9. Chemical Equilibrium

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9.1 Chemical Equilibrium in a Mixture of Ideal Gases

Consider a chemical reaction

$$aA \quad + bB \quad \rightarrow \quad cC \quad + \quad eE$$

The Gibbs free energy of the system is given by

$$dG = -S dT + V dp + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_E dn_E$$

At constant T and p

$$dG = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_E dn_E$$

The changes in the number of moles of each compound as the reaction advances by an amount ξ.

$$\begin{array}{ccccc} aA & + bB & \rightarrow & cC & + \; eE \\ -a\xi & -b\xi & & +c\xi & +e\xi \end{array}$$

For an infinitesimally small advancement $d\xi$, $dn_A = a d\xi$, etc.

$$dG = - \mu_A \, a d\xi - \mu_B \, b d\xi + \mu_C \, c \, d\xi + \mu_E \, e \, d\xi$$

$$dG = \{(c\mu_C + e\mu_E) - (a\mu_A + b\mu_B)\} \, d\xi$$

At constant p and T, the reaction Gibbs energy is defined as the slope $(\partial \boldsymbol{G}/\partial \xi)_{p,T}$ of the graph of the Gibbs energy plotted against extent of reaction ξ :

$$(\partial \boldsymbol{G}/\partial \xi)_{p,T} = (c\mu_C + e\mu_E) - (a\mu_A + b\mu_B)$$

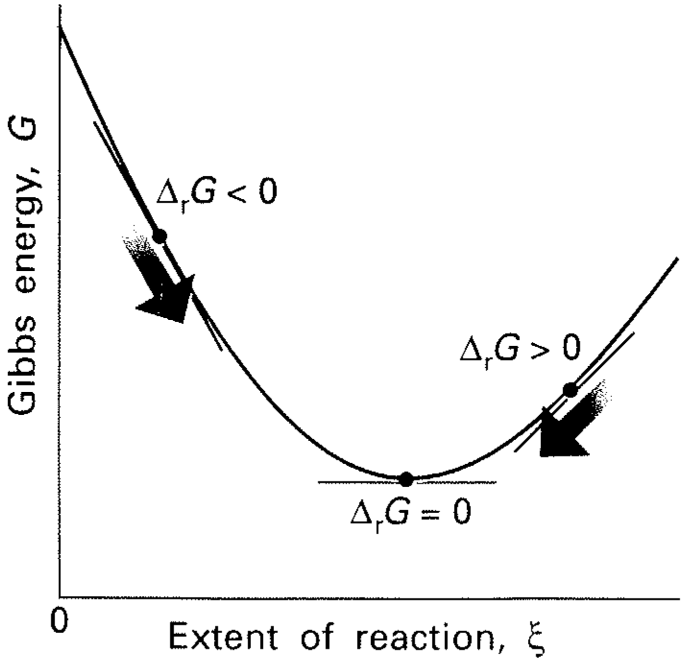
The difference between the chemical potentials of the products and reactants at the composition of the reaction mixture is given by

$$\Delta_{rxn}\boldsymbol{G} = (c\mu_C + e\mu_E) - (a\mu_A + b\mu_B)$$

When equilibrium is reached,

$$(\partial \boldsymbol{G}/\partial \xi)_{p,T} = 0$$

$$\{(c\mu_C + e\mu_E) - (a\mu_A + b\mu_B)\}_{\text{equil}} = 0$$



Now, if the reactants and products are entirely ideal gases, we can write for each one the chemical potential of an ideal gas in a mixture,

$$\mu_A(T) = \mu_A{}^{\ominus}{}_T + \mathrm{RT}\ln\frac{p_A}{1} \quad \text{for A}$$

where p_A is the partial pressure of the gas A in the mixture. Substitute expressions like this into the equation
$\Delta_{\mathrm{rxn}}\boldsymbol{G} = (\mathrm{c}\mu_\mathrm{C} + \mathrm{e}\mu_\mathrm{E}) - (\mathrm{a}\mu_\mathrm{A} + \mathrm{b}\mu_\mathrm{B})$
to get

$$\Delta_{\mathrm{rxn}}\boldsymbol{G} = (\mathrm{c}\mu_C{}^{\ominus}{}_T + \mathrm{e}\mu_E{}^{\ominus}{}_T - \mathrm{a}\mu_A{}^{\ominus}{}_T - \mathrm{b}\mu_B{}^{\ominus}{}_T) + \mathrm{c}RT\ln(p_C/1) + \mathrm{e}RT\ln(p_E/1) - \mathrm{a}RT\ln(p_A/1) - \mathrm{b}RT\ln(p_B/1)$$

