogen sulfide	H_2S	7.02	HS^-	6.98
Dihydrogen phosphate	$H_2PO_4^-$	7.198	HPO_4^{-2}	6.797
Bisulfite ion	HSO_3^-	7.172	SO_3^{-2}	6.823
Hypochlorous acid	$HOCl$	7.53	OCl^-	6.47
Hydrogen cyanide	HCN	9.21	CN^-	4.79
Boric acid	H_3BO_4	9.237	$B(OH)_4^-$	4.758
Ammonium ion	NH_4^+	9.245	NH_3	4.750
Bicarbonate	HCO_3^-	10.329	CO_3^{-2}	3.666
Hydrogen phosphate	HPO_4^{-2}	12.375	$PO4^{-3}$	1.620
Water[b]	H_2O	13.995	OH^-	0
Bisulfide	HS^-	~14	S^{-2}	~ 0
Ammonia	NH_3	~23	$NH2^-$	~ −9
Hydroxide ion	OH^-	~24	O^{-2}	~ −10

Increasing Acid Strength

Strong Bases

a. By common use. Based on $([CO_{2(aq)}] + [H_2CO_3])K_a = [HCO_3^-][H^+]$. $[H_2CO_3] \approx 0.002[CO_{2(aq)}]$ at 298.15 K. Thus, $(1.002[CO_{2(aq)}])K_a = [HCO_3^-][H^+]$ at 298.15 K.

b. If water is acting as a solute rather than a solvent, as it must if the acid strength of H_2O is being compared with that of other very weak acids, then $pK_{a,A} \sim 16$ should be used. See 1990. *J. Chem. Ed.* 67(5):386–388.

Strong Acid

$[Cl^-] = C_A$ material balance for complete dissociation 18.17

$K_{a,w} = [H^+][OH^-] = 10^{-14}$ equilibrium 18.18

$[H^+] = [Cl^-] + [OH^-]$ charge balance 18.19

$[H^+] = C_A + [OH^-]$ proton condition 18.20

$$K_{a,\,298} = [H^+][OH^-] = 10^{-14}$$

$[H^+]$ is large so $[OH^-]$ is very small, can be ignored

$pH \sim pC_A$

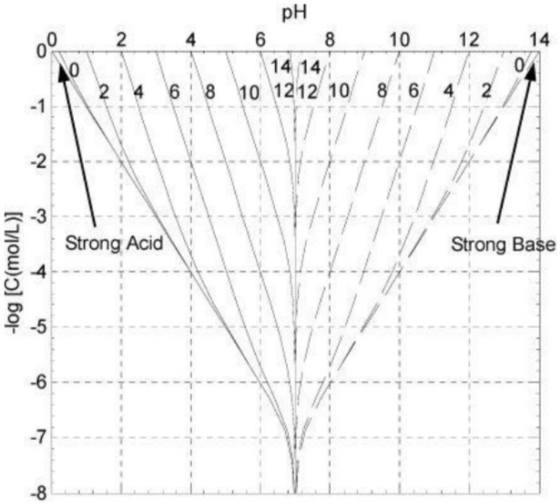


Figure 18.3. Flood diagram showing the behavior of strong monoprotic acids, weak monoprotic acids, salts of weak monoprotic bases, and strong monovalent bases.

Strong Base

$[\mathrm{Na}^+] = C_B$ material balance for complete dissociation

$K_{a,w} = [\mathrm{H}^+][\mathrm{OH}^-] = 10^{-14}$ equilibrium

$[\mathrm{H}^+] + [\mathrm{Na}^+] = [\mathrm{OH}^-]$ charge balance

$[\mathrm{H}^+] + C_B = [\mathrm{OH}^-]$ proton condition

$[\mathrm{OH}^-]$ is large so $[\mathrm{H}^+]$ is very small, can be ignored
$p\mathrm{OH} \sim p\mathrm{C_B}$

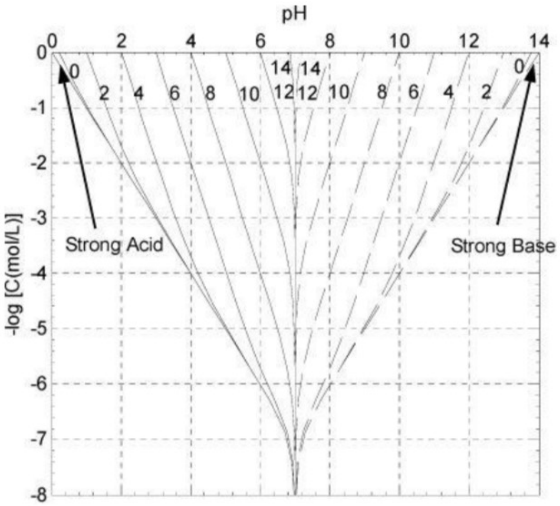


Figure 18.3. Flood diagram showing the behavior of strong monoprotic acids, weak monoprotic acids, salts of weak monoprotic bases, and strong monovalent bases.

Weak monoprotic Acid (Acetic Acid $pK_{a,A} = 4.7$)

$$[A^-] + [HA] = C_A \quad \text{material balance}$$

$$K_{a,A} = [H^+][A^-]/[HA] \quad \text{equilibrium}$$

$$K_{a,w} = [H^+][OH^-] = 10^{-14} \quad \text{equilibrium}$$

$$[H^+] = [A^-] + [OH^-] \quad \text{charge balance}$$

$$[H^+]^3 + K_{a,A}[H^+]^2 - (C_A K_{a,A} + K_{a,w})[H^+] - K_{a,A}K_{a,w} = 0 \quad \text{(Hint: limited utility)}$$

$$K_{a,A} = [H^+](C_A - [HA])/[HA]$$

$$\boxed{[HA] = C_A[H^+]/([H^+] + K_{a,A})} \quad \text{useful for undissociated acid}$$

$$\boxed{[A^-] = K_{a,A}C_A/([H^+] + K_{a,A})} \quad \text{useful for conjugate base}$$

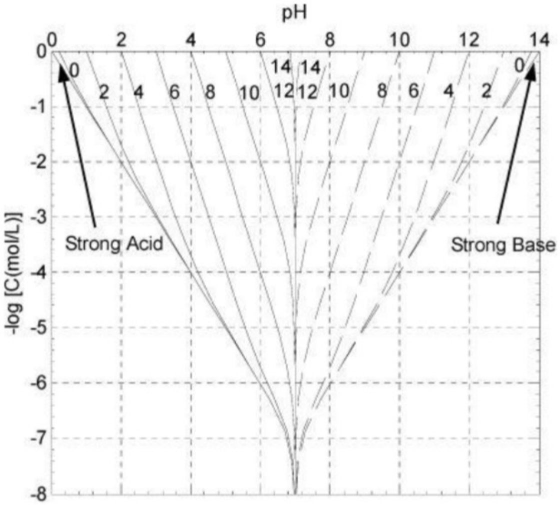


Figure 18.3. Flood diagram showing the behavior of strong monoprotic acids, weak monoprotic acids, salts of weak monoprotic bases, and strong monovalent bases.

Weak monoprotic Based (Acetate ion $pK_{a,B} = 9.3$)

$$A^- + H_2O \rightleftarrows HA + OH^-$$

$[Na^+] = [HA] + [A^-] = C_B$ material balance

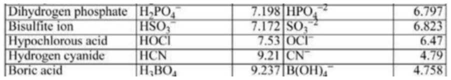
$K_{a,B} = [HA][OH^-]/[A^-]$ equilibrium

$K_{a,w} = [H^+][OH^-] = 10^{-14}$ equilibrium

$[H^+] + [Na^+] = [A^-] + [OH^-]$ charge balance

Start with sodium acetate which is a strong electrolyte, the resulting acetate ion is a weak base

$K_{a,B}[H^+]^3 + (C_B K_{a,B} + K_{a,w})[H^+]^2 - K_{a,B}K_{a,w}[H^+] - K_{a,w}^2 = 0$ limited use



Dihydrogen phosphate	$H_2PO_4^-$	7.198	HPO_4^{-2}	6.797
Bisulfite ion	HSO_3^-	7.172	SO_3^{-2}	6.823
Hypochlorous acid	HOCl	7.53	OCl^-	6.47
Hydrogen cyanide	HCN	9.21	CN^-	4.79
Boric acid	H_3BO_4	9.237	$B(OH)_4^-$	4.758

Convert to an acid equation and work with weak acid

$\boxed{[HA] = C_A[H^+]/([H^+] + K_{a,A})}$ useful for undissociated acid

$\boxed{[A^-] = K_{a,A}C_A/([H^+] + K_{a,A})}$ useful for conjugate base

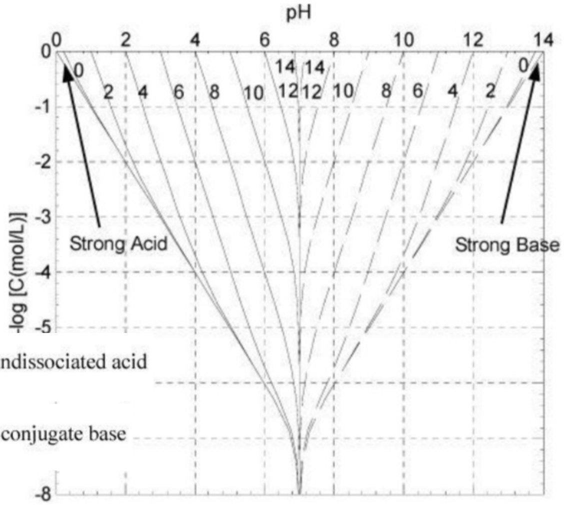


Figure 18.3. Flood diagram showing the behavior of strong monoprotic acids, weak monoprotic acids, salts of weak monoprotic bases, and strong monovalent bases.

Acid or Base Added to water

$$\boxed{pK_{a,A} + pK_{a,B} = pK_{a,w} \quad \text{or} \quad K_{a,A}K_{a,B} = K_{a,w}} \qquad 18.37$$

Example 18.4. Dissociation of fluconazole

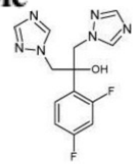


Figure 18.4. Structure of Fluconazole.

Base **Acid**

$$\text{Fluconazole} + H_2O \rightleftarrows \text{Fluconazole}^+ + OH^- \qquad 18.38$$

$$\ln(K_a) = -1.28 - 8000/T \qquad 18.39$$

Eqn. 18.39 represents $K_{a,B}$.

fluconazole and its ion and the hydroxyl are on the molality scale

Randall scale. Determine the percentage of fluconazole dissociated at pH 7 and pH 1.5 when the apparent amount of fluconazole in aqueous solution is 1.5E-3m. The molecular weight of fluconazole is 306.27. Assume ideal solutions.

Standard acid form of eqn. 18.38

$$\text{Fluconazole}^+ + H_2O \rightleftarrows \text{Fluconazole} + H_3O^+$$

At 298K, $K_{\text{a,B}}$ = 6.18 e-13 from eqn. 18.39

$K_{\text{a,A}}$ = 1e-14/6.18e-13 = 0.0162 or p$K_{\text{a,A}}$ = 1.79

Fluconazole is protonated below pH = 1.8 and neutral (undissociated) above

pH = 7

$$\boxed{[HA] = C_A[H^+]/([H^+] + K_{a,A})} \text{ useful for undissociated acid} \qquad 18.30$$

$$[\text{Fluc}^+] = C_{fluc}[H^+] / ([H^+] + K_{a,A}) = 1.5\text{E-}3\text{m}(10^{-7})/(10^{-7} + 0.01617) = 9.27\text{E-}9\text{m}.$$

None is dissociated so:

[Fluc] = 1.5E-3m, and the fraction protonated is 9.27E-9/(1.5E-3)· 100% = 0% (trace).

Example 18.4. Dissociation of fluconazole

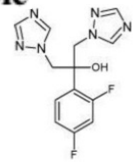


Figure 18.4. Structure of Fluconazole.

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$K_{a,A}$ = 1e-14/6.18 e-13 = 0.0162 or p$K_{a,A}$ = 1.79

Fluconazole is protonated below pH = 1.8 and neutral (undissociated) above

pH = 1.5 $\boxed{[HA] = C_A[H^+]/([H^+] + K_{a,A})}$ useful for undissociated acid 18.30

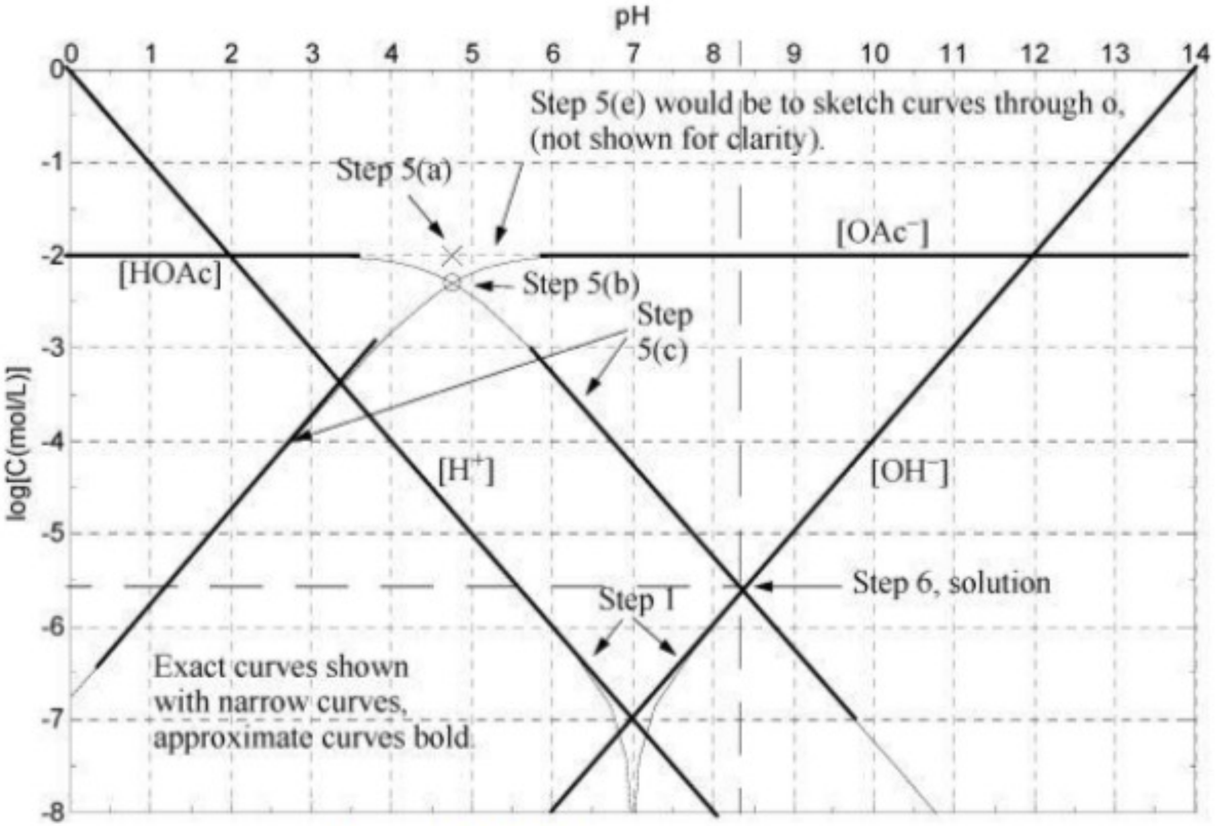
$[\text{Fluc}^+] = C_{fluc}[H^+] / ([H^+] + K_{a,A}) = 1.5\text{E-}3\text{m}(10^{-1.5})/(10^{-1.5} + 0.01617) = 9.9\text{E-}4\text{m}$

About half is dissociated:

$[\text{Fluc}] = 1.5\text{E-}3\text{m} - 9.9\text{E-}4\text{m} = 5.1\text{E-}4\text{m}$. protonated is $9.9\text{E-}4/(1.5\text{E-}3) \cdot 100\% = 66\%$.

Sillén Diagram or Bjerrum Plot or Hägg Diagram

$CH_3CO_2H + H_2O \rightleftarrows CH_3CO_2^- + H_3O^+$ 4.76 = pKa



Step 5(e) would be to sketch curves through o, (not shown for clarity).

Exact curves shown with narrow curves, approximate curves bold.

Figure 18.5. Sillèn plot for Example 18.5, acetate with an overall concentration 0.01 M.

Sillén Diagram

1. Create a coordinate system like the Flood diagram. (A template is available on the textbook web site.) Draw straight lines for the strong acid and strong base lines. The detail of the taper at pH = 7 should be ignored, and cross the lines. Note that the sum of the two lines is always –14 on the log scale and represents the ion product for water. Label these lines $[H^+]$ (left) and $[OH^-]$ (right).

2. Write the material balance for the dissociating species to relate the apparent species to the species in solution; for example, Eqn. 18.32.

$$[Na^+] = [HA] + [A^-] = C_B \quad \text{material balance} \qquad 18.32$$

3. Write the equilibria relations using the dissociation constants for weak acids or bases. If the acid/base is strong it will completely dissociate, and thus the relation is not needed. *Always write the reactions in the acid form* (even if bases are involved); for example, Eqn. 18.26 for acetate or acetic acid. Write the dissociation reaction for water. Using the acid form provides a consistent solution strategy, but is not theoretically required.

$$K_{a,A} = [H^+][A^-]/[HA] \quad \text{equilibrium} \qquad 18.26$$

$$K_{a,w} = [H^+][OH^-] = 10^{-14} \quad \text{equilibrium} \qquad 18.27$$

4. Write the electroneutrality constraint.

$$[H^+] = [A^-] + [OH^-] \quad \text{charge balance} \qquad 18.28$$

5. Sketch Eqns. 18.30 and 18.31 without calculations on the diagram using these steps. (See the example.) The steps are: **(a) create a system point** at C_A (or C_B) and p$K_{a,A}$; the procedure always uses p$K_{a,A}$, even for bases; **(b) create an acid/base intersection point** at (p$K_{a,A}$, logC_A – 0.3). (The value of 0.3 represents a decrease of 50% in the concentration, which is where the acid and base concentrations will match.); **(c) sketch diagonal lines** with slope +1 and –1 (parallel to the H+ and OH– lines) *below* C_A that project through the system point but extend downwards starting about logC_A – 1; **(d) draw horizontal lines** on either side of the system point leaving a gap of approximately 1 pH unit on either side of the system point and label the line on the left (low pH) as the acid and the line to the right (high pH) as the base; **(e) connect the sloping lines with the horizontal lines** with smooth curves that pass through the acid/base intersection point.

$$\boxed{[HA] = C_A[H^+]/([H^+] + K_{a,A})} \quad \text{useful for undissociated acid} \qquad 18.30$$

$$\boxed{[A^-] = K_{a,A}C_A/([H^+] + K_{a,A})} \quad \text{useful for conjugate base} \qquad 18.31$$

6. Decide which concentrations are largest and which are least significant. Let C_i be the apparent concentration. The goal is to simplify the balances and provide a good guess for true concentrations. This is almost always done by converting the charge balance to a proton condition by inserting the mass balance to eliminate terms that are largest and leave smaller terms that are more similar in magnitude. Use the diagram as a guide to decide which concentrations are insignificant in the pH range expected. The goal is to use the proton condition to identify the intersection of the positive and negative charges of the proton condition. Unless some of the diagonal curves are very close to each other this will be easy. There can be various proton conditions that are equally valid when many ions are present at similar concentrations. Hints: Remember that each unit on the log scale is an order of magnitude. Acids by themselves result in pH < 7; bases alone result in pH > 7; salts of a strong acid and weak base (e.g., $NH_4^+Cl^-$) are acidic; salts of a weak acid and strong base (e.g., NaOAc) are basic.

