Chapter 26: Chemical Equilibrium

Section 26-1 → gas phase reactions

\[ \Delta A(g) + \Delta B(g) \rightleftharpoons \Delta Y(g) + \Delta Z(g) \]

Define the "extent of reaction" $\xi$ such that

\[ \begin{align*}
N_A &= N_{A_0} - \Delta A \xi \\
N_B &= N_{B_0} - \Delta B \xi \\
N_Y &= N_{Y_0} + \Delta Y \xi \\
N_Z &= N_{Z_0} + \Delta Z \xi
\end{align*} \]

reactants \hspace{2cm} products

where $N_{j_0} = \text{initial \# moles for each species}$

Differentiating gives:

\[ \begin{align*}
dN_A &= -\Delta A d\xi \\
dN_B &= -\Delta B d\xi \\
dN_Y &= \Delta Y d\xi \\
dN_Z &= \Delta Z d\xi
\end{align*} \]

\[ \text{Why?} \quad \Delta A \text{ is just a number fixed by the stoichiometry.} \]

Recall that Gibbs energy is most useful under constant $T, P$ conditions.

We have $G = G(T, P, n_A, n_B, n_Y, n_Z)$ so that

\[ \begin{align*}
\frac{dG}{dT} &= \left( \frac{\partial G}{\partial T} \right)_{P, n_j} dt + \left( \frac{\partial G}{\partial P} \right)_{T, n_j} dP + \left( \frac{\partial G}{\partial n_A} \right)_{T, P, n_j, n_A^+} dN_A^+ \\
\Rightarrow \frac{dG}{dT} &= -S dt + V dP + \mu_A dN_A + \mu_B dN_B + \mu_Y dN_Y + \mu_Z dN_Z
\end{align*} \]

where $\mu_A = \left( \frac{\partial G}{\partial n_A} \right)_{T, P, n_B, n_Y, n_Z}$ = chemical potential.
At constant $T, P$ becomes
\[ dG = \sum_j \mu_j \, dn_j \quad \text{Does use the F equations:} \]
\[ dG = -dA \mu \, d\xi - dB \mu \, d\xi + \nu \mu \, d\xi + V \mu_2 \, d\xi \]
\[ = (\nu \mu_4 + V \mu_2 - dA \mu - dB \mu) \, d\xi \]
\[ \rightarrow \frac{\partial G}{\partial \xi} \bigg|_{T,P} = \nu \mu_4 + V \mu_2 - dA \mu - dB \mu \equiv \Delta G_{\text{rxn}} \]

$\Delta G_{\text{rxn}}$ is the change in Gibbs energy when the extent of reaction changes by one mole.

Now we need a result from Ch. 23, namely
\[ \mu_j(T, P) = \mu_j(T, P^0) + RT \ln \frac{P_j}{P^0} \quad \text{where} \quad P^0 = 1 \text{bar} \]
\[ = \mu_j^0(T) + RT \ln \frac{P_j}{P^0} \]

Let us derive this:
\[ \frac{\partial \mu_j}{\partial P} \bigg|_{T,n_j} = \frac{\partial}{\partial P} \left( \frac{\partial G}{\partial n_j} \right) = \frac{\partial}{\partial n_j} \left( \frac{\partial G}{\partial P} \right) \bigg|_{T,n_j} = \frac{\partial V}{\partial n_j} \bigg|_{T,P,n_i \neq j} \]
For a gas, $P_j V = n_j RT \Rightarrow \frac{\partial V}{\partial n_j} = RT / P_j$

Then
\[ \mu_j(T, P) = \mu_j(T, P^0) + \int_{P^0}^{P} \frac{\partial \mu_j}{\partial P} \bigg|_{T,n_j} \, dP \]
\[ = \mu_j^0(T) + RT \ln \frac{P_j}{P^0} \]
Using this gives
\[ \Delta G_{rxn} = \nu_Y \mu_Y^0(T) + \nu_Z \mu_Z^0(T) - \Delta H_M^0(T) - \nu_B \mu_B^0(T) \]
\[ + RT(\nu_Y \ln P_Y/p_o + \nu_Z \ln P_Z/p_o - \nu_A \ln P_A/p_o - \nu_B \ln P_B/p_o) \]