$$\Delta_{\mathrm{rxn}}\boldsymbol{G} = \Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_T + RT\{\ln(p_C/1)^\mathrm{c} + \ln(p_E/1)^\mathrm{e} - \ln(p_A/1)^\mathrm{a} - \ln(p_B/1)^\mathrm{b}\}$$

$$= \Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_{T}$$
$$+ RT \ln \{(p_C/1)^{\mathrm{c}}(p_E/1)^{\mathrm{e}}/(p_A/1)^{\mathrm{a}}(p_B/1)^{\mathrm{b}}\}$$

$\Delta_{\mathrm{rxn}}\boldsymbol{G} = \Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_{T} + RT \ln \mathrm{Q}_p$
where $\mathrm{Q}_p = \{(p_C/1)^{\mathrm{c}}(p_E/1)^{\mathrm{e}}/(p_A/1)^{\mathrm{a}}(p_B/1)^{\mathrm{b}}\}$
At equilibrium,
$\{(\mathrm{c}\mu_{\mathrm{C}} + \mathrm{d}\mu_{\mathrm{D}}) - (\mathrm{a}\mu_{\mathrm{A}} + \mathrm{b}\mu_{\mathrm{B}})\}_{\mathrm{equil}} = 0$ leads to

$\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_{T} +$
$RT \ln \{(p_C/1)^{\mathrm{c}}(p_E/1)^{\mathrm{e}}/(p_A/1)^{\mathrm{a}}(p_B/1)^{\mathrm{b}}\}_{\mathrm{equil}} = 0$
The quotient of equilibrium partial pressures is called K_p,
$K_p = \{(p_C/1)^{\mathrm{c}}(p_E/1)^{\mathrm{e}}/(p_A/1)^{\mathrm{a}}(p_B/1)^{\mathrm{b}}\}_{\mathrm{equil}}$

$$\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}{}_{T} = - RT \ln K_p$$

9.2 Chemical Equilibrium in a Mixture of Real Gases

For real gases

$K_f = \{(f_C/1)^c(f_E/1)^e/(f_A/1)^a(f_B/1)^b\}_{\text{equil}}$

based on, in a mixture of real gases,

$$\mu_A(T) = \mu_A{}^{\ominus}{}_T + RT \ln \frac{f_A}{1} \qquad \text{for A}$$

Chemical Equilibrium in Ideal solutions

In an ideal solution obeying Raoult's law,

$$\mu_A(T) = \mu_A{}^{\ominus}{}_T + RT \ln x_A \quad \text{(ideal solution)}$$

where $\mu_A{}^{\ominus}{}_T = \mu_A{}^*{}_T(T,p)$ is the chemical potential of the pure liquid A

$K_x = \{(x_C)^c(x_E)^e/(x_A)^a(x_B)^b\}_{\text{equil}}$

A more general definition of equilibrium constant K is in terms of activities,

$$\mu_A(T) = \mu_A{}^{\ominus}{}_T + RT \ln \, \boldsymbol{a}_A \quad \text{(non-ideal soln)}$$

where $\mu_A{}^{\ominus}{}_T = g_A(T,p)$ is the chemical potential of a hypothetical ideal solution of unit molality that obeys Henry's law
Thus, in the expression

$\Delta_{\text{rxn}}\boldsymbol{G}^{\ominus}{}_T = - RT \ln K$ for the reaction

$$\text{aA} + \text{bB} \rightarrow \text{cC} + \text{eE}$$

$$\Delta_{\text{rxn}}\boldsymbol{G}^{\ominus}{}_T = \{(\text{c}\mu_{\text{C}}{}^{\ominus}{}_T + \text{d}\mu_{\text{D}}{}^{\ominus}{}_T) - (\text{a}\mu_{\text{A}}{}^{\ominus}{}_T + \text{b}\mu_{\text{B}}{}^{\ominus}{}_T)\}$$

and

$$K = \{(\boldsymbol{a}_C/1)^{\text{c}}(\boldsymbol{a}_E/1)^{\text{e}}/(\boldsymbol{a}_A/1)^{\text{a}}(\boldsymbol{a}_B/1)^{\text{b}}\}_{\text{equil}}$$

$$K = K_\gamma \times K_m$$

each expressed in the same form.