7. Check the result. The results can be checked by iterating on charge balance pH by inserting Eqns. 18.30 and 18.31 or the analogs.

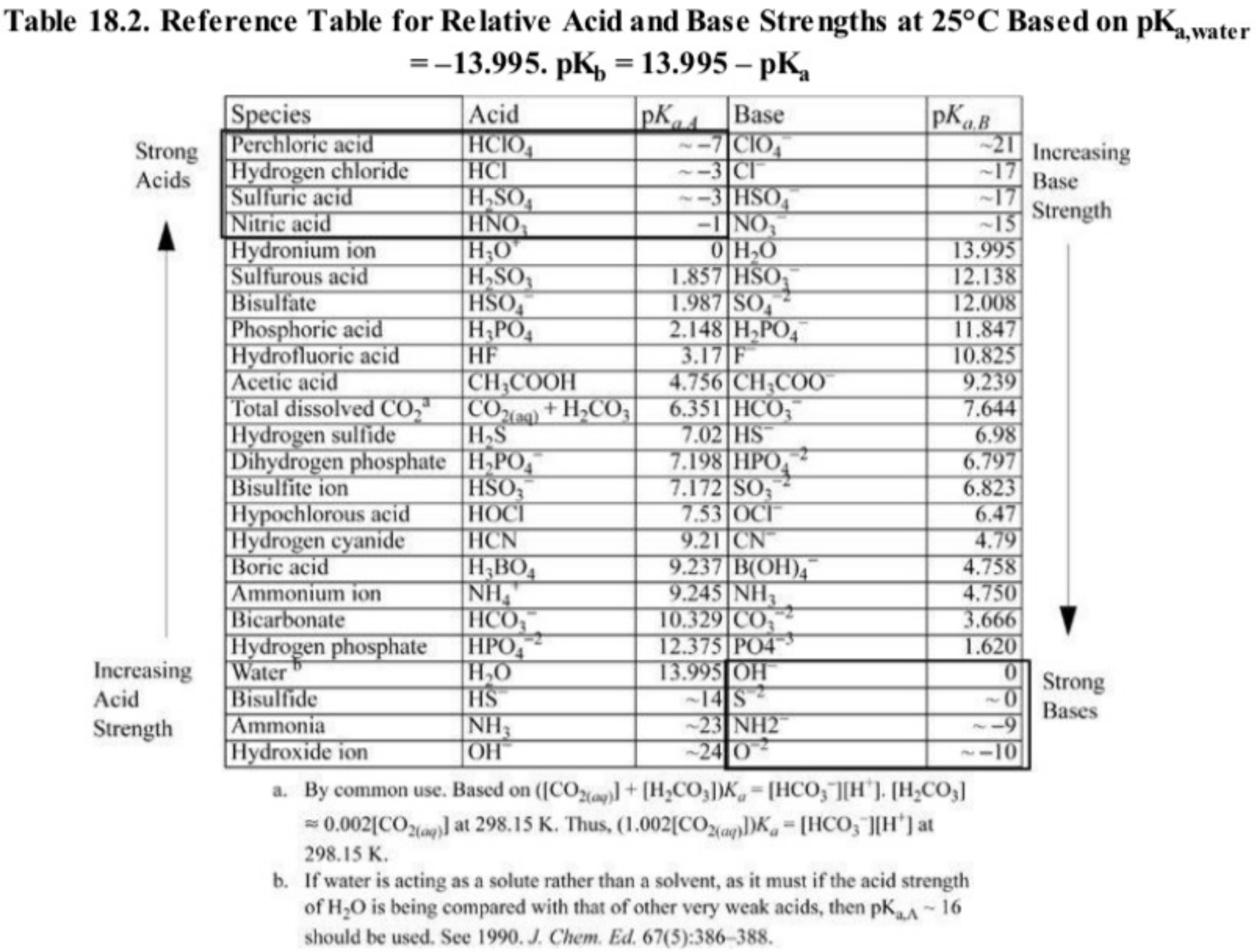


Table 18.2. Reference Table for Relative Acid and Base Strengths at 25°C Based on $pK_{a,water}$ =–13.995. $pK_b = 13.995 - pK_a$

Strong Acids

Increasing Base Strength

Species	Acid	$pK_{a,A}$	Base	$pK_{a,B}$
Perchloric acid	$HClO_4$	~–7	ClO_4^-	~21
Hydrogen chloride	HCl	~–3	Cl^-	~17
Sulfuric acid	H_2SO_4	~–3	HSO_4^-	~17
Nitric acid	HNO_3	–1	NO_3^-	~15
Hydronium ion	H_3O^+	0	H_2O	13.995
Sulfurous acid	H_2SO_3	1.857	HSO_3^-	12.138
Bisulfate	HSO_4^-	1.987	SO_4^{-2}	12.008
Phosphoric acid	H_3PO_4	2.148	$H_2PO_4^-$	11.847
Hydrofluoric acid	HF	3.17	F^-	10.825
Acetic acid	CH_3COOH	4.756	CH_3COO^-	9.239
Total dissolved CO_2[a]	$CO_{2(aq)} + H_2CO_3$	6.351	HCO_3^-	7.644
Hydrogen sulfide	H_2S	7.02	HS^-	6.98
Dihydrogen phosphate	$H_2PO_4^-$	7.198	HPO_4^{-2}	6.797
Bisulfite ion	HSO_3^-	7.172	SO_3^{-2}	6.823
Hypochlorous acid	$HOCl$	7.53	OCl^-	6.47
Hydrogen cyanide	HCN	9.21	CN^-	4.79
Boric acid	H_3BO_4	9.237	$B(OH)_4^-$	4.758
Ammonium ion	NH_4^+	9.245	NH_3	4.750
Bicarbonate	HCO_3^-	10.329	CO_3^{-2}	3.666
Hydrogen phosphate	HPO_4^{-2}	12.375	$PO4^{-3}$	1.620
Water[b]	H_2O	13.995	OH^-	0
Bisulfide	HS^-	~14	S^{-2}	~0
Ammonia	NH_3	~23	$NH2^-$	~–9
Hydroxide ion	OH^-	~24	O^{-2}	~–10

Increasing Acid Strength

Strong Bases

a. By common use. Based on $([CO_{2(aq)}] + [H_2CO_3])K_a = [HCO_3^-][H^+]$. $[H_2CO_3] \approx 0.002[CO_{2(aq)}]$ at 298.15 K. Thus, $(1.002[CO_{2(aq)}])K_a = [HCO_3^-][H^+]$ at 298.15 K.

b. If water is acting as a solute rather than a solvent, as it must if the acid strength of H_2O is being compared with that of other very weak acids, then $pK_{a,A} \sim 16$ should be used. See 1990. *J. Chem. Ed.* 67(5):386–388.

Example 18.5. Sillèn diagram for HOAc and NaOAc

Sodium acetate, NaOAc, is dissolved in water at an apparent concentration of $C_B = 10^{-2}$ mol/L. Construct a Sillèn diagram and estimate the pH. For acetic acid, $pK_{a,A} = 4.76$ at room temperature in dilute solutions.

$[OH^-][H^+]=10^{-14}$ so $\log [OH^-]+\log[H^+] = 14$ (two lines as drawn)

Step 1: The lines for $[H^+]$ and $[OH^-]$ have been drawn and labeled in the figure.

Step 2: $[Na^+] = [HOAc] + [OAc^-] = C_B$ material balance 18.40

When one component is small the other is C_B

Step 3: $K_{a,A} = [OAc^-][H^+]/[HOAc]$ equilibrium 18.41

When $[OAc^-] = [HOAc]$ then $K_{a,A} = [H^+]$

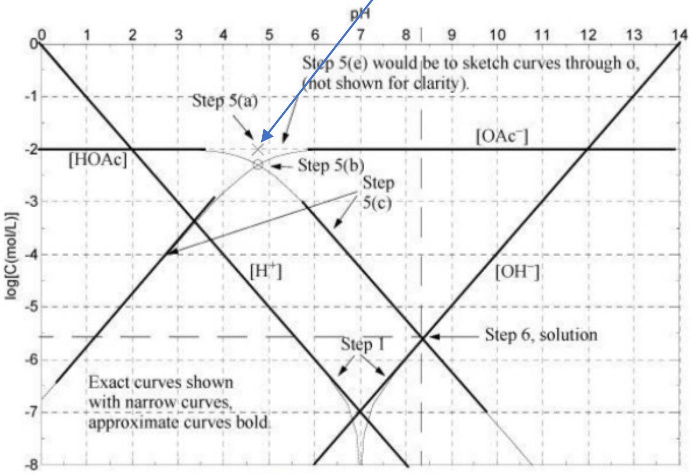
$K_{a,w} = [H^+][OH^-] = 10^{-14}$ equilibrium 18.42

Step 4: $[H^+] + [Na^+] = [OAc^-] + [OH^-]$ charge balance 18.43

$[H^+] + [HOAc] = [OH^-]$ proton condition 18

$[HA] = C_A[H^+]/([H^+] + K_{a,A})$

$[HOAc]$ is parallel to $[H^+]$ when $[H^+]$ is small



Strong Base/Weak Acid,
Answer is Basic
In Basic region
$[H^+] << [HOAc]$
So $[HOAc] \sim [OH^-]$ for
solution at pH 8.4

$[A^-] = K_{a,A}C_A/([H^+] + K_{a,A})$

$[H^+]=10^{-14}/[OH^-]$ so $[OAc^-]$ is parallel to $[OH^-]$ when $[OH^-]$ is small

Step 5: See the diagram labels denoting steps 5(a) and 5(b). Referring to the procedure above indicates the system point (**x**) should be at C_B and p$K_{a,A}$. On the diagram below, use a straight edge to verify that the lines for step 5(c) extrapolate through the **x** from step 5(a). Note that the curves for step 5(e) are not shaded for clarity, but it is obvious that the curves could be easily drawn through o. Recall that step 5 plots Eqns. 18.30 and 18.31 without calculations.

$$\boxed{[\mathrm{HA}] = C_A[\mathrm{H}^+]/([\mathrm{H}^+] + K_{a,A})} \quad \text{useful for undissociated acid} \qquad 18.30$$

$$\boxed{[\mathrm{A}^-] = K_{a,A}C_A/([\mathrm{H}^+] + K_{a,A})} \quad \text{useful for conjugate base} \qquad 18.31$$

Step 6: Develop the proton condition. This step is very important and can be the most confusing. It is best understood by using equations together with the diagram. Since we have dissolved the salt of a weak acid and strong base, we expect the pH to be above 7. Looking at the diagram in this range, $[\mathrm{OAc}^-] >> [\mathrm{HOAc}]$ and we will be unable to reliably calculate $[\mathrm{HOAc}] = C_B - [\mathrm{OAc}^-]$ with the material balance because the last two terms are nearly equal. Let us use the material balance to eliminate the large terms $[\mathrm{Na}^+]$ and $[\mathrm{OAc}^-]$ from the charge balance. Note that we can replace $[\mathrm{Na}^+]$ with C_B and $[\mathrm{OAc}^-] = C_B - [\mathrm{HOAc}]$. This causes all the largest terms to drop from the charge balance, giving

$$[\mathrm{H}^+] + [\mathrm{HOAc}] = [\mathrm{OH}^-] \quad \text{proton condition} \qquad 18.44$$

Eqns. 18.40–18.43 are now all condensed to using Eqn. 18.44 with the graph, looking for where the proton condition is satisfied. Looking at the lines on the graph where pH > 7, it is obvious that [HOAc] is almost three orders of magnitude larger than $[\mathrm{H}^+]$ above pH = 5. Thus, the left side of the proton condition becomes $[\mathrm{HOAc}] + [\mathrm{H}^+] = [\mathrm{HOAc}] + ...$ where ... denotes a very small number. The proton condition becomes $[\mathrm{HOAc}] + ... = [\mathrm{OH}^-]$, and the solution is given for practical purposes by the intersection of the [HOAc] curve with the $[\mathrm{OH}^-]$ curve as shown in the diagram. The approximate concentrations are

$$\mathrm{pH} = 8.4,\ \mathrm{pOH} = 14 - 8.4 = 5.6,\ [\mathrm{HOAc}] = 10^{-5.6},\ [\mathrm{Na}^+] = [\mathrm{OAc}^-] = 10^{-2}$$

Step 7: The proton condition is in terms of Eqns. 18.27 and 18.30, and avoiding taking differences, $[OH^-] = 10^{-14}/[H^+] = [H^+] + [HOAc] = [H^+] + C_A[H^+] / ([H^+] + K_{a.A})$

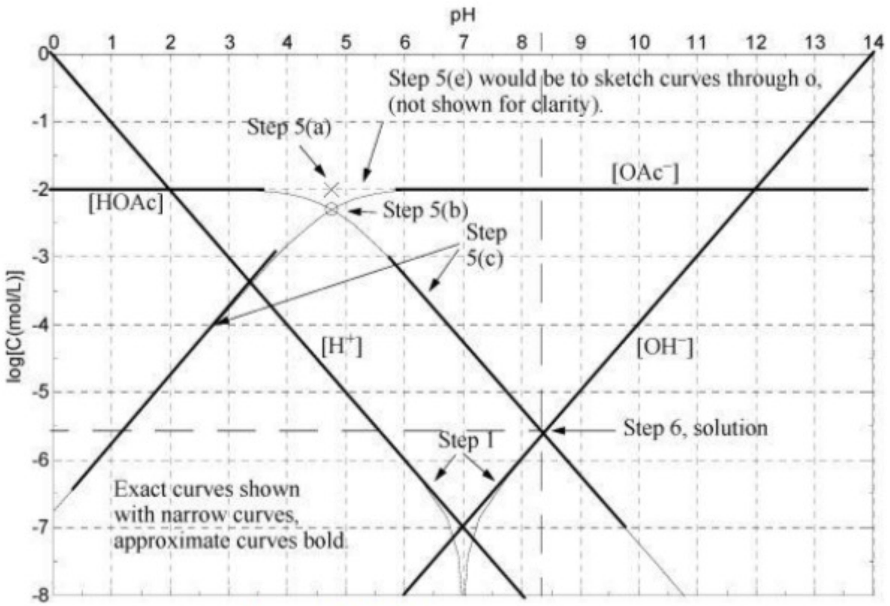
Rearranging for successive substitution on $[H^+]$, and inserting the initial guess of pH = 8.4, iterate on the highest power of $[H^+]$,

$$[H^+]^2 = 10^{-14} / (1 + C_A / ([H^+] + K_{a,A})) = 10^{-8.4} + (10^{-2})(10^{-8.4})/(10^{-8.4} + 10^{-4.76})$$

$$[H^+] = \sqrt{10^{-14}/(1 + C_A/([H^+] + K_{a,A}))} = \sqrt{10^{-14}/(1 + 10^{-2}/(10^{-8.4} + 10^{-4.76}))}$$

$$= 4.165E\text{-}9$$

pH = 8.38. Plugging this back in results in no further changes. Recall that if successive substitution results in divergence rather than convergence, that the equation needs to be rearranged. See Appendix A, Section A.4.