We can write this as  \[ \Delta G_{rxn} = \Delta G_{rxn}^0 + RT \ln Q \]
where \[ \Delta G_{rxn}^0 = \nu_Y \mu_Y^0(T) + \nu_Z \mu_Z^0(T) - \Delta H_M^0(T) - \nu_B \mu_B^0(T) \]
and \[ Q = \left( \frac{P_Y}{P_o} \right)^{\nu_Y} \left( \frac{P_Z}{P_o} \right)^{\nu_Z} \]
\[ \left( \frac{P_A}{P_o} \right)^{\nu_A} \left( \frac{P_B}{P_o} \right)^{\nu_B} \]

At equilibrium, \[ \Delta G_{rxn} = \frac{\partial G}{\partial \Phi} \bigg|_{T, P} = 0 \]
This gives, in \[ \bullet \]
\[ \Delta G_{rxn}^0(T) = -RT \ln \left( \frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{eq} \equiv -RT \ln K_p(T) \]
where we have dropped the \[ P_o = 1 \text{ bar} \] parts of Q, but they are still present to make Q unitless.
\[ K_p(T) \] is the equilibrium constant of the reaction.
Consider \( \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \)

with \( K_p(T) = \frac{P_{\text{PCl}_3}P_{\text{Cl}_2}}{P_{\text{PCl}_5}} \)

Suppose the total pressure is \( P \) and we begin with one mole of \( \text{PCl}_5(g) \) and no products. When \( x \) moles of reactants have converted to products, and equilibrium is achieved, work out the partial pressures of each species:

\[ \text{Initial:} \quad 1 \quad 0 \quad 0 \]

\[ \text{Change:} \quad -x \quad +x \quad +x \]

\[ \text{Final:} \quad 1-x \quad x \quad x \]

Total moles: \( (1-x)+x+x = 1+x \)

\[ PV = n_{\text{TOT}} \cdot RT = (n_{\text{PCl}_5} + n_{\text{PCl}_3} + n_{\text{Cl}_2}) \cdot RT \]

Define \( P_{\text{PCl}_5} = \frac{n_{\text{PCl}_5} \cdot RT}{\sqrt{V}} \); \( P = P_{\text{TOT}} = P_{\text{PCl}_5} + P_{\text{PCl}_3} + P_{\text{Cl}_2} \)

\[ \Rightarrow P_{\text{PCl}_5} = (1-x) \frac{P}{n_{\text{TOT}}} = \frac{(1-x)P}{1+x} \]

\[ P_{\text{PCl}_3} = P_{\text{Cl}_2} = \frac{x \cdot P}{1+x} \]

\[ \Rightarrow K_p(T) = \frac{P_{\text{eq}}^2}{1-P_{\text{eq}}} \]
This makes it look like \( K_p(T) \) depends on \( P \).
But it doesn't. What is going on?

What happens is that \( F \) shifts as \( P \) shifts to keep \( K \) constant. *See Fig 26.1*

This is an example of Le Châtelier's principle:

If a chemical reaction at equilibrium is subjected to a change in conditions, the reaction adjusts to partially offset the change.

Here an increase in pressure shifts the equilibrium such that \( N_{TOT} \) decreases.

Instead of equil pressures, we could use equil concentrations for \( K \) through \( P = cHT = \left( \frac{n}{V} \right) RT \)

This looks like:

\[
K_p = \frac{C_y^{v_y} C_z^{v_z}}{C_A^{v_A} C_B^{v_B}} \left( \frac{RT}{P_0} \right)^{v_y + v_z - v_A - v_B}
\]

or \( K_p = K_c \left( \frac{c^0 RT}{P_0} \right)^{v_y + v_z - v_A - v_B} \)

With \( K_c = \frac{(C_y/c_0)^{v_y} (C_z/c_0)^{v_z}}{(C_A/c_0)^{v_A} (C_B/c_0)^{v_B}} \)
Section 26-3: ΔG° data can be used to compute K.

Ex: calculate ΔG°rxn and Kp at 298.15 K for

\[ \text{NH}_3(g) \rightarrow \frac{3}{2} \text{H}_2(g) + \frac{1}{2} \text{N}_2(g) \]

\[ \Delta G_{\text{rxn}} = \frac{3}{2} (0) + \frac{1}{2} (0) - (1 \times 16.364 \text{ kJ/mol}) = 16.364 \text{ kJ/mol} \]

Then \( \ln K_p(T) = - \frac{\Delta G_{\text{rxn}}}{RT} = - \frac{16.364 \text{ kJ/mol}}{8.3145 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} \)

\[ = -6.6 \Rightarrow K_p(T) = 1.36 \times 10^{-3} \text{ at 298 K} \]

Section 26-4: What does G vs Φ look like?