$\gamma_B = (\boldsymbol{a}_B / m_B)$. As $m_B \rightarrow 0$, we find

$\boldsymbol{a}_B \rightarrow m_B$ $\quad \gamma_B \rightarrow 1$ $\quad K_\gamma \rightarrow 1$ and $K_m \rightarrow K$.

9.3 The Temperature Dependence of an Equilibrium Constant

$$\Delta_{\text{rxn}}\boldsymbol{G}^{\ominus}{}_{T} = -RT\ln K$$

Recall that we had derived, using only the definition $\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$, the general relation called the Gibbs-Helmholtz eq.:

$$\boxed{(\partial(\Delta \boldsymbol{G}/T)/\partial T)_p \quad = -(\Delta \boldsymbol{H}/T^2)}$$

We now apply it to $\Delta_{\text{rxn}}\boldsymbol{G}^{\ominus}{}_{T}/T = -R\ln K$

$$(\partial(\Delta_{\text{rxn}}\boldsymbol{G}^{\ominus}/T)/\partial T)_p \quad = -(\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}/T^2)$$

$$(\partial(-R\ln K)/\partial T)_p \quad = -(\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}/T^2)$$

$$\boxed{\mathrm{d}\ln K/\mathrm{d}T = \Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}/RT^2}$$

If $\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}$ is positive (exothermic reaction) ln K and therefore K itself decreases as the temperature rises.

Aside:

Applications of Gibbs-Helmholtz eqn

$\Delta \boldsymbol{G}/T$ as a function of T :

$(\partial(\boldsymbol{G}/T)/\partial T)_p = -(\boldsymbol{H}/T^2)$ Gibbs- Helmholtz

$(\partial(\Delta\boldsymbol{G}/T)/\partial T)_p = -(\Delta\boldsymbol{H}/T^2)$

$d(\Delta\boldsymbol{G}/T)_p = -(\Delta\boldsymbol{H}/T^2)\,dT = \Delta\boldsymbol{H}\,d(1/T)$

e. g., $d(\Delta_{fus}\boldsymbol{G}/T)_p = \Delta_{fus}\boldsymbol{H}\,d(1/T)$

or $d(\Delta_{vap}\boldsymbol{G}/T)_p = \Delta_{vap}\boldsymbol{H}\,d(1/T)$

$\int d(\Delta\boldsymbol{G}/T)_p = \int \Delta\boldsymbol{H}\,d(1/T)$

$$\boxed{\begin{aligned}&(\Delta\boldsymbol{G}/T)_{T2,p} - (\Delta\boldsymbol{G}/T)_{T1,p}\\ &\qquad = \Delta\boldsymbol{H}\{(1/T_2) - (1/T_1)\}\end{aligned}}$$

equilibrium constant as a function of T :

$d(\Delta\boldsymbol{G}^{\ominus}/T)_p = \Delta\boldsymbol{H}^{\ominus}\,d(1/T)$

$\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus} = -RT\ln\boldsymbol{K}$

$d(\Delta_{\mathrm{rxn}}\boldsymbol{G}^{\ominus}/T)_p = -R\,d\ln\boldsymbol{K} = \Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}\,d(1/T)$

$\int d\ln\boldsymbol{K} = -(1/R)\int \Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}\,d(1/T)$

Integrate between T_1 and T_2

$$\boxed{-\ln[\boldsymbol{K}_{T2}/\boldsymbol{K}_{T1}] = (\Delta_{\mathrm{rxn}}\boldsymbol{H}^{\ominus}/R)\{(1/T_2) - (1/T_1)\}}$$

non-volatile solute,

boiling point elevation:

$\mu^*_{A,\text{liquid}}(T,p) + RT \ln x_A = \mu^*_{A,\text{vapor}}(T,p)$

$\ln x_A = [\mu^*_{A,\text{vapor}}(T,p) - \mu^*_{A,\text{liquid}}]/RT$

$= \Delta_{vap}\boldsymbol{G}/RT = (1/R)(\Delta_{vap}\boldsymbol{G}/T)$

$(\partial(\ln x_A/\partial T)_p = (1/R)(\partial(\Delta_{vap}\boldsymbol{G}/T)/\partial T)_p$