Polyprotic Acids and Bases

The phosphoric system (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) and the CO_2 (CO_2, HCO_3^-, CO_3^{2-}) systems are important for both biology and environmental applications. Succinic acid, a dicarboxylic acid produced by fermentation, is expected to become more widely produced via fermentation in future years, typically as a salt. Amino acids, the building blocks for proteins, combine a basic amine and a carboxylic acid on the same molecule. Let us begin by considering the nonvolatile phosphate system.

$$\frac{[H_2PO_4^-]}{[H_3PO_4]} = \frac{K_{a1}}{[H^+]} \qquad 18.45$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{K_{a2}}{[H^+]} \text{ or } \frac{[HPO_4^{2-}]}{[H_3PO_4]} = \frac{K_{a1}K_{a2}}{[H^+]^2} \qquad 18.46$$

$$\frac{[PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{K_{a3}}{[H^+]} \text{ or } \frac{[PO_4^{3-}]}{[H_3PO_4]} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} \qquad 18.47$$

$$C = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \qquad 18.48$$

$$\alpha_3 = \frac{[H_3PO_4]}{C},\ \alpha_2 = \frac{[H_2PO_4^-]}{C},\ \alpha_1 = \frac{[HPO_4^{2-}]}{C},\ \alpha_0 = \frac{[PO_4^{3-}]}{C} \qquad 18.49$$

$$\frac{1}{\alpha_3} = \frac{C}{[H_3PO_4]} = 1 + \frac{[H_2PO_4^-]}{[H_3PO_4]} + \frac{[HPO_4^{2-}]}{[H_3PO_4]} + \frac{[PO_4^{3-}]}{[H_3PO_4]} = 1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} \qquad 18.50$$

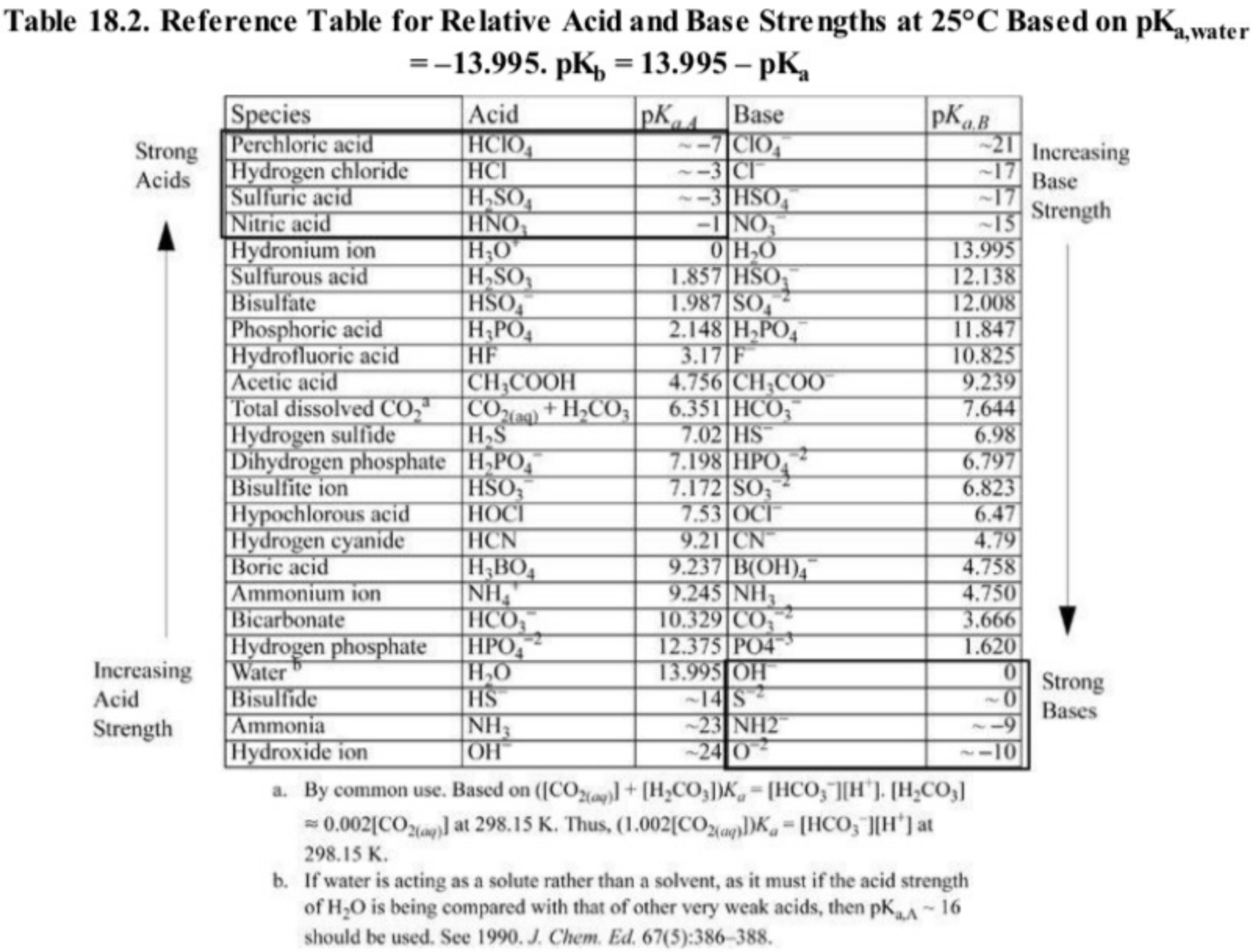
$$\alpha_3 = \frac{[H_3PO_4]}{C} = \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \qquad 18.51$$

$$\alpha_2 = \frac{[H_2PO_4^-]}{C} = \frac{[H_3PO_4]}{C}\frac{[H_2PO_4^-]}{[H_3PO_4]} = \alpha_3\frac{K_{a1}}{[H^+]}$$

$$\alpha_2 = \frac{[H_2PO_4^-]}{C} = \frac{K_{a1}[H^+]^2}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \qquad 18.52$$

$$\alpha_1 = \frac{[HPO_4^{2-}]}{C} = \frac{K_{a1}K_{a2}[H^+]}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \qquad 18.53$$

$$\alpha_0 = \frac{[PO_4^{3-}]}{C} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \qquad 18.54$$



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Species	Acid	$pK_{a,A}$	Base	$pK_{a,B}$
Perchloric acid	$HClO_4$	~ −7	ClO_4^-	~21
Hydrogen chloride	HCl	~ −3	Cl^-	~17
Sulfuric acid	H_2SO_4	~ −3	HSO_4^-	~17
Nitric acid	HNO_3	−1	NO_3^-	~15
Hydronium ion	H_3O^+	0	H_2O	13.995
Sulfurous acid	H_2SO_3	1.857	HSO_3^-	12.138
Bisulfate	HSO_4^-	1.987	SO_4^{-2}	12.008
Phosphoric acid	H_3PO_4	2.148	$H_2PO_4^-$	11.847
Hydrofluoric acid	HF	3.17	F^-	10.825
Acetic acid	CH_3COOH	4.756	CH_3COO^-	9.239
Total dissolved CO_2[a]	$CO_{2(aq)} + H_2CO_3$	6.351	HCO_3^-	7.644
Hydrogen sulfide	H_2S	7.02	HS^-	6.98
Dihydrogen phosphate	$H_2PO_4^-$	7.198	HPO_4^{-2}	6.797
Bisulfite ion	HSO_3^-	7.172	SO_3^{-2}	6.823
Hypochlorous acid	$HOCl$	7.53	OCl^-	6.47
Hydrogen cyanide	HCN	9.21	CN^-	4.79
Boric acid	H_3BO_4	9.237	$B(OH)_4^-$	4.758
Ammonium ion	NH_4^+	9.245	NH_3	4.750
Bicarbonate	HCO_3^-	10.329	CO_3^{-2}	3.666
Hydrogen phosphate	HPO_4^{-2}	12.375	$PO4^{-3}$	1.620
Water[b]	H_2O	13.995	OH^-	0
Bisulfide	HS^-	~14	S^{-2}	~ 0
Ammonia	NH_3	~23	$NH2^-$	~ −9
Hydroxide ion	OH^-	~24	O^{-2}	~ −10

a. By common use. Based on $([CO_{2(aq)}] + [H_2CO_3])K_a = [HCO_3^-][H^+]$. $[H_2CO_3] \approx 0.002[CO_{2(aq)}]$ at 298.15 K. Thus, $(1.002[CO_{2(aq)}])K_a = [HCO_3^-][H^+]$ at 298.15 K.

b. If water is acting as a solute rather than a solvent, as it must if the acid strength of H_2O is being compared with that of other very weak acids, then $pK_{a,A} \sim 16$ should be used. See 1990. *J. Chem. Ed.* 67(5):386–388.

The Sillèn diagram for the phosphate system is slightly more complicated than a monoprotic system, but can still be quickly drawn by hand. The concentration of each species *i* can rigorously be calculated at each pH by $\alpha_i C$ where α_i is calculated from Eqns. 18.51–18.54. The exact

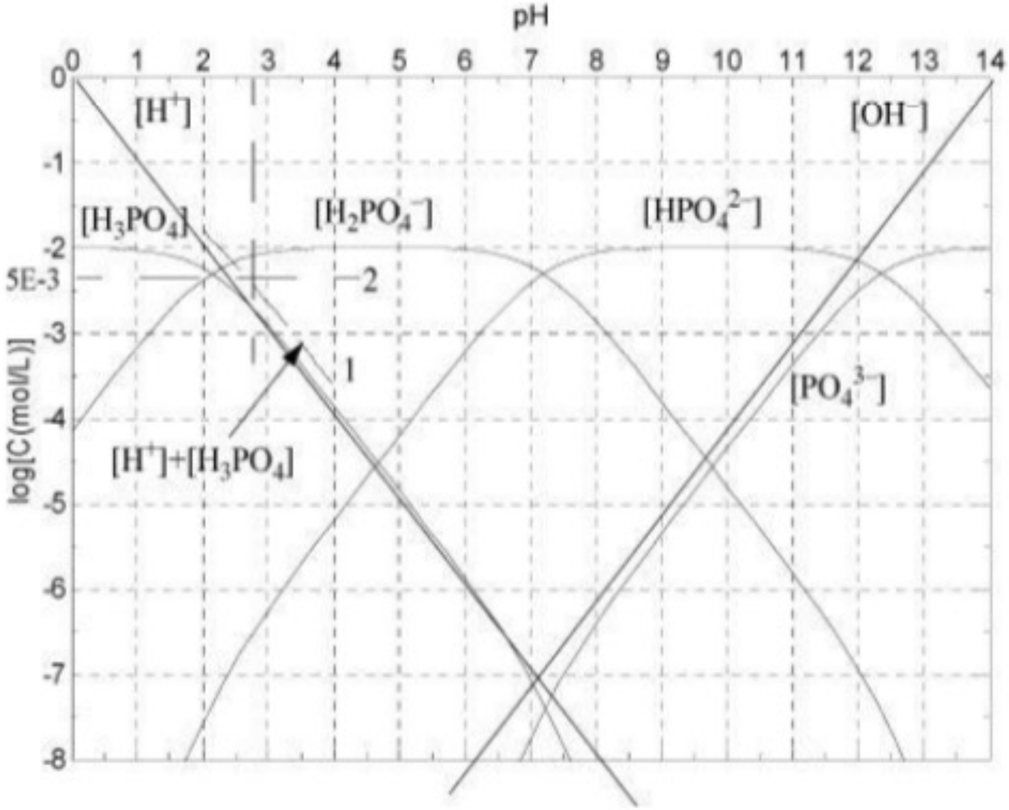


Figure 18.6. Phosphoric system at $C = 10^{-2}$ mol/L discussed in Example 18.6.

Example 18.6. Phosphate salt and strong acid

A solution of NaH_2PO_4 and HCl is prepared such that the total phosphorous concentration is 1E-2 M and the total Cl concentration is 5E-3M. Calculate the pH and concentrations of species present.

$$1\times10^{-2}\text{M} = [H_3PO_4]+[H_2PO_4^-]+[HPO_4^{2-}]+[PO_4^{3-}] = [Na^+] \qquad 18.55$$

$$[Cl^-] = 5\times10^{-3}\text{M} \qquad 18.56$$

$$[H^+]+[Na^+] = [H_2PO_4^-]+2[HPO_4^{2-}]+3[PO_4^{3-}]+[OH^-]+[Cl^-] \text{ charge balance} \qquad 18.57$$

Step 6. The proton condition is developed by eliminating $[Na^+]$ and $[Cl^-]$ using the material balances since they are both known constants. The material balance for phosphate is also inserted, resulting in

$$[H^+]+10^{-2} = 10^{-2}-[H_3PO_4]+[HPO_4^{2-}]+2[PO_4^{3-}]+[OH^-]+5\cdot10^{-3} \qquad 18.58$$

which becomes

$$[H^+]+[H_3PO_4] = [HPO_4^{2-}]+2[PO_4^{3-}]+[OH^-]+5\cdot10^{-3} \text{ proton condition} \qquad 18.59$$

Understanding where to find the solution requires some thought and reasoning rather than a direct numerical manipulation. Both terms on the left side of the proton condition are almost equal at $2.5 < \text{pH} < 7$. The values are added on the short dashed line marked “1” (since they are virtually equal in most of the range, the sum is double, or about 0.3 units higher on the $\log_{10}$ scale). Note that $[H_2PO_4^-]$ does not appear in the proton condition. On the right-hand side, the term 5E-3 dominates at pH < 6. Solutions at high pH are impossible because the decreasing right-hand side is too small to balance the value of 5E-3 plus increasing concentrations of the negative phosphate and hydroxide ions in the proton condition. Therefore, the solution must be a low pH where the concentration of negative phosphate and hydroxide ions in the proton condition are small. The solution occurs where $[H^+] + [H_3PO_4] = 5\text{E-}3$ (the line marked “2”), and pH = 2.6. The approximate concentrations from the diagram are $[H^+] = [H_3PO_4] = 2.5\text{E-}3$. Eqn. 18.45 simplifies to $[H_2PO_4^-] = K_{a1} = 10^{-2.15}$, $[HPO_4^{2-}] = 10^{-6.5}$, $[Na^+] = 1\text{E-}2$, $[Cl^-] = 5\text{E-}3$.

$$\frac{[H_2PO_4^-]}{[H_3PO_4]} = \frac{K_{a1}}{[H^+]} \qquad 18.45$$

Step 7. The detailed calculations are often tedious. Inserting Eqn. 18.51 into the proton condition, where the first three terms on the right side are negligible,

$$[\mathrm{H}^+] + \frac{C[\mathrm{H}^+]^3}{[\mathrm{H}^+]^3 + K_{a1}[\mathrm{H}^+]^2 + K_{a1}K_{a2}[\mathrm{H}^+] + K_{a1}K_{a2}K_{a3}} = 5\text{E-3} + \ldots \tag{18.60}$$

$$\begin{gathered}[\mathrm{H}^+]\left(1 + \frac{C[\mathrm{H}^+]^2}{[\mathrm{H}^+]^3 + K_{a1}[\mathrm{H}^+]^2 + K_{a1}K_{a2}[\mathrm{H}^+] + K_{a1}K_{a2}K_{a3}}\right) = \\ [\mathrm{H}^+]\left(1 + \frac{C/[\mathrm{H}^+]}{1 + K_{a1}/[\mathrm{H}^+] + (K_{a1}K_{a2})/[\mathrm{H}^+]^2 + (K_{a1}K_{a2}K_{a3})/[\mathrm{H}^+]^3}\right) = 5\text{E-3}\end{gathered} \tag{18.61}$$

Inserting the initial guess,

$$[\mathrm{H}^+] = (5\text{E-3})/\left[1 + \frac{C/[\mathrm{H}^+]}{1 + K_{a1}/[\mathrm{H}^+] + (K_{a1}K_{a2})/[\mathrm{H}^+]^2 + (K_{a1}K_{a2}K_{a3})/[\mathrm{H}^+]^3}\right] \tag{18.62}$$

$$[\mathrm{H}^+] = (5\text{E-3})/\left[1 + \frac{10^{-2}/[\mathrm{H}^+]}{1 + 10^{-2.148}/[\mathrm{H}^+] + \ldots}\right]$$

$$= (5\text{E-3})/\left[1 + \frac{10^{-2}/10^{-2.6}}{1 + 10^{-2.148}/10^{-2.6} + \ldots}\right] = (5\text{E-3})/\left[1 + \frac{3.981}{1 + 2.8314 + \ldots}\right] \tag{18.63}$$

$$(5\text{E-3})/[2.039] = 2.45\text{E-3} = 10^{-2.611}$$

Repeating the iteration results in $[\mathrm{H}^+] = 2.44\text{E-3}$, pH = 2.613. Note how close we were with the graphical value of pH = 2.6.

Amino Acids (Zwiterions)

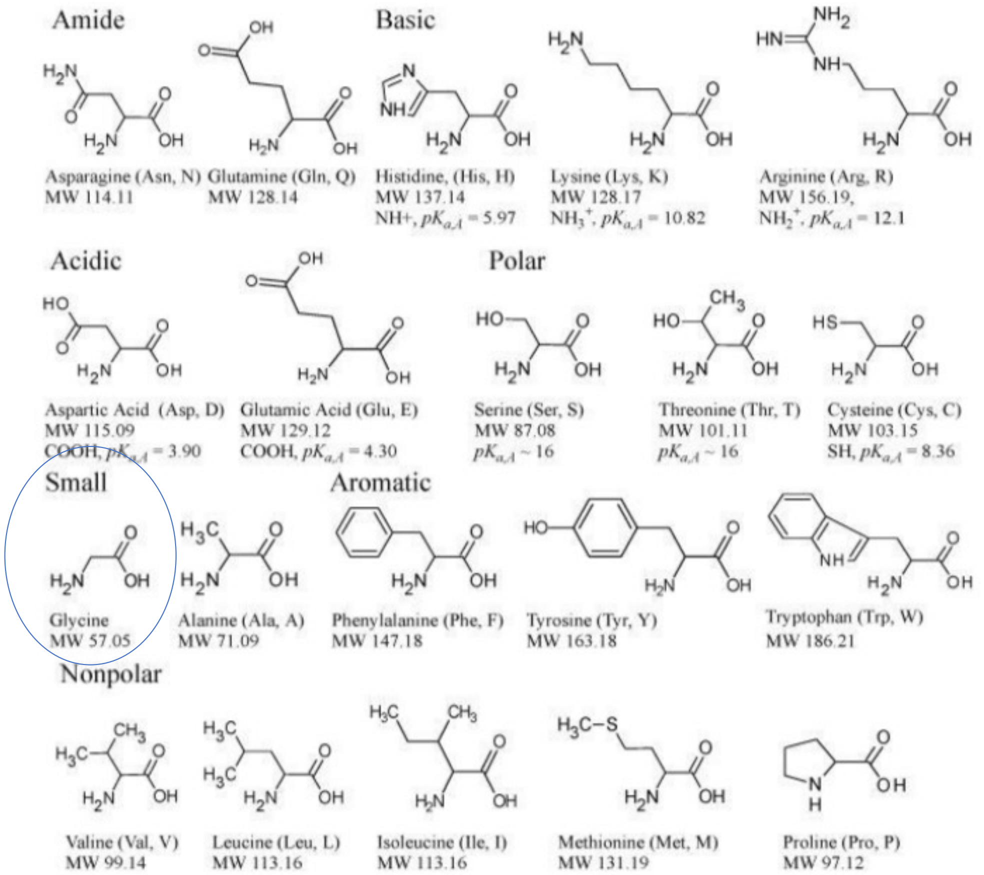


Figure 18.7. Summary of 20 amino acids encoded by the universal genetic code. The amine and carboxylic groups on the bottom of each molecule are where the amino acid is linked into the biomolecule. The acidic and basic side chains are shown uncharged.

Amino Acids (Zwiterions)

glycinium	glycine	glycinate
H_2Gly^+	HGly	Gly^-
$pH < 2.35$	$2.35 < pH < 9.78$	$pH > 9.78$

$$^+H_3NCH_2COOH \rightleftarrows {}^+H_3NCH_2COO^- \rightleftarrows H_2NCH_2COO^-$$

$$pK_{a,A} = 2.35 \qquad pK_{a,A} = 9.78$$

Figure 18.8. Dominant species for glycine at various pH levels. $pK_{a,A} = 2.35$ for the carboxylic acid and $pK_{a,A} = 9.78$ for NH_3^+. The top line shows the nomenclature and the second line shows abbreviations.

$$K_{a1} = \frac{[H^+][HGly]}{[H_2Gly^+]} \text{ or } \frac{[HGly]}{[H_2Gly^+]} = \frac{K_{a1}}{[H^+]} \qquad 18.64$$

$$K_{a2} = \frac{[H^+][Gly^-]}{[HGly]} \text{ or } \frac{[Gly^-]}{[HGly]} = \frac{K_{a2}}{[H^+]} \text{ or } \frac{[Gly^-]}{[H_2Gly^+]} = \frac{K_{a1}K_{a2}}{[H^+]^2} \qquad 18.65$$

Example 18.7. Distribution of species in glycine solution

a. Calculate the pH of a 0.1 M solution of glycine.

b. What is the distribution of species for glycine at a physiological pH of 7.4?