We expect, in general, that G is a minimum at equilibrium.

Look at \( \text{N}_2\text{O}_4(g) \rightarrow 2 \text{N}_2\text{O}_2(g) \) at 298 K, 1 bar.

Begin with 1 mol \( \text{N}_2\text{O}_4 \), zero mols \( \text{N}_2\text{O}_2 \).

Then \( N_{\text{N}_2\text{O}_4} = (1-Φ) \); \( N_{\text{N}_2\text{O}_2} = 2Φ \); \( Φ \in (0, 1) \)

\[ G(Φ) = (1-Φ) \Delta G_{\text{N}_2\text{O}_4} + 2Φ \Delta G_{\text{N}_2\text{O}_2} \]

\[ = (1-Φ) \Delta G_{\text{N}_2\text{O}_4} + 2Φ \Delta G_{\text{N}_2\text{O}_2} + (1-Φ)RT \ln P_{\text{N}_2\text{O}_4} + 2ΦRT \ln P_{\text{N}_2\text{O}_2} \]

\[ P_{\text{N}_2\text{O}_4} = \frac{1-Φ}{1+Φ} \quad \text{and} \quad P_{\text{N}_2\text{O}_2} = \frac{2Φ}{1+Φ} \]

Also, \( \Delta G_{\text{N}_2\text{O}_4} = ΔG°(\text{N}_2\text{O}_4) \) and \( \Delta G_{\text{N}_2\text{O}_2} = ΔG°(\text{N}_2\text{O}_2) \).

\[ \Rightarrow G(Φ) = (1-Φ) \times 94.787 \text{ kJ/mol} + 2Φ \times 51.258 \text{ kJ/mol} \]

\[ + (1-Φ)RT \ln \frac{1-Φ}{1+Φ} + 2ΦRT \ln \frac{2Φ}{1+Φ} \]

\[ \text{minimum = equilibrium} \Rightarrow Φ = 0.1892 \text{ mol} \]
We had \( \Delta G_{\text{rxn}} = \Delta G^\circ_{\text{rxn}} + RT \ln \frac{P_y^{d_y} P_z^{d_z}}{P_A^{d_A} P_B^{d_B}} \)

for \( n_A + n_B \rightarrow n_Y + n_Z \)

We write this in terms of \( Q \) and \( K \) as
\[
\Delta G_{\text{rxn}} = -RT \ln K_p + RT \ln Q_p = RT \ln \frac{Q_p}{K_p}
\]

At equil. \( \Delta G_{\text{rxn}} = 0 \) and \( Q_p = K_p \)

If \( Q_p < K_p \) then \( Q_p \) must increase as the reaction proceeds towards equil, which means the partial pressures of the products must increase and those of the reactants must decrease.

In other words, the reaction proceeds from left to right as written.

If \( Q_p > K_p \) the reaction goes from right to left.
section 26-6: What is the difference between \( \Delta G^\circ \)_rxn and \( \Delta G^\circ \)?

The ° means everything is at 1 bar (all reactants and products).

If \( \Delta G^\circ \_\text{rxn} > 0 \), then \( K_p < 1 \) meaning that the reaction will go from products to reactants if all the species are mixed at 1 bar partial pressures.

Consider \( \text{N}_2\text{O}_4 (g) \rightleftharpoons 2\text{NO}_2 (g) \)

where \( \Delta G^\circ = 4.729 \text{ KJ/mol} \) at 298 K.

\[ \Delta G = \Delta G^\circ + RT \ln Q_p = 4.729 + 2.479 \ln \frac{P_{\text{NO}_2}}{P_{\text{N}_2\text{O}_4}} \]

Place 0.8 bar \( \text{N}_2\text{O}_4 \) and 0.2 bar \( \text{NO}_2 \) in a flask.

Then \( \Delta G = 4.729 + 2.479(-3) = -2.7 \).

So the reaction proceeds forwards even though \( \Delta G^\circ > 0 \).