But, $(\partial(\Delta\boldsymbol{G}/T)/\partial T)_p = -(\Delta\boldsymbol{H}/T^2)$

$\therefore\ (\partial(\ln x_A/\partial T)_p = -(1/R)(\Delta_{vap}\boldsymbol{H}/T^2)$

$d(\ln x_A) = (1/R)\Delta_{vap}\boldsymbol{H}\, d(1/T)$

Now integrate between

pure solvent ($x_A = 1$, $T = T^*$)

and solution (x_A , T):

$\int_1^{xA} d\ln x_A = (1/R) \int_{T^*}^{T} \Delta_{vap}\boldsymbol{H}\, d(1/T)$

If further, $\Delta_{vap}\boldsymbol{H}$ is nearly independent of temperature,

$$\boxed{\ln x_A = \Delta_{vap}\boldsymbol{H}/R \left[\frac{1}{T} - \frac{1}{T^*} \right]}$$

non-volatile solute,

freezing point depression:

$\mu_{A,\mathrm{solid}}(T,p) = \mu^*_{A,\mathrm{liquid}}(T,p) + RT \ln x_A$

$\ln x_A \quad = [\mu_{A,\mathrm{solid}}(T,p) - \mu^*_{A,\mathrm{liquid}}]/RT$

$\quad = - \Delta_{fus}\mathbf{G}/RT = - (1/R)(\Delta_{fus}\mathbf{G}/T)$

$(\partial(\ln x_A /\partial T)_p = - (1/R)(\partial(\Delta_{fus}\mathbf{G} /T) /\partial T)_p$

But, $(\partial(\Delta \mathbf{G} /T) /\partial T)_p = - (\Delta \mathbf{H} /T^2)$

$\therefore \quad (\partial(\ln x_A /\partial T)_p = +(1/R)(\Delta_{fus}\mathbf{H} /T^2)$

$\quad d(\ln x_A) = (1/R)\Delta_{fus}\mathbf{H}\, d(-1/T)$

Integrate between

pure solvent ($x_A = 1$, $T=T^*$)

and solution (x_A , T)

$\int_1^{xA} d\ln x_A = (1/R) \int_{T^*}^{T} \Delta_{fus}\mathbf{H}\, d(-1/T)$

If further, $\Delta_{fus}\mathbf{H}$ is nearly independent of temperature,

$$\boxed{\ln x_A = \Delta_{fus}\mathbf{H}/R \left[-\frac{1}{T} + \frac{1}{T^*} \right]}$$

9.4 LeChatelier's Principle

LeChatelier's principle predicts that a system at equilibrium will tend to shift towards the direction that absorbs heat if the temperature is raised.

For an exothermic reaction, an increase in temperature would favor the reactants. Thus, Le Chatelier's principle predicts that ln K decreases with increasing temperature for an exothermic reaction. This is exactly what we had derived using only the definition $\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$ and $(\partial \boldsymbol{G}/\partial T)_p = -\boldsymbol{S}$.

9.5 Activities in Solutions of Electrolytes

Assume a solution of an electrolyte which is completely dissociated into ions in solvent A.

$\boldsymbol{G} = n_A\mu_A + n_+\mu_+ + n_-\mu_-$

If each formula unit M_pX_q of the electrolyte dissociates into s=p+q ions, then in a solution of molality *m* in the electrolyte,

$m_+ = pm$ and $m_- = qm$.

and $\mu = p\mu_+ + q\mu_-$

We can define a mean ionic chemical potential $\mu_\pm$

$s\mu_\pm = p\mu_+ + q\mu_-$

We define the activities accordingly,

$\mu(T) = \mu^{\ominus}{}_T + RT \ln \boldsymbol{a}$

$\mu_+(T) = \mu_+{}^{\ominus}{}_T + RT \ln \boldsymbol{a}_+$ ditto for -

$\mu_{\pm}(T) = \mu_{\pm}{}^{\ominus}{}_{T} + RT \ln a_{\pm}$

and $\mu^{\ominus}{}_{T} = \mathrm{p}\mu_{+}{}^{\ominus}{}_{T} + \mathrm{q}\mu_{-}{}^{\ominus}{}_{T} = \mathrm{s}\mu_{\pm}{}^{\ominus}{}_{T}$

We write the various activity coefficients in terms of γ and m,

$a_{\pm} = \gamma_{\pm} m_{\pm} \qquad a_{+} = \gamma_{+} m_{+} \qquad a_{-} = \gamma_{-} m_{-}$