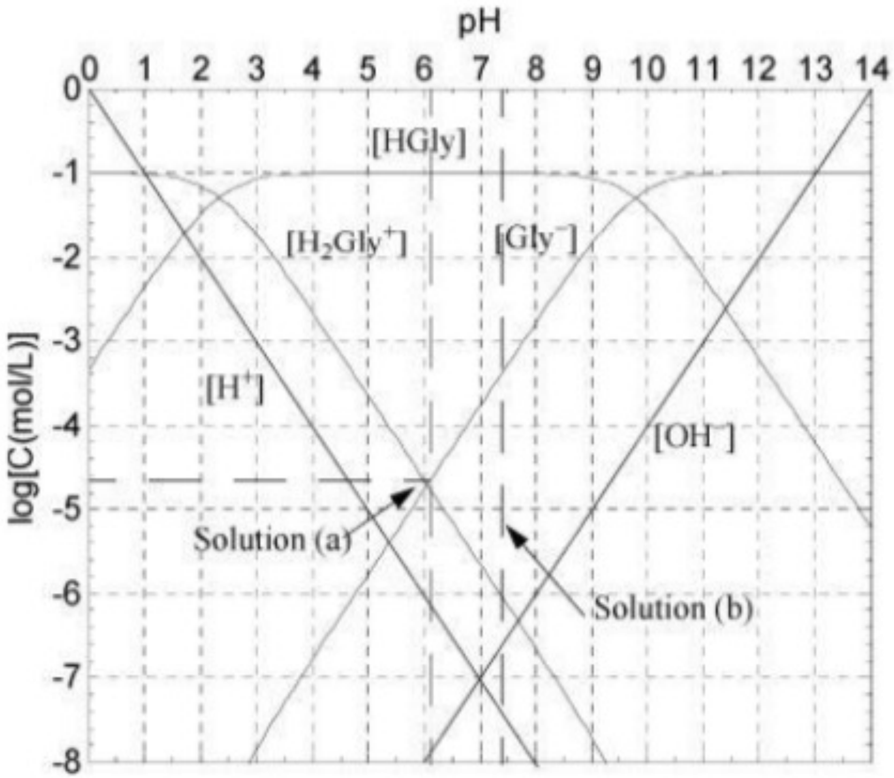


Figure 18.9. Sillèn diagram for 0.1 M glycine discussed in Example 18.7.

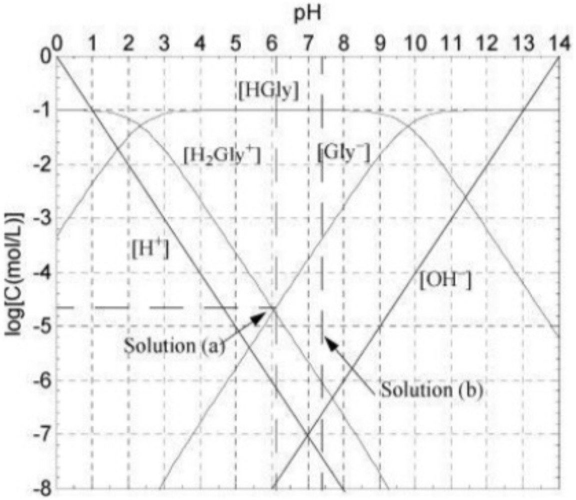
$$K_{a1} = \frac{[\mathrm{H^+}][\mathrm{HGly}]}{[\mathrm{H_2Gly^+}]} \text{ or } \frac{[\mathrm{HGly}]}{[\mathrm{H_2Gly^+}]} = \frac{K_{a1}}{[\mathrm{H^+}]} \qquad 18.64$$

$$K_{a2} = \frac{[\mathrm{H^+}][\mathrm{Gly^-}]}{[\mathrm{HGly}]} \text{ or } \frac{[\mathrm{Gly^-}]}{[\mathrm{HGly}]} = \frac{K_{a2}}{[\mathrm{H^+}]} \text{ or } \frac{[\mathrm{Gly^-}]}{[\mathrm{H_2Gly^+}]} = \frac{K_{a1}K_{a2}}{[\mathrm{H^+}]^2} \qquad 18.65$$

$$C = [\mathrm{H_2Gly^+}] + [\mathrm{HGly}] + [\mathrm{Gly^-}] = 0.1M \qquad 18.66$$

$$[\mathrm{H^+}] + [\mathrm{H_2Gly^+}] = [\mathrm{Gly^-}] + [\mathrm{OH^-}] \qquad 18.67$$

Charge balance (18.67) is reached about where 1.1[H_2Gly^+] = [Gly^-], a little above p*H* = 6



glycinium	glycine	glycinate
H_2Gly^+	HGly	Gly^-
$pH < 2.35$	$2.35 < pH < 9.78$	$pH > 9.78$

$$\mathrm{^+H_3NCH_2COOH} \rightleftarrows \mathrm{^+H_3NCH_2COO^-} \rightleftarrows \mathrm{H_2NCH_2COO^-}$$

Buffer: a salt and an acid that share a common ion

Acetic Acid and Sodium Acetate

$$[\mathrm{HA}] + [\mathrm{A}^-] = C_A + C_B \text{ and } [\mathrm{Na}^+] = C_B \quad \text{material balances} \qquad 18.69$$

$$K_{a,A} = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}] \quad \text{equilibrium} \qquad 18.70$$

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 10^{-14} \quad \text{equilibrium} \qquad 18.71$$

$$[\mathrm{Na}^+] + [\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{OH}^-] \quad \text{charge balance} \qquad 18.72$$

$$[\mathrm{A}^-] = C_B + [\mathrm{H}^+] - [\mathrm{OH}^-] \qquad 18.73$$

$$[\mathrm{HA}] = C_A - [\mathrm{H}^+] + [\mathrm{OH}^-] \qquad 18.74$$

$$[\mathrm{H}^+] = K_{a,A}\frac{C_A - [\mathrm{H}^+] + [\mathrm{OH}^-]}{C_B + [\mathrm{H}^+] - [\mathrm{OH}^-]} \qquad 18.75$$

Henderson-Hasselbalch Equation

$$[\mathrm{H}^+] \approx K_{a,A}\frac{C_A}{C_B} \text{ or } \mathrm{pH} \approx \mathrm{p}K_{a,A} - \log\frac{C_A}{C_B} = \mathrm{p}K_{a,A} + \log\frac{C_B}{C_A}$$

Buffer: a salt and an acid that share a common ion

Acetic Acid and Sodium Acetate

$$[\mathrm{HA}] + [\mathrm{A}^-] = C_A + C_B \text{ and } [\mathrm{Na}^+] = C_B \quad \text{material balances} \qquad 18.69$$

$$K_{a,A} = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}] \quad \text{equilibrium} \qquad 18.70$$

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 10^{-14} \quad \text{equilibrium} \qquad 18.71$$

$$[\mathrm{Na}^+] + [\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{OH}^-] \quad \text{charge balance} \qquad 18.72$$

$$[\mathrm{A}^-] = C_B + [\mathrm{H}^+] - [\mathrm{OH}^-] \qquad 18.73$$

$$[\mathrm{HA}] = C_A - [\mathrm{H}^+] + [\mathrm{OH}^-] \qquad 18.74$$

$$[\mathrm{H}^+] = K_{a,A}\frac{C_A - [\mathrm{H}^+] + [\mathrm{OH}^-]}{C_B + [\mathrm{H}^+] - [\mathrm{OH}^-]} \qquad 18.75$$

Better equation:

$$\mathrm{pH} \approx \mathrm{p}K_{a,A} - \log\frac{C_A - [\mathrm{H}^+]}{C_B + [\mathrm{H}^+]} \text{ (acidic p}K_{a,A}\text{) or } \mathrm{pH} \approx \mathrm{p}K_{a,A} - \log\frac{C_A + [\mathrm{OH}^-]}{C_B - [\mathrm{OH}^-]} \text{ (basic p}K_{a,A}\text{)} \; 18.77$$

Isoelectric Point

For a zwitterion like an amino acid amines protonate at neutral p*H* and carboxylic acids are deprotonated. When there is no net charge the p*H* = p*I* is the isoelectric point. Solubility is at a minimum at the isoelectric point.

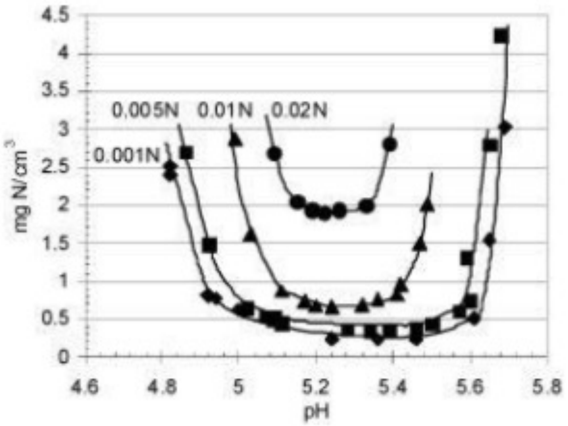


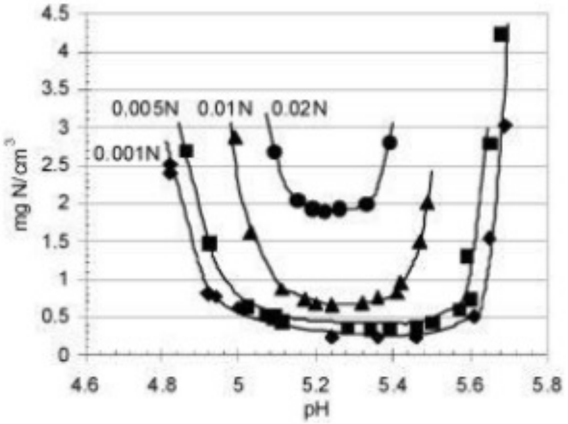
Figure 18.10. Salting in and illustration of minimum solubility at the isoelectric point for milk protein β-lactoglobulin as a function of pH and ionic strength. Gronwall, A., 1942. C.R. Trav. Lab. Carlsberg, Ser. Chim. 24:185-200.

Ionic Strength (salt concentration)

For low ionic strength, as ionic strength increases, solubility increases (salting in).

For high ionic strength, as ionic strength increases, solubility decreases (salting out).

Maximum solubility at intermediate salt concentrations.



Salting in

Figure 18.10. Salting in and illustration of minimum solubility at the isoelectric point for milk protein β-lactoglobulin as a function of pH and ionic strength. Gronwall, A., 1942. C.R. Trav. Lab. Carlsberg, Ser. Chim. 24:185-200.

Donnan Equilibria

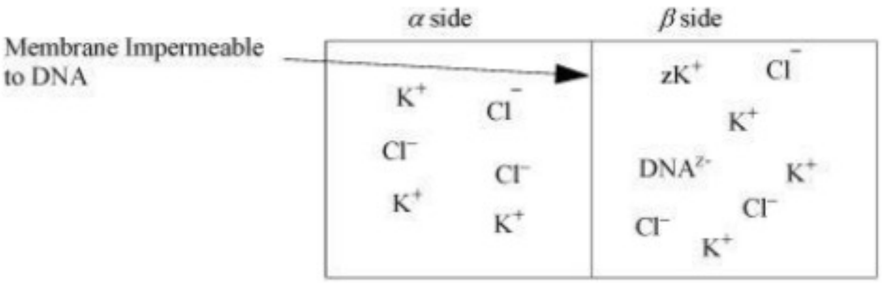


Figure 18.11. Illustration of Donnan Equilibria for DNA. DNA cannot cross the membrane. A larger concentration of ions will exist on the β side, creating higher pressure on the β side due to osmotic pressure.

$$(a_{K^+}a_{Cl^-})_\alpha = (a_{K^+}a_{Cl^-})_\beta \qquad 18.78$$

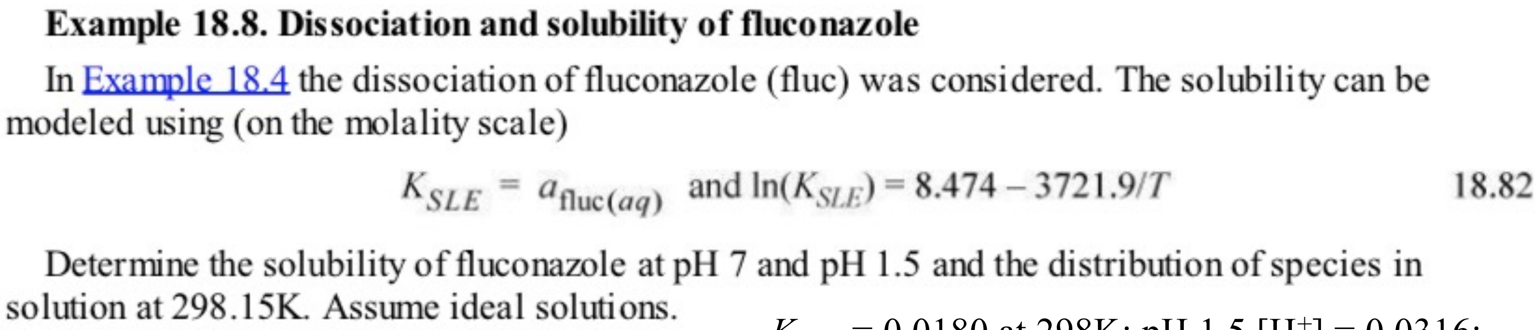
$$[K^+]_\alpha = [Cl^-]_\alpha \quad \text{and} \quad [K^+]_\beta = z[DNA^{z-}]_\beta + [Cl^-]_\beta \qquad 18.79$$

$$[K^+]_\alpha = [K^+]_\beta\left(1 - \frac{z[DNA^{z-}]}{[K^+]_\beta}\right)^{1/2} \qquad 18.80$$

$$[Cl^-]_\alpha = [Cl^-]_\beta\left(1 + \frac{z[DNA^{z-}]}{[Cl^-]_\beta}\right)^{1/2} \qquad 18.81$$

Solubility

Solubility and vapor pressure rely on equilibria with the un-ionized species.
So solubility depends on p*H*. *Remember, the activity of a solid is 1.*

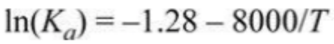


Example 18.8. Dissociation and solubility of fluconazole

In Example 18.4 the dissociation of fluconazole (fluc) was considered. The solubility can be modeled using (on the molality scale)

$$K_{SLE} = a_{\text{fluc}(aq)} \quad \text{and } \ln(K_{SLE}) = 8.474 - 3721.9/T \qquad 18.82$$

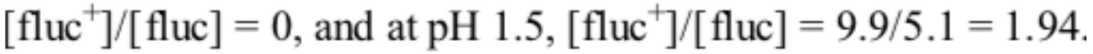
Determine the solubility of fluconazole at pH 7 and pH 1.5 and the distribution of species in solution at 298.15K. Assume ideal solutions.



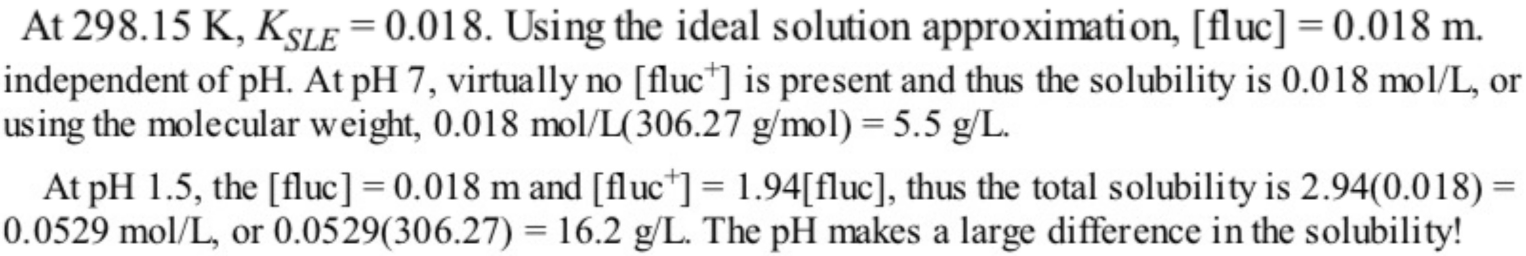
$\ln(K_a) = -1.28 - 8000/T$

K_{SLE} = 0.0180 at 298K; pH 1.5 [H$^+$] = 0.0316; pH 7 [H$^+$] = 1e-7; K_a = 6.18 e-13; pK_a = 1.8 so protonated below pH 1.8 and undissociated above pH 7

From slide 18 example 18.4



[fluc$^+$]/[fluc] = 0, and at pH 1.5, [fluc$^+$]/[fluc] = 9.9/5.1 = 1.94.



At 298.15 K, K_{SLE} = 0.018. Using the ideal solution approximation, [fluc] = 0.018 m. independent of pH. At pH 7, virtually no [fluc$^+$] is present and thus the solubility is 0.018 mol/L, or using the molecular weight, 0.018 mol/L(306.27 g/mol) = 5.5 g/L.

At pH 1.5, the [fluc] = 0.018 m and [fluc$^+$] = 1.94[fluc], thus the total solubility is 2.94(0.018) = 0.0529 mol/L, or 0.0529(306.27) = 16.2 g/L. The pH makes a large difference in the solubility!