Next consider \( 2\text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(l) \)

with \( \Delta G^\circ \_\text{rxn} = -237 \text{ KJ per mole of H}_2\text{O formed at 298K} \).

So \( \text{H}_2\text{O}(l) \) at 1 bar and 298K is much more stable than a mixture of \( \text{H}_2(g) \) and \( \text{O}_2(g) \) under the same conditions.

But the reaction does not proceed without a spark or a catalyst because there is a large barrier in going from reactants to products.
Thermodynamics vs Kinetics

If thermodynamics says a reaction should proceed spontaneously, we may observe the reaction, but the rate could be zero for kinetic reasons.

If thermodynamics says a reaction will NOT proceed spontaneously, we will not observe the reaction.

Section 26.7: Temperature dependence of $K_p$.

We begin with the Gibbs-Helmholtz equation (22.61)

$$\frac{\partial A^0 (T)}{\partial T} = -\frac{\Delta H^0}{T^2}$$

and substitute $A^0 = -RT \ln K_p$ to obtain

$$\frac{\partial \ln K_p (T)}{\partial T} = \frac{\Delta H_{\text{rxn}}}{RT^2} = \frac{d \ln K_p (T)}{dT}$$

Integrate to get

$$\ln \frac{K_p (T_2)}{K_p (T_1)} = \int_{T_1}^{T_2} \frac{\Delta H_{\text{rxn}} (T)}{RT^2} dT$$

If we assume $\Delta H_{\text{rxn}}$ is independent of $T$ we get

$$\ln \frac{K_p (T_2)}{K_p (T_1)} = -\frac{\Delta H_{\text{rxn}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Van't Hoff Equation

$$\ln K_p \propto \text{linear, slope} = -\frac{\Delta H_{\text{rxn}}}{R} \quad \text{endothermic}$$

$1/T$
had: \( \mu_j = \mu_j^0 + RT \ln \frac{p_j}{p_0} \) for ideal gas from which we obtained \( \Delta G_{rxn} = \Delta G_{rxn}^0 + RT \ln Q_p \)

\[ Q_p \left( = \frac{K_p \text{ at equil}}{P} \right) = \frac{P^{\nu_y} P^{\nu_z}}{P^{\nu_A} P^{\nu_B}} \text{ for } \nu_A + \nu_B \rightleftharpoons \nu_Y + \nu_Z \]

(suppress 1° ref. state)

Can use concentrations instead:

\[ Q_c \left( = \frac{K_c \text{ at equil}}{C} \right) = \frac{C^{\nu_y} C^{\nu_z}}{C^{\nu_A} C^{\nu_B}} \]

Generalize to \( \mu_j = \mu_j^0 (T) + RT \ln a_j \)

which means we use \( Q_a \left( = \frac{K_a \text{ at equil}}{a} \right) = \frac{a^{\nu_y} a^{\nu_z}}{a^{\nu_A} a^{\nu_B}} \)

**Standard state**: gases: ideal gas at 1 bar

pure solid, liquid: pure substance in normal state at 1 bar

solutions: solvent: Raoult's law std. state

solute: Henry's law std. state

Activity accounts for state (gas, solid, solution) and also deviations from ideal behavior (ideal depends on state)

real gases: \( a_j = \gamma_j \frac{p_j}{p_0} \) activity coefficient

pure solid or liquid: at fixed \( T \), \( \mu = \mu^0 + RT \ln a \Rightarrow \gamma_j = \frac{RT \text{ dlna}}{\text{dP}} \)

Also \( \frac{\partial \mu}{\partial P} = \frac{2}{\partial P} \frac{2V}{\partial n} = \frac{2V}{\partial n} \Rightarrow \gamma_j = \frac{V}{T} \text{ dP} \)

Combine \( V \text{ dP} = RT \text{ dlna} \Rightarrow \text{ dlna} = \frac{1}{RT} V \text{ dP} \Rightarrow \ln a = \frac{1}{RT} \int_0^p V \text{ dP} \approx \frac{V}{RT} (p - 1) \) since liquids, solids incommunicable (roughly)
Recall, previously, we had:

$$\mu_j(T, P) = \mu_j^0(T) + \int_{P_0}^P \frac{\partial \mu_j}{\partial P} \, dP$$

for an ideal gas, which was how we obtained the expression:

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^0 + RT \ln Q_p$$.