We find the mean ionic molality $m_{\pm}$ and the mean ionic activity coefficient $\gamma_{\pm}$:

$(\gamma_{\pm})^{\mathrm{s}} (m_{\pm})^{\mathrm{s}} = (\gamma_{+} m_{+})^{\mathrm{p}} (\gamma_{-} m_{-})^{\mathrm{q}}$

$(\gamma_{\pm})^{\mathrm{s}} = (\gamma_{+})^{\mathrm{p}} (\gamma_{-})^{\mathrm{q}}$ and

$(m_{\pm})^{\mathrm{s}} = (m_{+})^{\mathrm{p}} (m_{-})^{\mathrm{q}} = (\mathrm{p}^{\mathrm{p}} \mathrm{q}^{\mathrm{q}}) m^{\mathrm{s}}$

Example:

in a 1:1 electrolyte e.g., $CaSO_4$ or NaCl

$\mathrm{p} = \mathrm{q} = 1$, $\mathrm{s} = 2$, $\quad m_{\pm} = m$, $\quad (\gamma_{\pm})^2 = \gamma_{+}\gamma_{-}$

in a 1:2 electrolyte such as Na_2SO_4,

$\mathrm{p} = 2$, $\mathrm{q} = 1$, $\mathrm{s} = 3$, $(\gamma_{\pm})^3 = (\gamma_{+})^2 (\gamma_{-})^1$ and

$(m_{\pm})^3 = (2^2 1^1) m^3$, leads to $m_{\pm} = 1.587m$.

In terms of the mean ionic activity,

$$\mu(T) = \mu^{\ominus}_{T} + RT \ln (a_{\pm})^{s}$$

$$\mu(T) = \mu^{\ominus}_{T} + RT \ln(p^{p}q^{q}) + sRT \ln m$$
$$+ sRT \ln(\gamma_{\pm})$$

$\gamma_{\pm}$ can be determined from freezing point depression measurements, or other colligative properties.

Equilibria in ionic solutions

$$HA \rightarrow H^{+} + A^{-}$$
$$K = a_{H+}\, a_{A-} / a_{HA}$$

The activity of the solvent (H_2O, for example, is very nearly that of the pure solvent, $a_{H2O} = 1$). By definition,

$$a_{H+} = \gamma_{+} m_{H+}\,,\quad a_{A-} = \gamma_{-} m_{A-}\,,\quad a_{HA} = \gamma_{HA} m_{HA}$$
$$K = (\gamma_{H+}\gamma_{A-}/\gamma_{HA})(m_{H+}\, m_{A-}/m_{HA})$$
$$= (\gamma_{\pm}^{2}/\gamma_{HA})(m_{H+}\, m_{A-}/m_{HA})$$

If the degree of dissociation is α,

$m_{\mathrm{H+}}=\alpha m$, $m_{\mathrm{A-}}=\alpha m$, $m_{\mathrm{HA}}=(1-\alpha)m$

$$K = (\gamma_{\pm}{}^{2}/\gamma_{\mathrm{HA}}) \times [\alpha^{2}/(1-\alpha)]\, m$$

$$K = K_{\gamma} \times K_{m}$$

A plot of ln K_m versus m extrapolated to infinite dilution should provide K and K_{γ}. If the solution is dilute we may set $\gamma_{\mathrm{HA}}=1$ and if K is small, $1-\alpha \approx 1$

$K \approx \gamma_{\pm}{}^{2}\alpha^{2}m$ or $\alpha \approx (K/m)^{1/2}/\gamma_{\pm}$

Consider now the equilibrium of a slightly soluble salt:

$$\mathrm{AgCl(s)} \rightarrow \mathrm{Ag^{+}} + \mathrm{Cl^{-}}$$

where the solubility of AgCl is C_s moles per kg water, so that $m_{\mathrm{Ag+}} = m_{\mathrm{Cl-}} = C_s$

The solubility product constant is

$$K = a_{\mathrm{Ag+}}\, a_{\mathrm{Cl-}} / a_{\mathrm{AgCl}}$$

The activity of pure AgCl solid is 1

$$K = (\gamma_{+} m_{\mathrm{Ag+}}\, \gamma_{-}\, m_{\mathrm{Cl-}}) = \gamma_{\pm}{}^{2}\, C_s{}^{2}$$

In general, $K = p^{p} q^{q} \gamma_{\pm}{}^{s}\, C_s{}^{2}$

Debye-Hückel theory

Recall

$\mu_B(T,p,x) - \mu_{B\,(ideal)}(T,p,x) = RT\ln\gamma_B$

Imagine a solution with all the ions in their same locations but with the charges turned off. The difference between the molar Gibbs energy of the ideal solution (no charges) and the real solution (with charges) is equal to the electrical work W_{elec} of charging the system in this arrangement.