Common ion effect

Add NaCl to a KCl saturated solution causes precipitation

$$\mathrm{KCl}_{(s)} \rightleftarrows \mathrm{K}^{+}{}_{(aq)} + \mathrm{Cl}^{-}{}_{(aq)} \quad K_{sp} = a_{\mathrm{K}^{+}} a_{\mathrm{Cl}^{-}} \tag{18.83}$$

Redox Reactions OILRIG

Lose or gain electrons

Electrochemical Cell (discharge)
Anode: $LiC_6 \rightleftarrows C_6 + Li^+ + e^-$ Oxidation (OIL)
Cathode: $CoO_2 + Li^+ + e^- \rightleftarrows LiCoO_2$ Reduction (RIG)
3.9 Volts

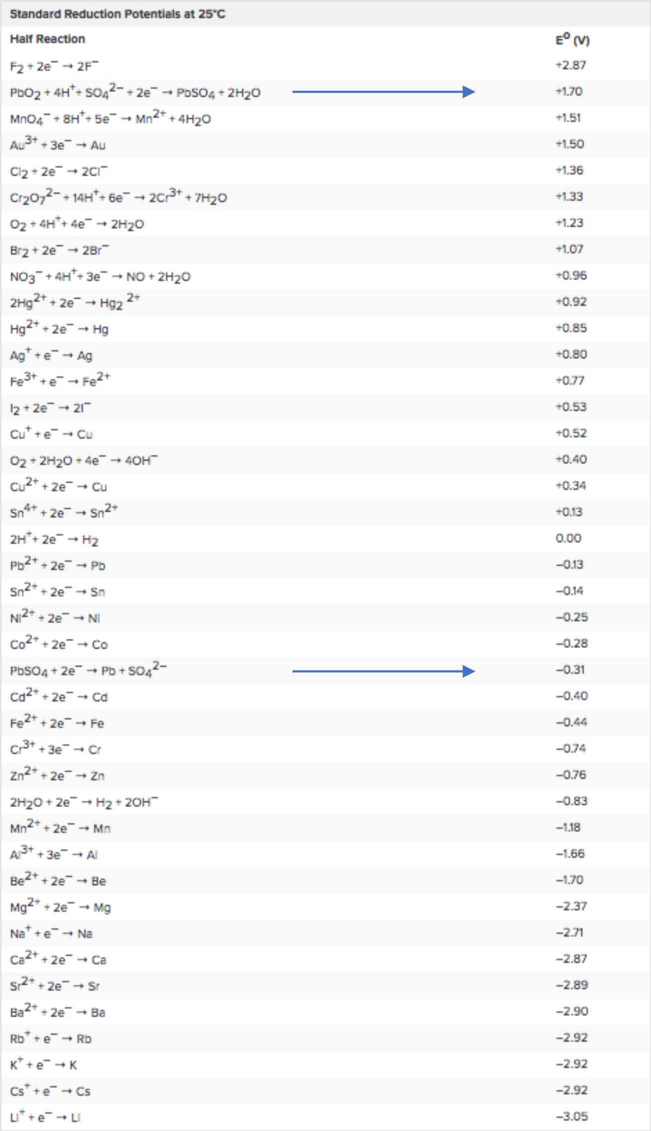
Reference voltage is platinum electrode:H_2(g) electrode at pH = 0; 298K; 1 bar

$2H^+ + 2e^- \rightleftarrows H_{2(g)}$ Reduction of H^+ Potential set to 0 as reference

$$\boxed{\Delta G^\circ = -n_e F E^\circ = -RT \ln K_a} \qquad 18.84$$

Faraday's constant 96,485 J/V, and $E^\circ = E^\circ_{red} - E^\circ_{ox}$

$$\Delta G^\circ = -n_e F E^\circ_{\text{red}} + n_e F E^\circ_{ox}$$



Standard Reduction Potentials at 25°C

Half Reaction	E^{o} (V)
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	+1.70
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51
$Au^{3+} + 3e^- \rightarrow Au$	+1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.07
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+0.96
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+0.92
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.85
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$I_2 + 2e^- \rightarrow 2I^-$	+0.53
$Cu^+ + e^- \rightarrow Cu$	+0.52
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.13
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.25
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.31
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$Be^{2+} + 2e^- \rightarrow Be$	−1.70
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Na^+ + e^- \rightarrow Na$	−2.71
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.87
$Sr^{2+} + 2e^- \rightarrow Sr$	−2.89
$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$Rb^+ + e^- \rightarrow Rb$	−2.92
$K^+ + e^- \rightarrow K$	−2.92
$Cs^+ + e^- \rightarrow Cs$	−2.92
$Li^+ + e^- \rightarrow Li$	−3.05

Redox Reactions OILRIG

$$\boxed{\Delta G^\circ = -n_e F E^\circ = -RT \ln K_a} \tag{18.84}$$

$$\Delta G^\circ = - n_e F E^\circ_{\text{red}} + n_e F E^\circ_{ox}$$

$$\Delta G = \Delta G^\circ + RT \ln \prod a_i^{v_i} \quad \text{or} \quad n_e F E = n_e F E^\circ - RT \ln \prod a_i^{v_i} \tag{18.85}$$

$$\boxed{E = E^\circ - \frac{RT}{n_e F} \ln \prod a_i^{v_i} = E^\circ - \frac{0.05916}{n_e} \log \prod a_i^{v_i}} \quad \text{Nernst equation} \tag{18.86}$$

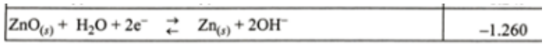
Example 18.9. Alkaline dry-cell battery

Consumer portable electronics are commonly powered by ‘alkaline’ dry-cell batteries. These cells use an alkaline paste instead of an aqueous solution. The moisture content is low to minimize leakage, and the alkaline solution is used instead of acid because the degradation of the electrodes is slower in alkali compared to acid. The relevant species are $Zn_{(s)}$, $ZnO_{(s)}$, γ-$MnO_{2(s)}$, and α-$MnOOH_{(s)}$. A new battery has $Zn_{(s)}$ and γ-$MnO_{2(s)}$ electrodes.

> **a.** Determine the balanced reactions for H^+ and then transform them to use OH^-. Then provide the balanced overall reaction. (b) Determine the voltage generated by the cell when $[OH^-] = 1$ m and $[OH^-] = 1.1$ m, and the Gibbs energy of reaction.

a. For Mn, the half-cell reduction reaction is found to be $\gamma\text{-}MnO_{2(s)} + H^+ + e^- \rightleftarrows \alpha\text{-}MnOOH_{(s)}$, through the following procedure. Start with the Mn species (MnO2 and MnOOH) on each side of the reaction (more reduced on the right). The reduction requires one electron to go from +4 to +3, so one electron is added to the left. At this point, the O is already balanced, and one H^+ is added to the left to balance hydrogen. The total charge is 0 on each side of the reaction. To convert to the base form, we add $H_2O \rightleftarrows H^+ + OH^-$, giving $\gamma\text{-}MnO_{2(s)} + H_2O + e^- \rightleftarrows \alpha\text{-}MnOOH_{(s)} + OH^-$ and the total charge is –1 on each side of the reaction.

$\gamma\text{-}MnO_{2(s)} + H_2O + e^- \rightleftarrows \alpha\text{-}MnOOH_{(s)} + OH^-$	0.30



$ZnO_{(s)} + H_2O + 2e^- \rightleftarrows Zn_{(s)} + 2OH^-$	–1.260

For the other electrode, the half-cell reduction reaction is found to be $ZnO_{(s)} + 2H^+ + 2e^- \rightleftarrows Zn_{(s)} + H_2O$ through the following procedure. After writing the Zn species on each side (more reduced on the right), we note that the reaction requires two electrons and add them to the left, water is added on the right side to balance oxygen, then $2H^+$ are added to the left side to balance H. The total charge is 0 on each side. To convert to the base form, we add $2H_2O \rightleftarrows 2H^+ + 2OH^-$, giving $ZnO_{(s)} + H_2O + 2e^- \rightleftarrows Zn_{(s)} + 2OH^-$.

For the overall reaction, to balance electrons, two Mn must be reduced for each Zn oxidized. Combining, $Zn_{(s)} + 2\gamma\text{-}MnO_{2(s)} + H_2O \rightleftarrows ZnO_{(s)} + 2\alpha\text{-}MnOOH_{(s)}$.

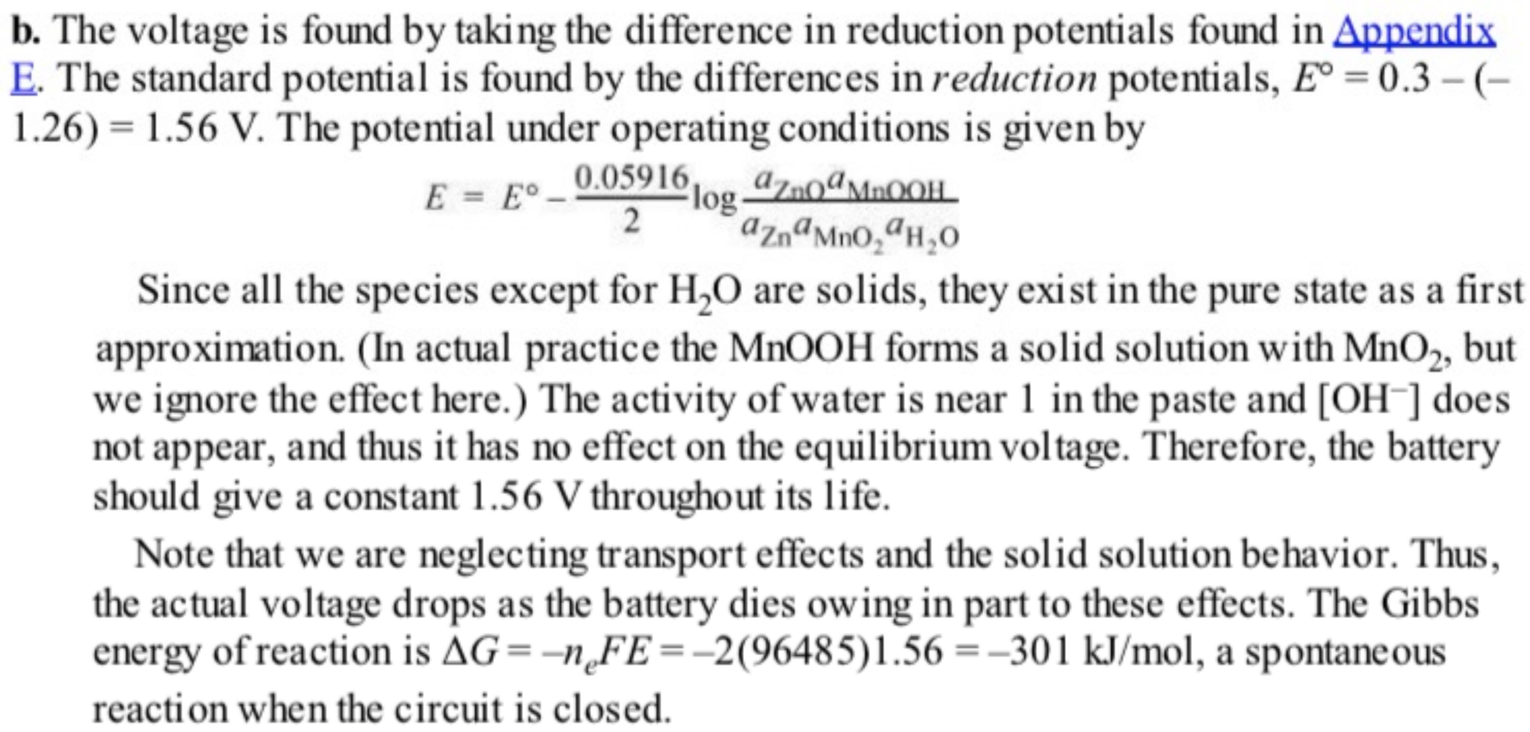
Reaction[a]	E° (volts)	dE°/dT (mV/K)
Copper		
$Cu^+ + e^- \rightleftarrows Cu_{(s)}$	0.518	–0.754
$Cu^{2+} + 2e^- \rightleftarrows Cu_{(s)}$	0.339	0.011
$Cu^{2+} + e^- \rightleftarrows Cu^+$	0.161	0.776
$Cu(OH)_{2(s)} + 2e^- \rightleftarrows Cu_{(s)} + 2OH^-$	–0.222	
Hydrogen		
$2H^+ + 2e^- \rightleftarrows H_{2(g)}$	0.000	0
$H_2O + e^- \rightleftarrows \frac{1}{2}H_{2(g)} + OH^-$	–0.8280	–0.8360
Iron		
$FeO_4^{2-} + 3H_2O + 3e^- \rightleftarrows FeOOH_{(s)} + 5OH^-$	0.80	–1.59
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	0.771	1.175
$FeOOH_{(s)} + 3H^+ + e^- \rightleftarrows Fe^{2+} + 2H_2O$	0.74	–1.05
$Fe(glutamate)^{3+} + e^- \rightleftarrows Fe(glutamate)^{2+}$	0.240	
$FeOH^+ + H^+ + 2e^- \rightleftarrows Fe_{(s)} + H_2O$	–0.16	0.07
$Fe^{2+} + e^- \rightleftarrows Fe_{(s)}$	–0.44	0.07
$FeCO_{3(s)} + 2e^- \rightleftarrows Fe_{(s)} + CO_3^{2-}$	–0.756	–1.293
Lead		
$PbO_{2(s)} + 4H^+ + 2e^- \rightleftarrows Pb^{2+} + 2H_2O$	1.458	–0.253
$3PbO_{2(s)} + 2H_2O + 4e^- \rightleftarrows Pb_3O_{4(s)} + 4OH^-$	0.269	–1.136
$Pb_3O_{4(s)} + H_2O + 2e^- \rightleftarrows 3PbO_{(s,red)} + 2OH^-$	0.224	–1.211
$Pb_3O_{4(s)} + H_2O + 2e^- \rightleftarrows 3PbO_{(s,yellow)} + 2OH^-$	0.207	–1.177
$Pb^{2+} + 2e^- \rightleftarrows Pb_{(s)}$	–0.126	–0.395
Manganese		
$MnO_4^- + 4H^+ + 3e^- \rightleftarrows \beta\text{-}MnO_{2(s)} + 2H_2O$	1.692	–0.671
$Mn^{3+} + e^- \rightleftarrows Mn^{2+}$	1.56	1.8
$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 2H_2O$	1.507	–0.646
$Mn_2O_{3(s)} + 6H^+ + 2e^- \rightleftarrows 2Mn^{2+} + 3H_2O$	1.485	–0.926
$\beta\text{-}MnO_{2(s)} + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$	1.23	–0.609
$MnO_4^- + e^- \rightleftarrows MnO_4^{2-}$	0.56	–2.05
$\gamma\text{-}MnO_{2(s)} + H_2O + e^- \rightleftarrows \alpha\text{-}MnOOH_{(s)} + OH^-$	0.30	
$3Mn_2O_{3(s)} + H_2O + 2e^- \rightleftarrows 2Mn_3O_{4(s)} + 2OH^-$	0.002	–1.256
$Mn_3O_{4(s)} + 4H_2O + 2e^- \rightleftarrows 3Mn(OH)_{2(s)} + 2OH^-$	–0.352	–1.61
$Mn^{2+} + 2e^- \rightleftarrows Mn_{(s)}$	–1.182	–1.129
$Mn(OH)_{2(s)} + 2e^- \rightleftarrows Mn_{(s)}$	–1.565	–1.10
Oxygen		
$O_{3(g)} + 2H^+ + 2e^- \rightleftarrows O_{2(g)} + H_2O$	2.075	–0.489
$H_2O_{2(g)} + 2H^+ + 2e^- \rightleftarrows 2H_2O$	1.763	–0.698
$\frac{1}{2}O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O$	1.2291	–0.8456
$O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O_2$	0.695	–0.993
Ruthenium		
$RuO_{4(s)} + H_2O \rightleftarrows H_2RuO_5$ $\quad \log[H_2RuO_5] = -0.88$		
$RuO_4^{2-} + 4H^+ + 2e^- \rightleftarrows RuO_{2(s)} + 2H_2O$	2.005	
$RuO_4^- + 4H^+ + 3e^- \rightleftarrows RuO_{2(s)} + 2H_2O$	1.533	
$H_2RuO_5 + 4H^+ + 4e^- \rightleftarrows RuO_{2(s)} + 3H_2O$	1.40	
$RuO_{4(s)} + 4H^+ + 4e^- \rightleftarrows RuO_{2(s)} + 2H_2O$	1.387	
$H_2RuO_5 + e^- \rightleftarrows RuO_4^- + H_2O$	1.001	
$RuO_4^- + e^- \rightleftarrows RuO_4^{2-}$	0.589	
Zinc		
$ZnOH^+ + H^+ + 2e^- \rightleftarrows Zn_{(s)} + H_2O$	–0.497	0.03
$Zn^{2+} + 2e^- \rightleftarrows Zn_{(s)}$	–0.762	0.119
$Zn(OH)_3^- + 2e^- \rightleftarrows Zn_{(s)} + 3OH^-$	–1.183	
$Zn(OH)_4^{2-} + 2e^- \rightleftarrows Zn_{(s)} + 4OH^-$	–1.199	
$Zn(OH)_{2(s)} + 2e^- \rightleftarrows Zn_{(s)} + 2OH^-$	–1.249	
$ZnO_{(s)} + H_2O + 2e^- \rightleftarrows Zn_{(s)} + 2OH^-$	–1.260	

a. Most values from Harris, D.C. 2007. *Quantitative Chemical Analysis*. 7th ed., New York NY: W.H. Freeman. A good source for more values is Bratsch, S.G. 1989. *J. Chem. Ref. Data* 18:1, available at www.nist.gov/data/PDFfiles/jperd355.pdf (Oct 2011), and Bard, A.J., Parsons, R., Jordan, J. 1985. *Standard Potentials in Aqueous Solution*, New York: Marcel Dekker.

E.8 BIOCHEMICAL DATA

Standard state for soluble species is an ideal solution at 1 M except for water, which is relative to the Lewis-Randall standard state. The data are for the untransformed Gibbs energies and enthalpies.

Name[a]	$\Delta G^o_{f,298.15}$ (kJ/mol)	$\Delta H^o_{f,298.15}$ (kJ/mol)	z_i	N_H	N_{Mg}
NADox	0	0	–1	26	0
NADred	22.65	–31.94	–2	27	0
ATP^{4-}	–2768.1	–3619.21	–4	12	0
ATP^{3-}	–2811.48	–3612.91	–3	13	0
ATP^{2-}	–2838.18	–3627.91	–2	14	0
$MgATP^{2-}$	–3258.68	–4063.31	–2	12	1
$MgHATP^{1-}$	–3287.5	–4063.01	–1	13	1
Mg_2ATP	–3729.33	–4519.51	0	12	2



b. The voltage is found by taking the difference in reduction potentials found in Appendix E. The standard potential is found by the differences in *reduction* potentials, $E° = 0.3 - (-1.26) = 1.56$ V. The potential under operating conditions is given by

$$E = E° - \frac{0.05916}{2} \log \frac{a_{\text{ZnO}} a_{\text{MnOOH}}}{a_{\text{Zn}} a_{\text{MnO}_2} a_{\text{H}_2\text{O}}}$$

Since all the species except for H_2O are solids, they exist in the pure state as a first approximation. (In actual practice the MnOOH forms a solid solution with MnO_2, but we ignore the effect here.) The activity of water is near 1 in the paste and $[OH^-]$ does not appear, and thus it has no effect on the equilibrium voltage. Therefore, the battery should give a constant 1.56 V throughout its life.

Note that we are neglecting transport effects and the solid solution behavior. Thus, the actual voltage drops as the battery dies owing in part to these effects. The Gibbs energy of reaction is $\Delta G = -n_e FE = -2(96485)1.56 = -301$ kJ/mol, a spontaneous reaction when the circuit is closed.