We now generalize this expression to:

$$\mu_j = \mu_j^0(T) + RT \ln a_j$$

→ standard state value

Note: for gases, the standard state is the corresponding ideal gas at 1 bar pressure; for pure solids and liquids, the standard state is the pure substance in its normal state at 1 bar pressure; for solutions, we have a Raoult's Law standard state for the solvent and a Henry's Law standard state for the solute. (we will define these later)

The activity accounts for the state (gas, solid, solution, ...)

and also for deviations from "ideal" behavior.

Note: "ideal" behavior means something different for gas vs solution...
ex: for "real" gases, we write $a_j = \gamma_j \frac{P_j}{P_0}$ where $\gamma_j$ is the activity coefficient (given, or look up in tables...)

ex: for pure condensed phases we obtain the activity by:
$\mu = \mu^0(T) + RT \ln \alpha$ \implies $d\mu = RT \, d \ln \alpha$  \hspace{2cm} \xRightarrow{fix \ the \ temperature} \hspace{2cm} \frac{dP}{P} = \frac{dV}{V} \hspace{1cm} \frac{\partial P}{\partial V} = -\frac{1}{V}$

Thus $d \ln \alpha = \frac{1}{RT} \, \bar{V} \, dP \implies \ln \alpha = \frac{1}{RT} \int \bar{V} \, dP$

$\bar{V}$ is essentially constant for condensed phases, giving
$\ln \alpha = \frac{\bar{V}}{RT} (P - 1)$

ex: for ionic species, we do the following using acetic acid as an example:

\[ \text{CH}_3\text{COO}^- (aq) \rightarrow \text{H}^+ (aq) + \text{CH}_3\text{COO}^- (aq) \]

$\alpha_{\text{HAc}} = C_{\text{HAc}} \hspace{1cm} \text{concentration in molarity} \hspace{1cm} (y = 1)$

$\alpha_{\text{H}^+} \alpha_{\text{Ac}^-} = C_{\text{H}^+} C_{\text{Ac}^-} \gamma_+^2 \hspace{1cm} \text{activity coefficient} \hspace{1cm} \gamma_+$

We use $K = K_c$ in molarity so we use concentrations.

One choice for $\gamma_+$, specific to aqueous solutions at 298 K is

\[ \ln \gamma_+ = -\frac{1.173 (1 + \gamma_+ - 1) I_c^{1/2}}{1 + I_c^{1/2}} \hspace{1cm} \text{where} \hspace{0.5cm} I_c = \frac{1}{2}(C_{\text{H}^+} + C_{\text{Ac}^-}) \hspace{1cm} \text{ionic strength} \]
Where does this expression for $\gamma$ come from?

- First, we cannot treat the anions and cations separately because solutions are always electrically neutral.

- Second, each ion in solution is surrounded by an ionic atmosphere of the opposite charge. This is because Coulomb's Law tends to attract counterions and repel ions of like charge. There is only a slight imbalance of charge around a given ion because random thermal motion tends to keep all the ions distributed uniformly throughout the solution.

Because each ion is in an atmosphere of opposite charge, its energy is lower than in a uniform, ideal solution and therefore its chemical potential is lower than in an ideal solution.

This means $\gamma < 1$ (ln $\gamma < 0$).

Debye and Hückel worked out an approximate expression, which is the one given.
Usually the activities of pure solids and liquids are not included in equilibrium constant expressions.

Note: from \( \mu_j = \mu_j^0 + RT \ln a_j \) and \( v_1 A + v_2 B \rightleftharpoons v_1 Y + v_2 Z \)

we have \( \Delta G_{rxn}^0 = \Delta H_{rxn}^0 + RT \ln Q_a \) and \( \Delta G_{rxn}^0 = -RT \ln K_a \)

where \( K_a(T) = \left( \frac{a_y}{a_z} \right) \frac{a_z^{v_1}}{a_y^{v_2}} \), eq.