For a salt M_pX_q, $s = p+q$,

$$RT\ln(\gamma_\pm)^s = W_{elec}$$

First find the final distribution of the ions and then find the work of charging them in that distribution.

For a bare charge Q, the electric potential is just $(Q/\varepsilon)r^{-1}$ in cgs units or $(Q/4\pi\varepsilon)r^{-1}$ in SI units. The presence of all the other ions makes the potential drop off with distance.

The potential due to the atmosphere of all other ions is $\{\exp[-r/r_D]r^{-1} - r^{-1}\}(Q/\varepsilon)$. The potential at the *i*th ion itself due to the ionic atmosphere is the same as that of a single charge of equal magnitude but at a distance r_D away. The potential at its location, due to the ionic atmosphere is

$$-(Q/\varepsilon)r_D^{-1}.$$

Energy = charge×electric potential

The work of adding dQ of charge to a region having this electric potential is,

$$-(Q/\varepsilon)r_D^{-1}\,dQ$$

Therefore the <u>molar work</u> of fully charging the ions is

$$N_{\mathrm{Avog}}\int_0^{ze} -(Q/\varepsilon)r_D^{-1}\,dQ$$

$$= -N_{\mathrm{Avog}}(z_i e)^2/2\varepsilon r_D$$

$$RT\ln(\gamma_\pm)^s = W_{elec} = pW_{elec+}qW_{elec-} =$$

$$\ln\gamma_\pm = (pW_{elec+}qW_{elec-})/sRT$$

$$= z_+ z_- e^2 N_{Avog}/RT\ 2\varepsilon r_D = z_+ z_- e^2/\ 2\varepsilon k_B T\, r_D$$

The Debye length r_D is obtained from the statistical distribution of charged particles, where ρ is the density of the solvent and molarity = $m_i \rho$ and I is the ionic strength:

$r_D = \{1000\varepsilon k_B T/8\pi\, I\rho e^2 N_{Avog}\}^{1/2}$

Substituting r_D into $\ln(\gamma_\pm)$

$\ln \gamma_\pm = z_+ z_- e^2/\, 2\varepsilon k_B T \bullet$

$\{8\pi I\rho e^2 N_{Avog}/1000\varepsilon_0 k_B T\}^{1/2}$

$\ln \gamma_\pm = z_+ z_- I^{1/2}\, (e^2/10\varepsilon k_B T)^{3/2}\, \{2\pi\rho N_{Avog}\}^{1/2}$

This is the limiting Debye-Hückel eqn.

Atkins has an extra $(4\pi)^{-3/2}$ and b = 1 molal (reference state of solution)

$\ln \gamma_\pm = z_+ z_- I^{1/2}(e^2/4\pi\varepsilon k_B T)^{3/2}\{b 2\pi\rho N_{Avog}\}^{1/2}$

A more realistic form is obtained if multiplied by a factor $\{1 + B\, I^{1/2}\}^{-1}$

Debye Huckel limiting law provides

$\ln \gamma_{\pm} = (2\pi N_{Avog})^{1/2} (e^2/10\varepsilon k_B T)^{3/2} \; z_+ z_- I^{1/2}$

This gives us a limiting behavior for $\gamma_{\pm}$ in dilute solutions, for ions bearing charges $+z_+ e$ and $-z_- e$. The ionic strength is

$$I \equiv (1/2) \sum_{i=\text{all ions}} C_i \, z_i$$

where C_i is the molarity of the ith ion in the solution.

The dependence on ionic strength $I^{1/2}$ provides a means by which the limiting behavior of various equilibrium constants can be obtained.

A plot of $\ln K_m$ versus $I^{1/2}$ should approach a linear behavior as the solution becomes more dilute, obeying the Debye limiting law. Extrapolating the straight line to infinite dilution should provide $\ln K$ as the intercept.