Bioprocess Engineering (Fermentation)

Degree of Reduction

$\gamma_{red} = (4f + a - 2b - 3c + 6d + 5e)/f$ carbon-containing 18.88

$C_fH_aO_b + rO_2 \rightleftarrows fCO_2 + \frac{a}{2}H_2O$ 18.87

Stoichiometry $r = f + a/4 - b/2.$

Oxidation State
O2 is 0; in products is -2
Moles of electrons transferred to oxygen

$$4r = 4f + a - 2b.$$

The degree of reduction multipliers are +4 for C; +1 for H; -2 for O; -3 for N (ammonia); +6 for S (H_2SO_4); +5 for P (phosphoric acid)

Reaction of acetaldehyde C_2H_4O Degree of reduction 2(4)+4(1)+1(-2)=10 *or* 5 per carbon.
To determine *r* for O_2, 2*r*(-2) = -10 so r = -2.5 to yield zero on the left of 18.88
On the right of 18.88, For CO_2, 1(4)+2(-2) = 0 and for H_2O, 2(1)+1(-2) = 0
Two sides balance

An average elemental formula for cell mass is $CH_{1.8}O_{0.5}N_{0.2}$, with a degree of reduction of 4.2 per *C*-mole, slightly higher than glucose. For compounds not containing carbon, the degree of reduction is expressed per mole of that compound. For the compound $H_aO_bN_cS_dP_e$,

$$\gamma_{\text{red}} = (a - 2b - 3c + 6d + 5e) \qquad \text{not carbon-containing} \tag{18.89}$$

A fermentation can be represented with a pseudo-reaction, balancing inputs and outputs. For example, on the basis of one *C*-mole of substrate $CH_aO_bN_cS_d$,

$$CH_aO_bN_cS_d + Y_o(O_2) + Y_n(NH_3) + Y_{aux}(CH_e\ O_fN_gS_h) \rightarrow Y_{biomass}(CH_iO_jN_kS_l) + Y_{product}(CH_m\ O_nN_pS_q) + Y_{CO_2}(CO_2) + Y_w(H_2O) + Y_S(H_2SO_4)$$

where the *Y* values on the left are for the nutrients and on the right are for the products and by-products. The number of moles for each species is the value of the corresponding coefficient *Y*.

Biological Equilibrium Reactions

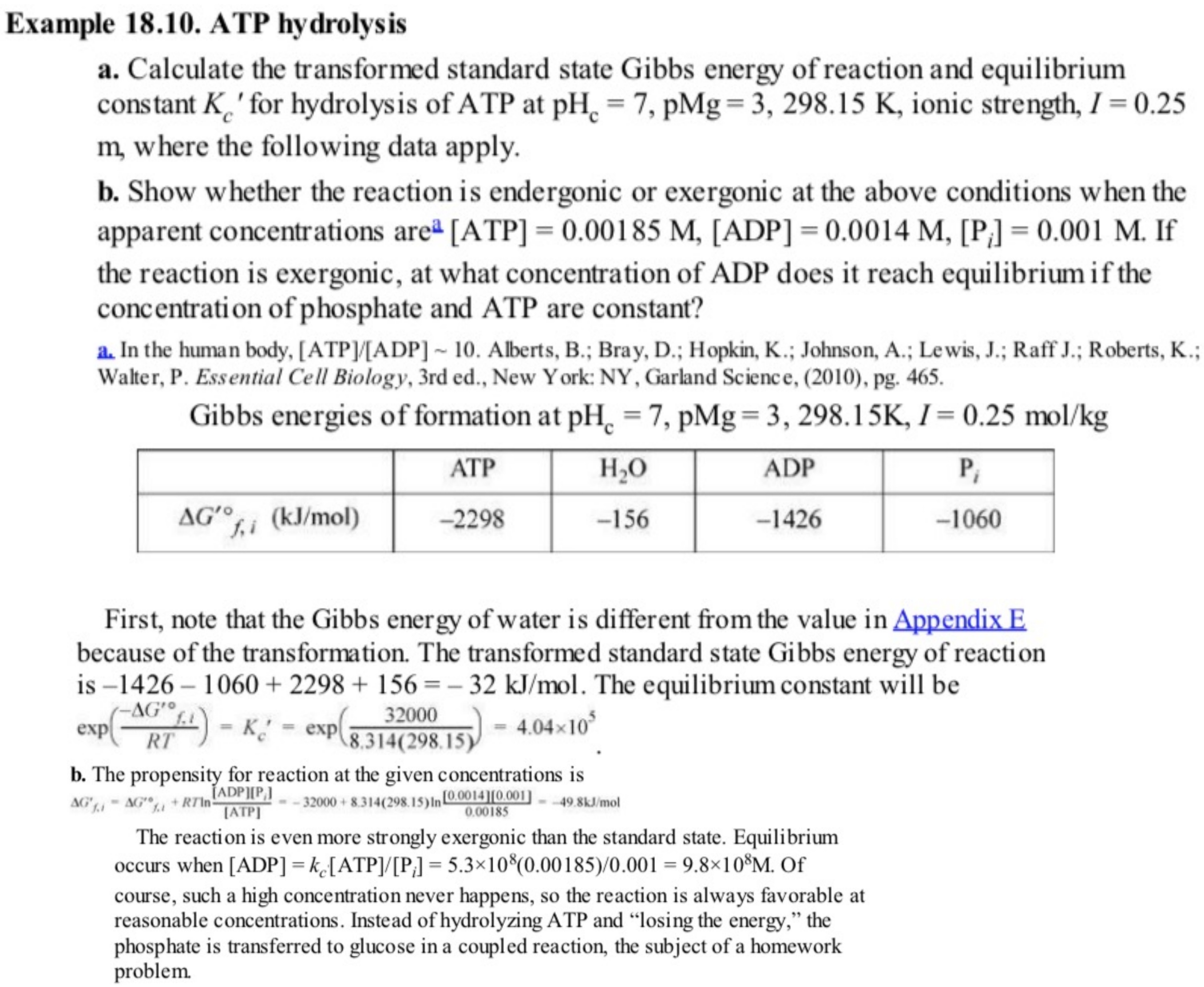
Reactions occur with a buffer so $[H^+]$ is ignored (indicated by prime)

$$ATP + H_2O \rightleftarrows ADP + H_3PO_4 \qquad \text{or} \qquad ATP + H_2O \rightleftarrows ADP + P_i \tag{18.94}$$

$$\boxed{\Delta G' = \Delta G'^{\circ} + RT \ln \prod_i [i]^{\nu_i} \qquad \Delta G'^{\circ} = -RT \ln K_c'} \tag{18.93}$$

$$K_c' = \frac{[ADP][P_i]}{[ATP]} = \exp\left(\frac{\Delta G'^{\circ}_{f,\,ADP} + \Delta G'^{\circ}_{f,\,P_i} - \Delta G'^{\circ}_{f,\,ATP} - \Delta G'^{\circ}_{f,\,H_2O}}{RT}\right) \tag{18.95}$$

Water is pure so activity is 1



Example 18.10. ATP hydrolysis

a. Calculate the transformed standard state Gibbs energy of reaction and equilibrium constant K_c' for hydrolysis of ATP at $\mathrm{pH_c} = 7$, pMg = 3, 298.15 K, ionic strength, $I = 0.25$ m, where the following data apply.

b. Show whether the reaction is endergonic or exergonic at the above conditions when the apparent concentrations are[a] [ATP] = 0.00185 M, [ADP] = 0.0014 M, $[\mathrm{P}_i] = 0.001$ M. If the reaction is exergonic, at what concentration of ADP does it reach equilibrium if the concentration of phosphate and ATP are constant?

[a] In the human body, [ATP]/[ADP] ~ 10. Alberts, B.; Bray, D.; Hopkin, K.; Johnson, A.; Lewis, J.; Raff J.; Roberts, K.; Walter, P. *Essential Cell Biology*, 3rd ed., New York: NY, Garland Science, (2010), pg. 465.

Gibbs energies of formation at $\mathrm{pH_c} = 7$, pMg = 3, 298.15K, $I = 0.25$ mol/kg

	ATP	H_2O	ADP	P_i
$\Delta G'^{\circ}_{f,i}$ (kJ/mol)	–2298	–156	–1426	–1060

First, note that the Gibbs energy of water is different from the value in Appendix E because of the transformation. The transformed standard state Gibbs energy of reaction is –1426 – 1060 + 2298 + 156 = – 32 kJ/mol. The equilibrium constant will be

$$\exp\left(\frac{-\Delta G'^{\circ}_{f,i}}{RT}\right) = K_c' = \exp\left(\frac{32000}{8.314(298.15)}\right) = 4.04\times10^5$$

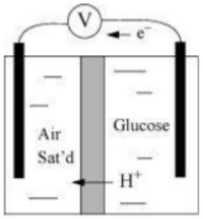
b. The propensity for reaction at the given concentrations is

$$\Delta G'_{f,i} = \Delta G'^{\circ}_{f,i} + RT\ln\frac{[\mathrm{ADP}][\mathrm{P}_i]}{[\mathrm{ATP}]} = -32000 + 8.314(298.15)\ln\frac{[0.0014][0.001]}{0.00185} = -49.8\,\mathrm{kJ/mol}$$

The reaction is even more strongly exergonic than the standard state. Equilibrium occurs when $[\mathrm{ADP}] = k_c[\mathrm{ATP}]/[\mathrm{P}_i] = 5.3\times10^8(0.00185)/0.001 = 9.8\times10^8$M. Of course, such a high concentration never happens, so the reaction is always favorable at reasonable concentrations. Instead of hydrolyzing ATP and "losing the energy," the phosphate is transferred to glucose in a coupled reaction, the subject of a homework problem.

Example 18.11. Biological fuel cell

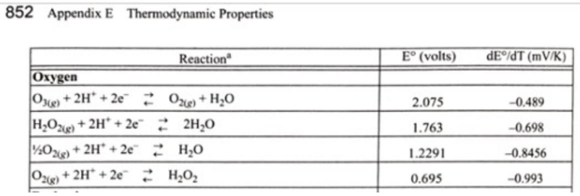
A biological fuel cell is a portable electrical source that can be refueled. Electrical current is generated by a biological redox couple. In an ideal fuel cell, the enzymes would be immobilized on the electrodes and maintain the same activity as if free. In the conceptualized fuel cell on the right, glucose is to be oxidized to gluconolactone in the right cell, catalyzed by immobilized glucose oxidase. Oxygen is excluded from the right cell to avoid loss of electrons by bulk oxidation. The left cell is saturated with air, and a reduction of O_2 to H_2O_2 catalyzed by immobilized laccase is envisioned. Electrons are to flow through the external circuit and H^+ is to flow through the membrane. Each side of the cell is buffered to $pH_c = 7$, $I = 0.25$ M at $T = 298.15$ K. Suppose the concentrations on the right side are [glucose] = 0.1 M, [gluconolactone] = 0.05 M, and on the left side $[H_2O_2] = 0.05$ M. Determine the transformed standard state half-cell potentials and the voltage expected from the cell under stated concentrations. The standard state Gibbs energies of relevant species are shown below at the stated conditions.



	$H_2O_{2(aq)}$	Glucose	Gluconolactone
$\Delta G'^{\circ}_{f,i}$ (kJ/mol)	–52	–427	–496

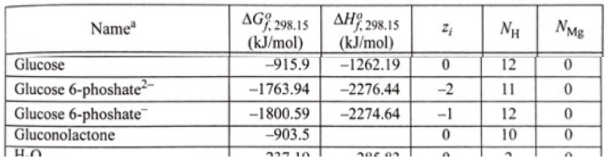
$$\text{glucose} \rightleftarrows \text{gluconolactone} + 2H^+ + 2e^-,$$

$$O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O_{2(aq)}$$

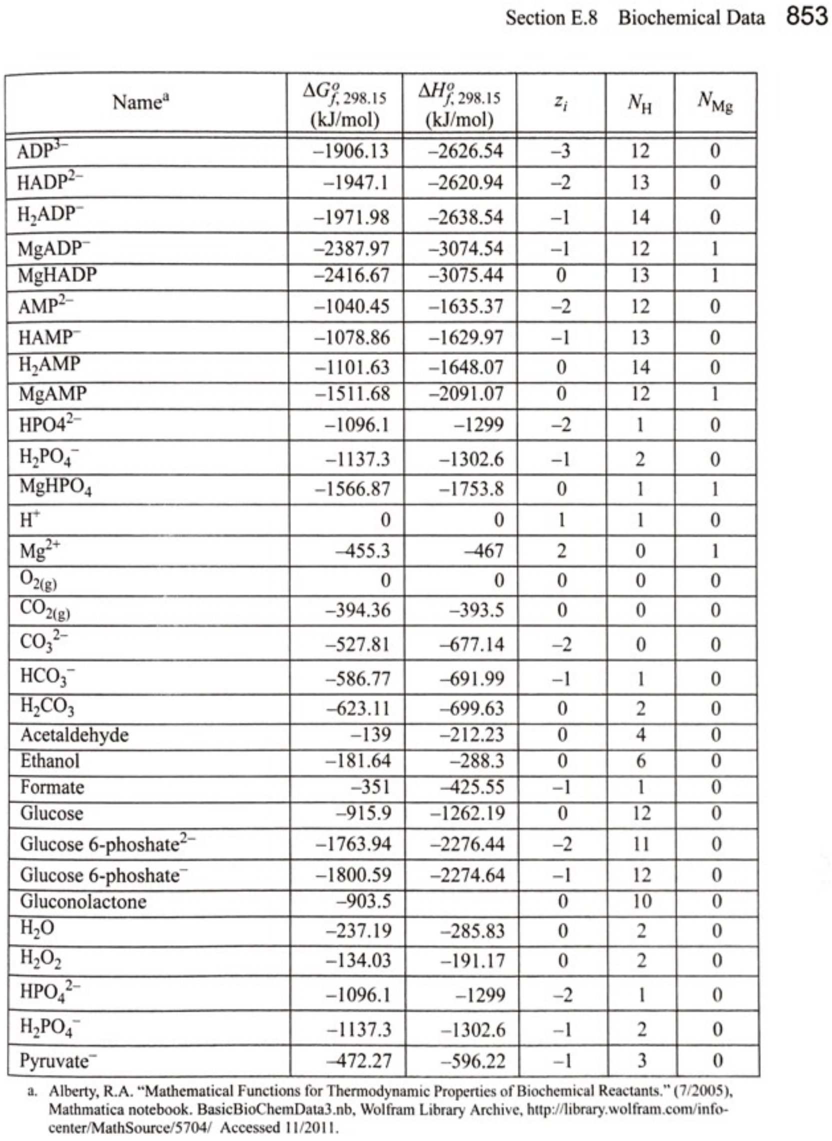


852 Appendix E Thermodynamic Properties

Reaction[a]	E° (volts)	dE°/dT (mV/K)
Oxygen		
$O_{3(g)} + 2H^+ + 2e^- \rightleftarrows O_{2(g)} + H_2O$	2.075	–0.489
$H_2O_{2(g)} + 2H^+ + 2e^- \rightleftarrows 2H_2O$	1.763	–0.698
$\frac{1}{2}O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O$	1.2291	–0.8456
$O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O_2$	0.695	–0.993

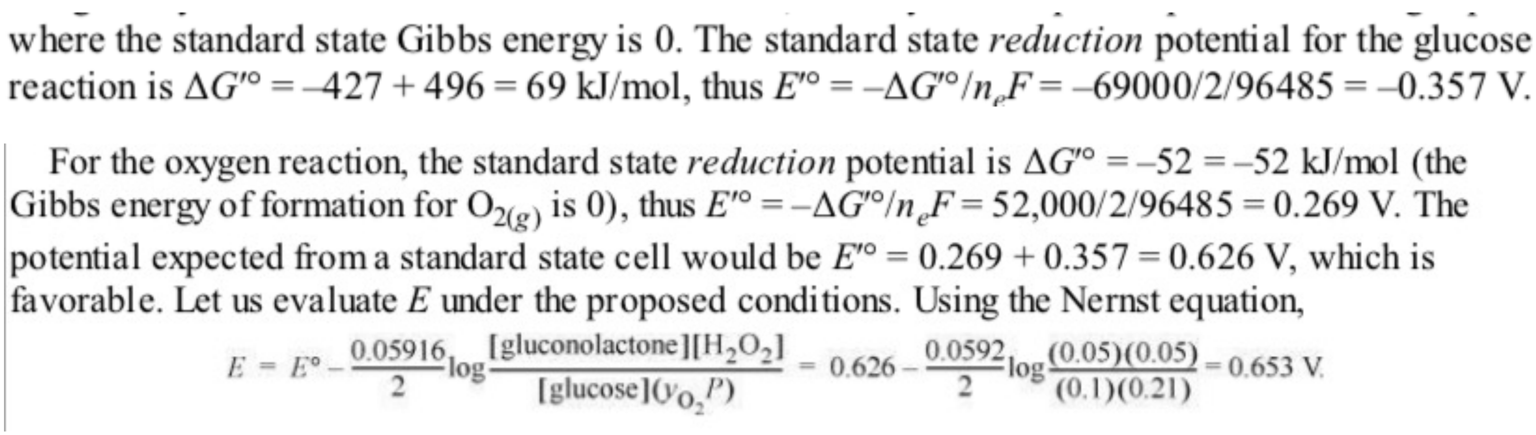


Name[a]	$\Delta G^o_{f,298.15}$ (kJ/mol)	$\Delta H^o_{f,298.15}$ (kJ/mol)	z_i	N_H	N_{Mg}
Glucose	–915.9	–1262.19	0	12	0
Glucose 6-phoshate^{2-}	–1763.94	–2276.44	–2	11	0
Glucose 6-phoshate$^-$	–1800.59	–2274.64	–1	12	0
Gluconolactone	–903.5		0	10	0



Name[a]	$\Delta G^o_{f,\,298.15}$ (kJ/mol)	$\Delta H^o_{f,\,298.15}$ (kJ/mol)	z_i	N_H	N_{Mg}
ADP^{3-}	–1906.13	–2626.54	–3	12	0
$HADP^{2-}$	–1947.1	–2620.94	–2	13	0
H_2ADP^-	–1971.98	–2638.54	–1	14	0
$MgADP^-$	–2387.97	–3074.54	–1	12	1
MgHADP	–2416.67	–3075.44	0	13	1
AMP^{2-}	–1040.45	–1635.37	–2	12	0
$HAMP^-$	–1078.86	–1629.97	–1	13	0
H_2AMP	–1101.63	–1648.07	0	14	0
MgAMP	–1511.68	–2091.07	0	12	1
$HPO4^{2-}$	–1096.1	–1299	–2	1	0
$H_2PO_4^-$	–1137.3	–1302.6	–1	2	0
$MgHPO_4$	–1566.87	–1753.8	0	1	1
H^+	0	0	1	1	0
Mg^{2+}	–455.3	–467	2	0	1
$O_{2(g)}$	0	0	0	0	0
$CO_{2(g)}$	–394.36	–393.5	0	0	0
CO_3^{2-}	–527.81	–677.14	–2	0	0
HCO_3^-	–586.77	–691.99	–1	1	0
H_2CO_3	–623.11	–699.63	0	2	0
Acetaldehyde	–139	–212.23	0	4	0
Ethanol	–181.64	–288.3	0	6	0
Formate	–351	–425.55	–1	1	0
Glucose	–915.9	–1262.19	0	12	0
Glucose 6-phoshate^{2-}	–1763.94	–2276.44	–2	11	0
Glucose 6-phoshate$^-$	–1800.59	–2274.64	–1	12	0
Gluconolactone	–903.5		0	10	0
H_2O	–237.19	–285.83	0	2	0
H_2O_2	–134.03	–191.17	0	2	0
HPO_4^{2-}	–1096.1	–1299	–2	1	0
$H_2PO_4^-$	–1137.3	–1302.6	–1	2	0
Pyruvate$^-$	–472.27	–596.22	–1	3	0

a. Alberty, R.A. "Mathematical Functions for Thermodynamic Properties of Biochemical Reactants." (7/2005), Mathmatica notebook. BasicBioChemData3.nb, Wolfram Library Archive, http://library.wolfram.com/infocenter/MathSource/5704/ Accessed 11/2011.