(recall heterogeneous equil. from general chemistry)

This is because these activities are \( \approx 1 \) so they don't contribute.

\[ a = 1.01 \quad \text{from} \quad \ln a = \frac{\bar{V}}{RT} (P-1) \]

\[ \bar{V} = 8.0 \text{ cm}^3 \text{ mol}^{-1} \]

\[ \bar{V} = 8.0 \text{ cm}^3 \text{ mol}^{-1} \]

\[ \bar{V} = 18.09 \text{ cm}^3 \text{ mol}^{-1} \]

Then \( 0.0424 \text{ bar} \rightarrow a = 0.9993 \)

\( 10 \text{ bar} \rightarrow 1.0065 = a \)

\( 100 \text{ bar} \rightarrow 1.0736 = a \)
Look at an example for ionic species:

Calculate the pH of an aqueous solution that is 0.100 M in acetic acid, given \( K_a = 1.74 \times 10^{-5} \).

\[
K_a = 1.74 \times 10^{-5} = \frac{a_{H^+} a_{Ac^-}}{a_{HAc}} = \frac{C_{H^+} C_{Ac^-} \gamma_+^2}{C_{HAc}}
\]

Ignore \( a_{H_2O} \)

\[
HAc \quad \Leftrightarrow \quad H^+ + Ac^-
\]

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Thus we have \( \frac{x^2 \gamma_+^2}{0.1-x} = 1.74 \times 10^{-5} \)

For \( \gamma_+ \), \( I_c = \frac{1}{2}(C_{H^+} + C_{Ac^-}) = C_{H^+} \). Also, \( Z_+ = 1, Z_- = -1, Z_0 = 0, \)

\[
\ln \gamma_+ = -\frac{1.173 \sqrt{C_{H^+}}}{1 + \sqrt{C_{H^+}}} = -\frac{1.173 \sqrt{x}}{1 + \sqrt{x}}
\]

This is a complicated expression in \( x \), namely the equation to find \( x \). We can solve it by the method of successive approximations.

1. put \( \gamma_+ = 1 \) and \( 0.1-x = 0.1 \) to get \( \frac{x^2}{0.1} = 1.74 \times 10^{-5} \)

\[
\Rightarrow x = 1.32 \times 10^{-3} \Rightarrow pH = 2.88
\]

2. put \( (0.1-x) = (0.1-1.32 \times 10^{-3}) = 0.09868 \)

and put \( \ln \gamma_+ = -\frac{1.173 \sqrt{1.32 \times 10^{-3}}}{1 + \sqrt{1.32 \times 10^{-3}}} = -0.04112 \Rightarrow \gamma_+^2 = 0.921 \)

\[
to \ get \ \frac{0.921 x^2}{0.0987} = 1.74 \times 10^{-5} \Rightarrow x = 1.37 \times 10^{-3} \Rightarrow pH = 2.86
\]

3. iterate again; still set \( pH = 2.86 \)
Was add 150 mM KCl which is roughly the physiological ionic strength = 0.15 M. Namely, calculate the pH of an aqueous solution that is 0.10 M in acetic acid and 0.15 M in KCl.

From the previous page, we have
\[
\frac{x^2 y_+^2}{0.1 - x} = 1.74 \times 10^{-5}
\]

1. Put \( y_+ = 1 \) and \( 0.1 - x = 0.1 \) to get
\[
\frac{x^2}{0.1} = 1.74 \times 10^{-5}
\]
\[\Rightarrow x = 1.32 \times 10^{-3} \Rightarrow pH = 2.88\]

2. Put \( (0.1 - x) = (0.1 - 1.32 \times 10^{-3}) = 0.09868 \)
   and put \( ln y_+ = -\frac{1.74 \sqrt{1.32 \times 10^{-3} + 0.15}}{1 + \sqrt{1.32 \times 10^{-3} + 0.15}} \approx -0.328 \)
\[\Rightarrow y_+^2 = 0.518\]
\[\text{to get} \quad \frac{0.518 x^2}{0.0987} = 1.74 \times 10^{-5} \Rightarrow x = 1.82 \times 10^{-3} \]
\[\Rightarrow pH = 2.74\]

3. Put \( (0.1 - x) = (0.1 - 1.82 \times 10^{-3}) = 0.09818 \)
   and put \( ln y_+ = -\frac{1.74 \sqrt{1.82 \times 10^{-3} + 0.15}}{1 + \sqrt{1.82 \times 10^{-3} + 0.15}} \approx -0.329 \)
\[\Rightarrow y_+^2 = 0.518\]
\[\text{to get} \quad \frac{0.518 x^2}{0.09818} = 1.74 \times 10^{-5} \Rightarrow x = 1.82 \times 10^{-3} \Rightarrow pH = 2.74\]

So the pH drops from 2.88 to 2.74 upon addition of physiological KCl!