For example, in AgCl, we had found

$$K = (\gamma_+ m_{\mathrm{Ag+}} \, \gamma_- \, m_{\mathrm{Cl-}}) = \gamma_{\pm}^{\;2} \, C_s^{\;2}$$

$\log_{10} K = 2 \log_{10} C_s + 2 \log_{10} \gamma_\pm$

Use the Debye-Huckel limiting eq.:

$\ln \gamma_\pm = (2\pi N_{Avog})^{1/2} (e^2/10\varepsilon k_B T)^{3/2} z_+ z_- I^{1/2}$

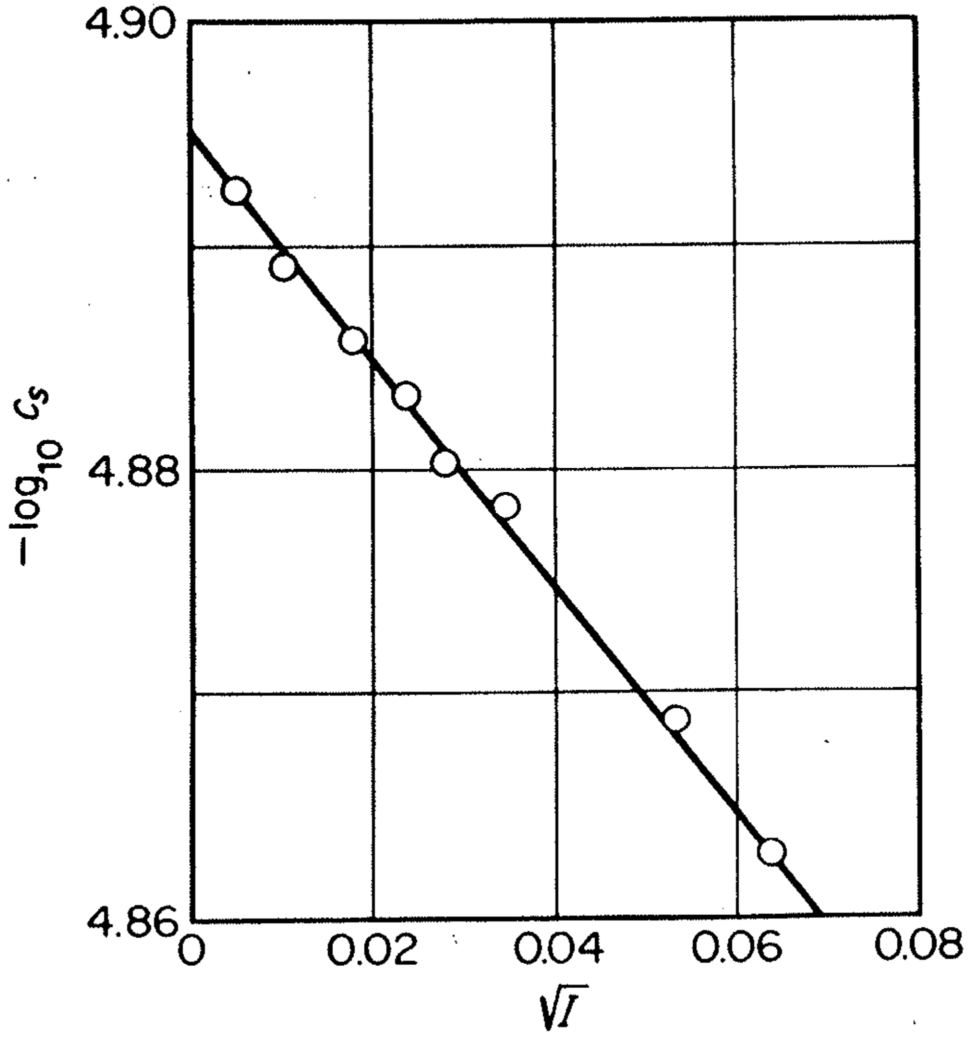
or $\log_{10} \gamma_\pm = A I^{1/2}$

$\log_{10} K = 2 \log_{10} C_s + 2A I^{1/2}$

$-\log_{10} C_s = A I^{1/2} - (1/2)\log_{10} K$

$y = \text{slope}\cdot x + \text{intercept}$

intercept is $-(1/2)\log_{10} K$, slope = A



Solubility of AgCl in $KNO_3(aq)$ at 25°C as a function of square root of ionic strength