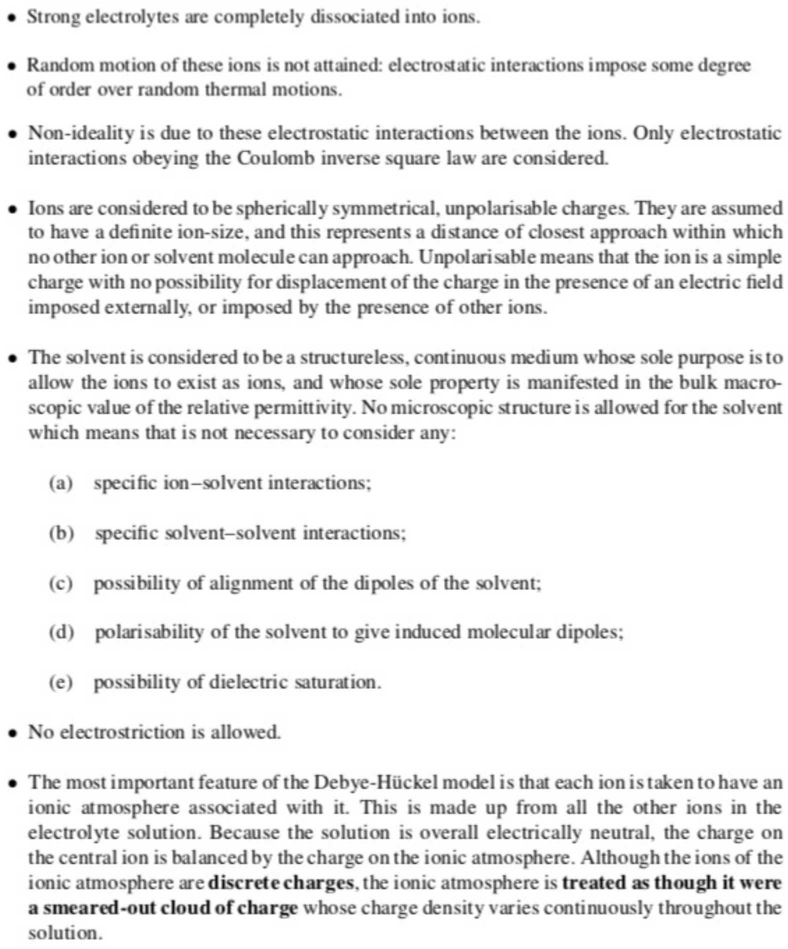


where the standard state Gibbs energy is 0. The standard state *reduction* potential for the glucose reaction is $\Delta G'^{\circ} = -427 + 496 = 69$ kJ/mol, thus $E'^{\circ} = -\Delta G'^{\circ}/n_eF = -69000/2/96485 = -0.357$ V.

For the oxygen reaction, the standard state *reduction* potential is $\Delta G'^{\circ} = -52 = -52$ kJ/mol (the Gibbs energy of formation for $O_{2(g)}$ is 0), thus $E'^{\circ} = -\Delta G'^{\circ}/n_eF = 52{,}000/2/96485 = 0.269$ V. The potential expected from a standard state cell would be $E'^{\circ} = 0.269 + 0.357 = 0.626$ V, which is favorable. Let us evaluate E under the proposed conditions. Using the Nernst equation,

$$E = E^{\circ} - \frac{0.05916}{2}\log\frac{[\text{gluconolactone}][\text{H}_2\text{O}_2]}{[\text{glucose}](y_{\text{O}_2}P)} = 0.626 - \frac{0.0592}{2}\log\frac{(0.05)(0.05)}{(0.1)(0.21)} = 0.653\text{ V.}$$

Debye-Hückel Model



- Strong electrolytes are completely dissociated into ions.
- Random motion of these ions is not attained: electrostatic interactions impose some degree of order over random thermal motions.
- Non-ideality is due to these electrostatic interactions between the ions. Only electrostatic interactions obeying the Coulomb inverse square law are considered.
- Ions are considered to be spherically symmetrical, unpolarisable charges. They are assumed to have a definite ion-size, and this represents a distance of closest approach within which no other ion or solvent molecule can approach. Unpolarisable means that the ion is a simple charge with no possibility for displacement of the charge in the presence of an electric field imposed externally, or imposed by the presence of other ions.
- The solvent is considered to be a structureless, continuous medium whose sole purpose is to allow the ions to exist as ions, and whose sole property is manifested in the bulk macroscopic value of the relative permittivity. No microscopic structure is allowed for the solvent which means that is not necessary to consider any:

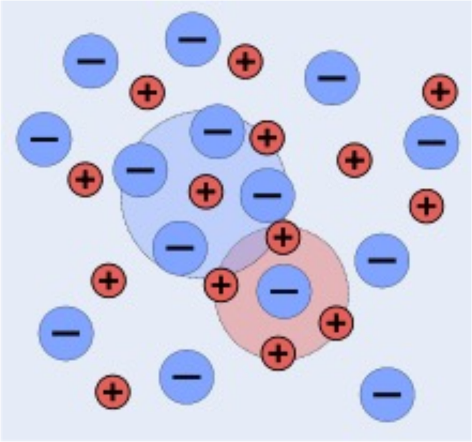
  (a) specific ion–solvent interactions;

  (b) specific solvent–solvent interactions;

  (c) possibility of alignment of the dipoles of the solvent;

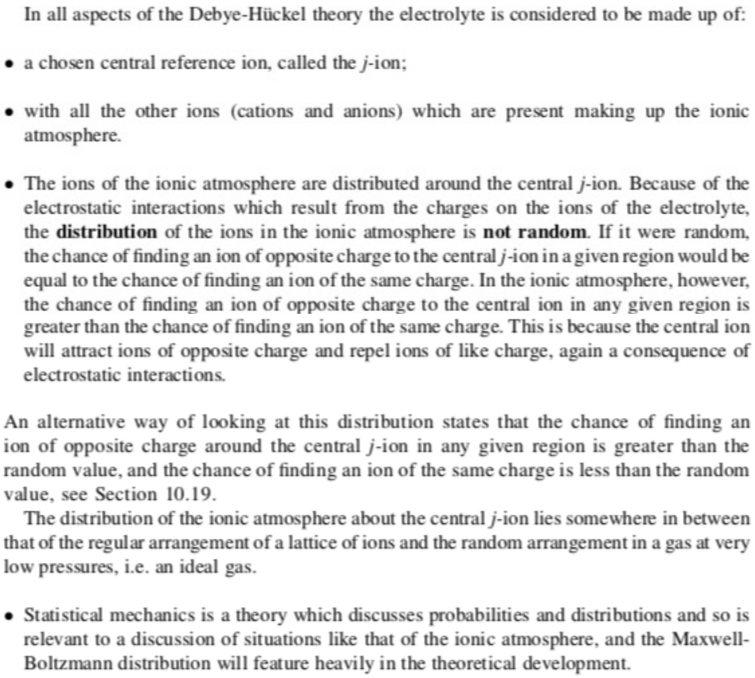
  (d) polarisability of the solvent to give induced molecular dipoles;

  (e) possibility of dielectric saturation.
- No electrostriction is allowed.
- The most important feature of the Debye-Hückel model is that each ion is taken to have an ionic atmosphere associated with it. This is made up from all the other ions in the electrolyte solution. Because the solution is overall electrically neutral, the charge on the central ion is balanced by the charge on the ionic atmosphere. Although the ions of the ionic atmosphere are **discrete charges**, the ionic atmosphere is **treated as though it were a smeared-out cloud of charge** whose charge density varies continuously throughout the solution.



Mean field

Debye-Hückel Model



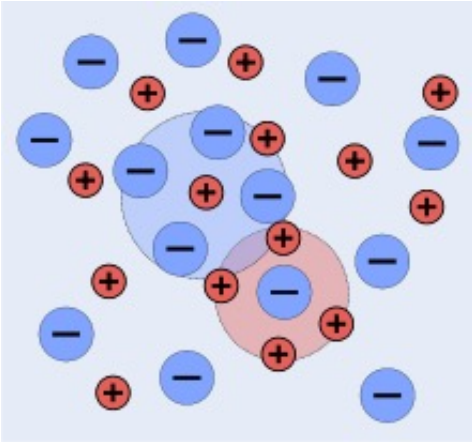
In all aspects of the Debye-Hückel theory the electrolyte is considered to be made up of:

- a chosen central reference ion, called the *j*-ion;
- with all the other ions (cations and anions) which are present making up the ionic atmosphere.
- The ions of the ionic atmosphere are distributed around the central *j*-ion. Because of the electrostatic interactions which result from the charges on the ions of the electrolyte, the **distribution** of the ions in the ionic atmosphere is **not random**. If it were random, the chance of finding an ion of opposite charge to the central *j*-ion in a given region would be equal to the chance of finding an ion of the same charge. In the ionic atmosphere, however, the chance of finding an ion of opposite charge to the central ion in any given region is greater than the chance of finding an ion of the same charge. This is because the central ion will attract ions of opposite charge and repel ions of like charge, again a consequence of electrostatic interactions.

An alternative way of looking at this distribution states that the chance of finding an ion of opposite charge around the central *j*-ion in any given region is greater than the random value, and the chance of finding an ion of the same charge is less than the random value, see Section 10.19.

The distribution of the ionic atmosphere about the central *j*-ion lies somewhere in between that of the regular arrangement of a lattice of ions and the random arrangement in a gas at very low pressures, i.e. an ideal gas.

- Statistical mechanics is a theory which discusses probabilities and distributions and so is relevant to a discussion of situations like that of the ionic atmosphere, and the Maxwell-Boltzmann distribution will feature heavily in the theoretical development.



Coulomb's Law

$$\text{force} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0\varepsilon_r r^2} \qquad (10.2)$$

$$w = \int_a^b f\,\mathrm{d}r$$

Work to place an ion in a solution of other ions

$$\text{potential energy} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0\varepsilon_r}\frac{1}{r}$$

Debye-Hückel Model

$$\frac{G^E}{RT} = \frac{-4x_s M_{w,s} A_\gamma}{1000(Ba)^3}\left[\ln(1 + Ba\sqrt{I}) - Ba\sqrt{I} + \frac{(Ba)^2 I}{2}\right] \qquad 18.102$$

$$\text{where } A_\gamma = \frac{N_A^2}{8\pi}\left(\frac{e^2}{\varepsilon_o \varepsilon_r RT}\right)^{3/2} \frac{(2000\rho_s)^{1/2}}{2.303} = \frac{1.8249\text{E}6(\rho_s)^{1/2}}{(\varepsilon_r T)^{3/2}} \qquad 18.103$$

$$\text{and } A_\gamma = 0.510(\text{kg/mol})^{1/2} \text{ for water at 25°C} \qquad 18.104$$

$$\text{ionic strength } I = 0.5\sum_{\text{ions}} m_i z_i^2 \qquad 18.105$$

where $e = 1.60218\text{E}{-19}$ C, $\varepsilon_o = 8.85419\text{E}{-12}$ $\text{C}^2\ \text{N}^{-1}\ \text{m}^{-2}$ is the permittivity of vacuum, ε_r is the dielectric constant or relative permittivity of the solvent, R is the gas constant in J/mol-K, T is the temperature in K, ρ_s is the density of the solvent in g/cm^3, z_i is the valence of the Coulombic charge on each ion type, and I is the ionic strength which characterizes the overall charges in the charge

of temperature are provided in Appendix E. The parameter a represents the average distance of closest approach, which is larger than the ion size due to water hydration which is always present. The term $1/(BI^{1/2})$ is an approximate distance known as the screening, shielding, or Debye length. It represents the screening of the coulombic potential due to the presence of other ions. A common assumption is $Ba = 1$ (kg/mol)$^{1/2}$, though in biological systems, $Ba = 1.6$ (kg/mol)$^{1/2}$.

$$\log_{10}\gamma_i^{\square} = \frac{-z_i^2 A_\gamma \sqrt{I}}{1 + Ba\sqrt{I}} \text{ up to } I = 0.1 \text{ m} \qquad 18.106$$

Activity Coefficient of Water

$$\log_{10}\gamma_s = \frac{2A_\gamma M_{w,s}}{1000(Ba)^3}\left\{1 + Ba\sqrt{I} - \frac{1}{1 + Ba\sqrt{I}} - 2\ln(1 + Ba\sqrt{I})\right\} \qquad 18.107$$

Can be determined by measuring the osmotic pressure

$$\Pi = \frac{RT}{V_s}\,\frac{M_{w,s}\sum\limits_{electrolytes} m_i}{1000}\Phi \qquad 18.109$$

$$\Phi = \frac{-1000}{M_{w,s}\sum\limits_{electrolytes} m_i}\ln a_s \qquad 18.108$$

Chlorination of Water

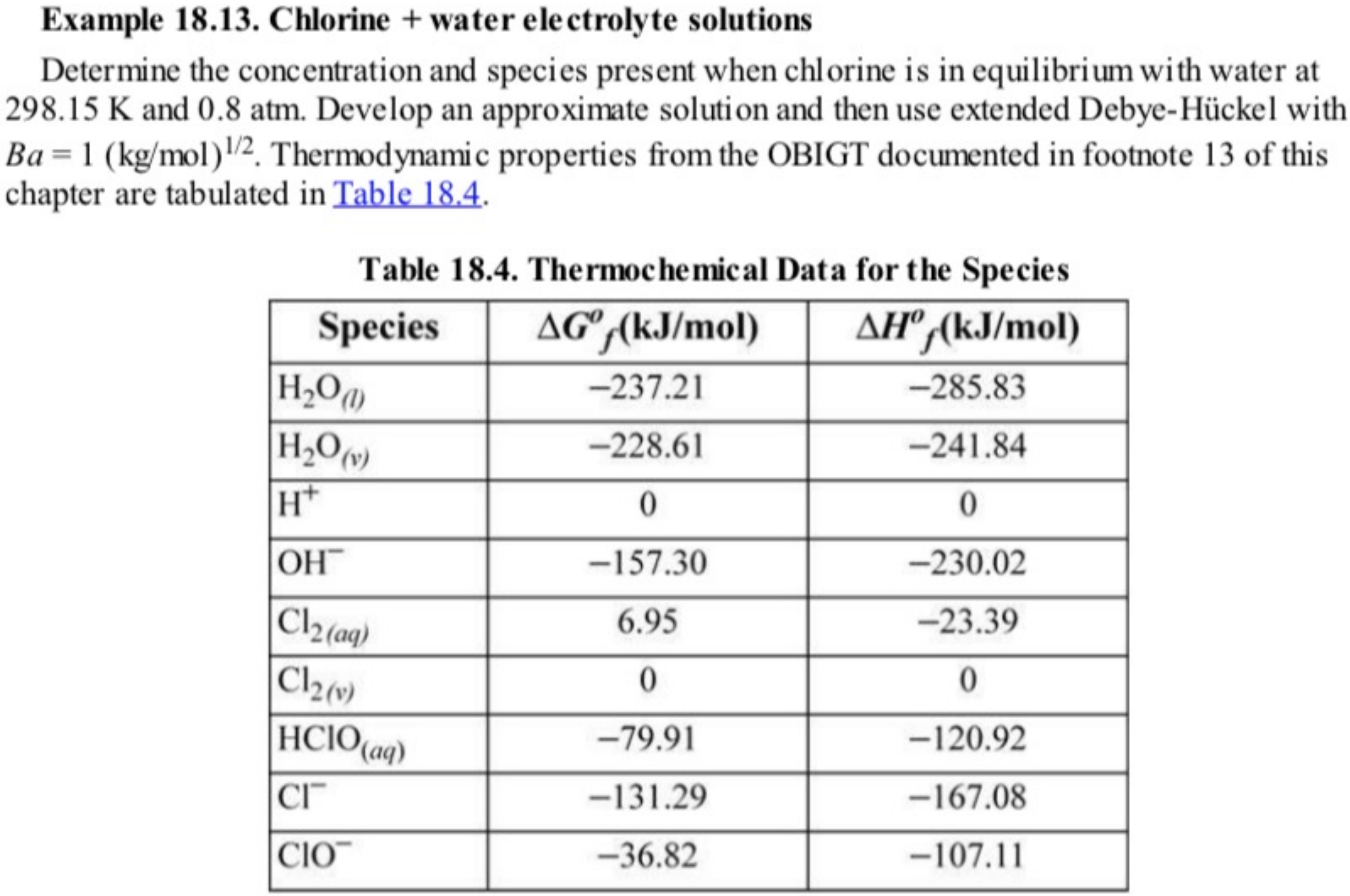
$$Cl_{2(aq)} + H_2O \rightleftarrows H^+ + Cl^- + HClO_{(aq)} \qquad K_{a1} = \frac{a_{H^+} a_{Cl^-} a_{HClO_{(aq)}}}{a_{Cl_{2(aq)}} a_{H_2O}} \qquad 18.127$$

$$HClO_{(aq)} \rightleftarrows H^+ + ClO^-{}_{(aq)} \qquad K_{a2} = \frac{a_{H^+} a_{ClO^-}}{a_{HClO_{(aq)}}} \qquad 18.128$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} \qquad 18.129$$

$$H_2O_{(v)} \rightleftarrows H_2O_{(l)} \qquad K = \frac{a_{H_2O}}{y_{H_2O} P} = \frac{1}{P^{sat}_{H_2O}} \qquad 18.130$$

$$Cl_{2(v)} \rightleftarrows Cl_{2(aq)} \qquad K_{H(Cl_2)} = \frac{a_{Cl_2}}{y_{Cl_2} P} \qquad 18.131$$

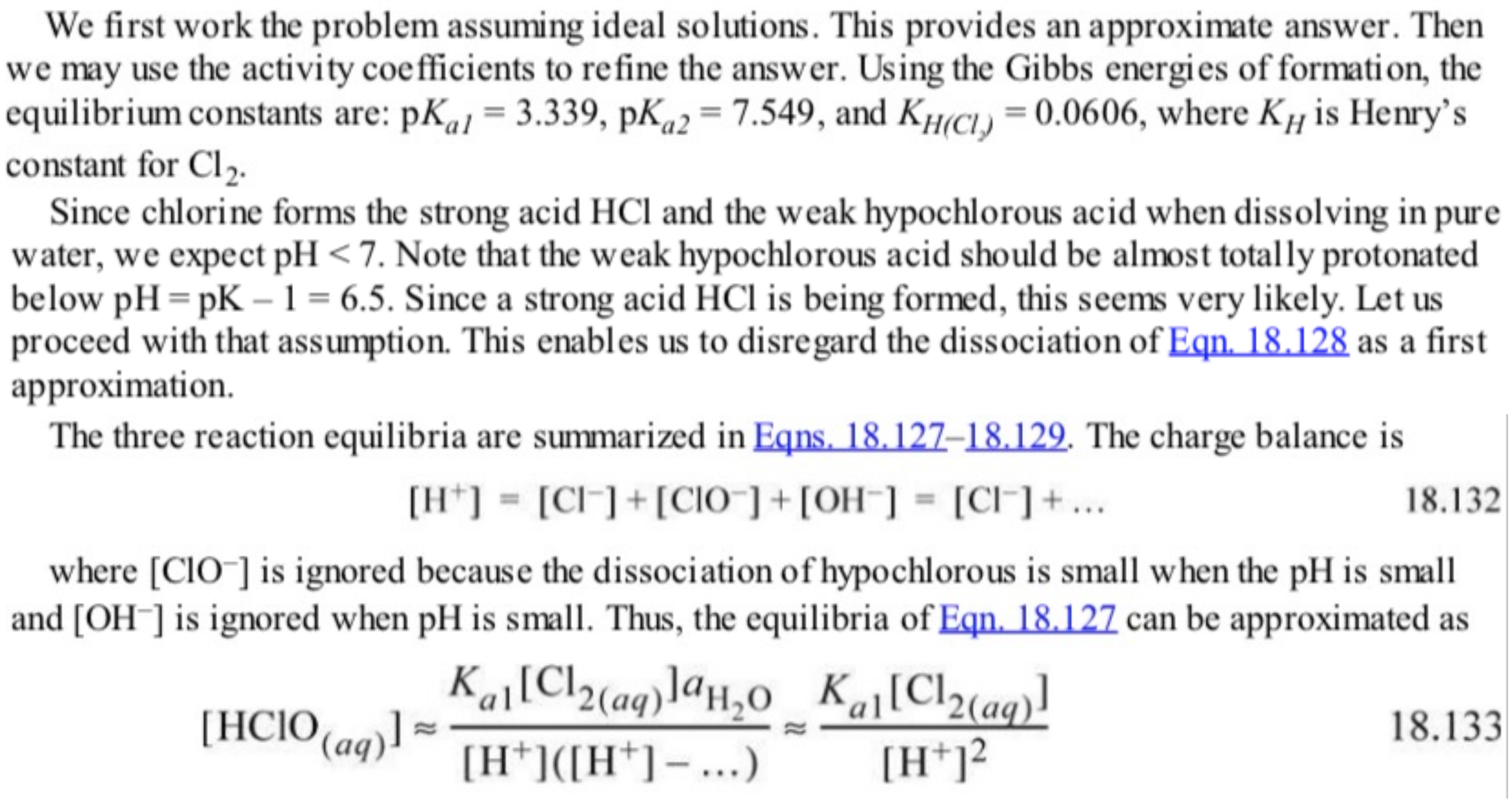


Example 18.13. Chlorine + water electrolyte solutions

Determine the concentration and species present when chlorine is in equilibrium with water at 298.15 K and 0.8 atm. Develop an approximate solution and then use extended Debye-Hückel with $Ba = 1\ (\text{kg/mol})^{1/2}$. Thermodynamic properties from the OBIGT documented in footnote 13 of this chapter are tabulated in Table 18.4.

Table 18.4. Thermochemical Data for the Species

Species	ΔG^o_f(kJ/mol)	ΔH^o_f(kJ/mol)
$H_2O_{(l)}$	–237.21	–285.83
$H_2O_{(v)}$	–228.61	–241.84
H^+	0	0
OH^-	–157.30	–230.02
$Cl_{2(aq)}$	6.95	–23.39
$Cl_{2(v)}$	0	0
$HClO_{(aq)}$	–79.91	–120.92
Cl^-	–131.29	–167.08
ClO^-	–36.82	–107.11



We first work the problem assuming ideal solutions. This provides an approximate answer. Then we may use the activity coefficients to refine the answer. Using the Gibbs energies of formation, the equilibrium constants are: $pK_{a1} = 3.339$, $pK_{a2} = 7.549$, and $K_{H(Cl_2)} = 0.0606$, where K_H is Henry's constant for Cl_2.

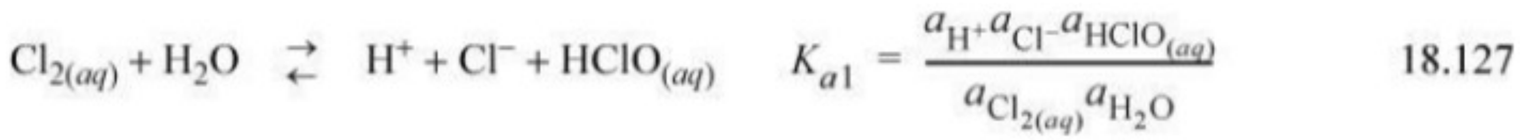
Since chlorine forms the strong acid HCl and the weak hypochlorous acid when dissolving in pure water, we expect pH < 7. Note that the weak hypochlorous acid should be almost totally protonated below pH = pK – 1 = 6.5. Since a strong acid HCl is being formed, this seems very likely. Let us proceed with that assumption. This enables us to disregard the dissociation of Eqn. 18.128 as a first approximation.

The three reaction equilibria are summarized in Eqns. 18.127–18.129. The charge balance is

$$[H^+] = [Cl^-] + [ClO^-] + [OH^-] = [Cl^-] + \ldots \qquad 18.132$$

where $[ClO^-]$ is ignored because the dissociation of hypochlorous is small when the pH is small and $[OH^-]$ is ignored when pH is small. Thus, the equilibria of Eqn. 18.127 can be approximated as

$$[HClO_{(aq)}] \approx \frac{K_{a1}[Cl_{2(aq)}]a_{H_2O}}{[H^+]([H^+] - \ldots)} \approx \frac{K_{a1}[Cl_{2(aq)}]}{[H^+]^2} \qquad 18.133$$



$$Cl_{2(aq)} + H_2O \rightleftarrows H^+ + Cl^- + HClO_{(aq)} \qquad K_{a1} = \frac{a_{H^+}a_{Cl^-}a_{HClO_{(aq)}}}{a_{Cl_{2(aq)}}a_{H_2O}} \qquad 18.127$$

Approximate Solution:

The partial pressure for water can be estimated by first assuming that the water is almost pure. This approximation can be refined later if we find significant concentrations of chlorine species. We also use molar concentrations to approximate molalities. Using Raoult's law for water, $y_{H_2O}P = P^{sat}_{H_2O}$. From the steam tables, $y_{H_2O}P = P^{sat}_{H_2O} = 0.0317$ bar = 0.0313 atm, and $y_{H_2O} = 0.0313/0.8 = 0.039$. Then $y_{Cl_2}P = 0.8 - 0.0313 = 0.7687$ atm, $y_{Cl_2} = 1 - 0.039 = 0.961$. Using Henry's law coefficient (K_H) for Cl_2 at 298.15 K, the concentration of $Cl_{2(aq)}$ is (independent of pH):

$$[Cl_{2(aq)}] = K_H(y_{Cl_2}P) = (0.0606)(0.7687) = 0.0484 \text{ mol/L} \qquad 18.134$$

The concentration $[HOCl_{(aq)}] = 10^{-3.339}(0.0484)/[H^+]^2$ (Eqn. 18.133) at small values of pH is plotted in a Sillèn diagram. The weak acid dissociation of hypochlorous acid $[OCl^-]$ is to be calculated from Eqn. 18.31 using the concentration of [HOCl] as a function of pH. As expected, the dissociation is small at low pH.

$$\boxed{[A^-] = K_{a,A}C_A/([H^+] + K_{a,A})} \quad \text{useful for conjugate base} \qquad 18.31$$

$$[HClO_{(aq)}] \approx \frac{K_{a1}[Cl_{2(aq)}]a_{H_2O}}{[H^+]([H^+] - \ldots)} \approx \frac{K_{a1}[Cl_{2(aq)}]}{[H^+]^2} \qquad 18.133$$

Double $[H^+]$ makes it about 0.3 higher

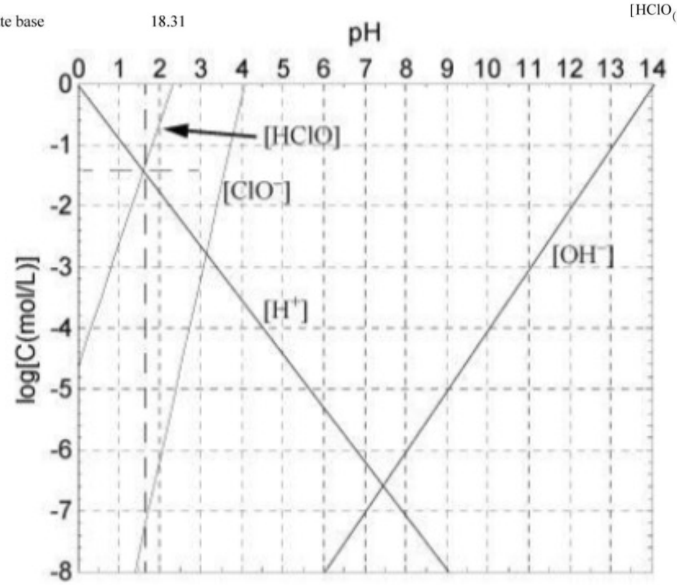


Figure 18.14. Determination of equilibria for the chlorine system.

The weak acid curve in Fig. 18.14 is much different from curves in previous examples because, in this case, the overall concentration of weak acid is changing rapidly with pH. Now consider the material balance associated with Eqns. 18.127 and 18.128. Since Eqn. 18.128 does not occur to a significant extent, to a good approximation by the stoichiometry of Eqn. 18.127 $[H^+] = [Cl^-] = [HOCl]$. This occurs at the intersection shown by the dotted lines. The approximate solution is pH = 1.55, $[H^+] = [Cl^-] = [HOCl] = 10^{-1.55} = 0.0282$ mol/L. Note on the diagram that $[OCl–] = 10^{-7.5} = 3.2E\text{-}8$. Now, we can use these as initial guesses in a more rigorous answer.

$$Cl_{2(aq)} + H_2O \rightleftarrows H^+ + Cl^- + HClO_{(aq)} \quad K_{a1} = \frac{a_{H^+}a_{Cl^-}a_{HClO_{(aq)}}}{a_{Cl_{2(aq)}}a_{H_2O}} \qquad 18.127$$

$$HClO_{(aq)} \rightleftarrows H^+ + ClO^-{}_{(aq)} \quad K_{a2} = \frac{a_{H^+}a_{ClO^-}}{a_{HClO_{(aq)}}} \qquad 18.128$$

$\boxed{[A^-] = K_{a,A}C_A/([H^+]+K_{a,A})}$ useful for conjugate base 18.31

$$[HClO_{(aq)}] \approx \frac{K_{a1}[Cl_{2(aq)}]a_{H_2O}}{[H^+]([H^+]-\ldots)} \approx \frac{K_{a1}[Cl_{2(aq)}]}{[H^+]^2} \qquad 18.133$$

Double $[H^+]$ makes it about 0.3 higher

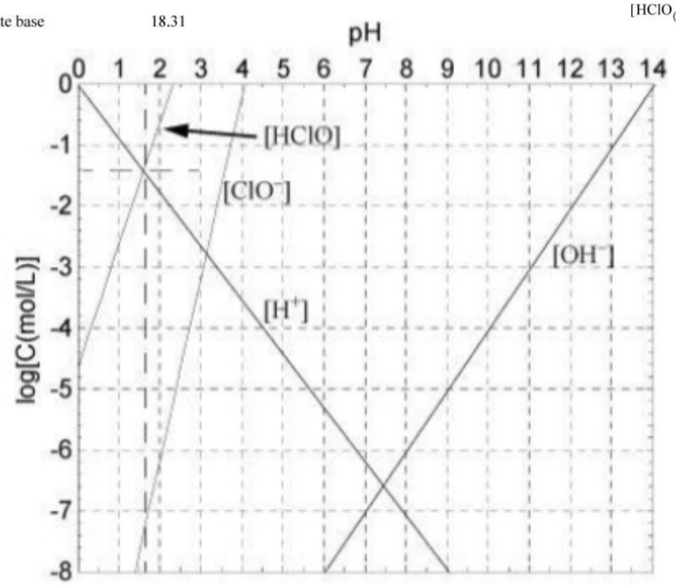


Figure 18.14. Determination of equilibria for the chlorine system.

Calculation with Activity Coefficients:

Thermodynamic properties for the components are tabulated below and in the spreadsheet: CL2H2O.xlsx. Note that the data tabulated below include values for Cl_2 and H_2O in both the vapor and aqueous phases. The Gibbs energies are used to calculate the VLE distribution coefficients as a "reaction."

To solve the nine equations (five equilibria, three atom balances, and one charge balance) simultaneously, we must identify nine unknowns. The nine unknowns selected here are the species listed in Table 18.4: the liquid moles of H_2O, Cl_2, HClO, H^+, Cl^-, ClO^-, and OH^-, and the vapor moles of $H_2O_{(v)}$ and $Cl_{2(v)}$. The basis is 1 liter of liquid water ($n^i_{H_2O} = 55.51$ moles) and $n^i_{Cl_2} = 0.9$ moles initially.

The detailed calculation are handled as a reactive flash. Three atom balances must be satisfied–H, O, Cl, along with the charge balance. The atom balances and charge balance are shown in Table 18.5 for the basis of 1 liter of liquid water and 0.9 moles of Cl_2. The compositions for iteration are summarized in Table 18.6.

Table 18.4. Thermochemical Data for the Species

Species	ΔG^o_f(kJ/mol)	ΔH^o_f(kJ/mol)
$H_2O_{(l)}$	−237.21	−285.83
$H_2O_{(v)}$	−228.61	−241.84
H^+	0	0
OH^-	−157.30	−230.02
$Cl_{2(aq)}$	6.95	−23.39
$Cl_{2(v)}$	0	0
$HClO_{(aq)}$	−79.91	−120.92
Cl^-	−131.29	−167.08
ClO^-	−36.82	−107.11

$$Cl_{2(aq)} + H_2O \rightleftarrows H^+ + Cl^- + HClO_{(aq)} \qquad K_{a1} = \frac{a_{H^+}a_{Cl^-}a_{HClO_{(aq)}}}{a_{Cl_{2(aq)}}a_{H_2O}} \qquad 18.127$$

$$HClO_{(aq)} \rightleftarrows H^+ + ClO^-_{(aq)} \qquad K_{a2} = \frac{a_{H^+}a_{ClO^-}}{a_{HClO_{(aq)}}} \qquad 18.128$$

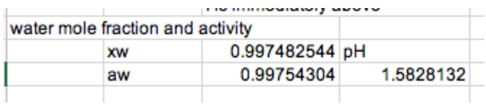
$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}} \qquad 18.129$$

$$H_2O_{(v)} \rightleftarrows H_2O_{(l)} \qquad K = \frac{a_{H_2O}}{y_{H_2O}P} = \frac{1}{P^{sat}_{H_2O}} \qquad 18.130$$

$$Cl_{2(v)} \rightleftarrows Cl_{2(aq)} \qquad K_{H(Cl_2)} = \frac{a_{Cl_2}}{y_{Cl_2}P} \qquad 18.131$$

Table 18.6. Electrolyte Component Mole Numbers and Activities at the Converged Composition

Liquid				Vapor		
Species	Moles	Molality	$\gamma^{\square}$	Species	Moles	y
H_2O	55.44564	----	1.000060649	H_2O	0.03322	3.88E-02
$Cl_{2(aq)}$	4.65E-02	0.046591564	1	Cl_2	0.82233	9.61E-01
HClO	3.11E-02	0.031168318	1	*sum*	0.85555	1.00
H^+	3.11E-02	0.031168399	0.838440619			
OH^-	4.55E-13	4.55732E-13	0.838440619	$y_{Cl2}P = 0.77$		
ClO^-	4.01E-08	4.01834E-08	0.838440619			
Cl^-	3.11E-02	0.031168359	0.838440619			
tot moles	55.5856					
Intermediate Calculations		$I = 0.03117$				
	$x_{H2O} = 0.99748$	$pH = -\log_{10}((0.0312)(0.838))$				
	$a_{H2O} = 0.9975$	$= 1.58$				



water mole fraction and activity			
	xw	0.997482544	pH
	aw	0.99754304	1.5828132

Mean (Geometric Mean) Ionic Activity Coefficients

Mean Molality: $\boxed{m_{\pm} \equiv (m_{+}^{\nu_{+}} m_{-}^{\nu_{-}})^{1/\nu}}$ 18.138

Mean Ionic Activity Coefficient: $\boxed{\gamma_{\pm} \equiv (\gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}})^{1/\nu}}$ 18.139

Stoichiometric Number $\nu \equiv (\nu_{+} + \nu_{-})$.

$$\log_{10} \gamma_{\pm} = \frac{-A_{\gamma} |z_{+} z_{-}| \sqrt{I}}{1 + Ba\sqrt{I}} \quad 18.141$$

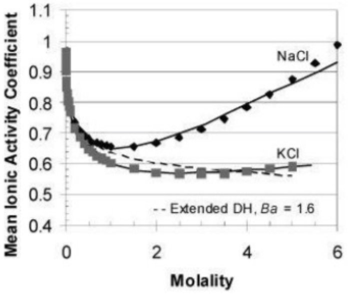


Figure 18.15. Mean ionic activity coefficient for NaCl, KCl and those predicted by the extended Debye-Hückel (DH) model at 298K. Dashed line is the extended Debye-Hückel, Solid lines are the unsymmetric eNRTL using default parameters in ASPEN Plus ver. 7.1. Experimental activity coefficients are from Hamer, W.J.; Wu, Y.-C., 1972. J. Phys. Chem. Ref. Data, 1:1047.