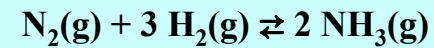
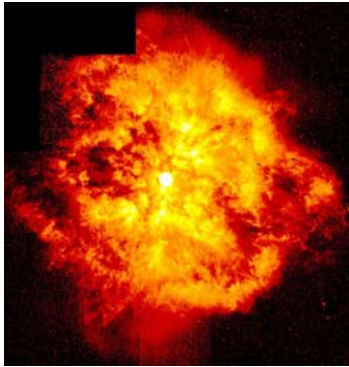
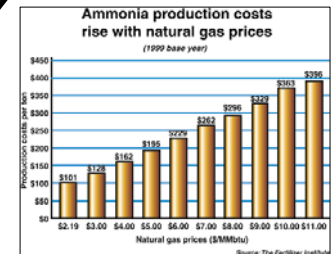


Chemistry BC3252y
VIII: Chemical Equilibria

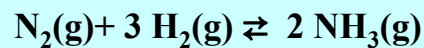


Not a trivial reaction!
Modern agriculture needs fertilizers that are ammonia based.
Ammonia synthesis is a multibillion dollar energy-intensive industry.

200 ton/day plant



2



Start with arbitrary amounts of each species, n_k°

As the reaction proceeds n_k values change

Let $k = \text{H}$ (for H_2), N (for N_2), and A (for NH_3).

Then $n_{\text{N}} = n_{\text{N}}^\circ + \Delta n_{\text{N}}$, $n_{\text{H}} = n_{\text{H}}^\circ + \Delta n_{\text{H}}$, etc.

Stoichiometry governs the changes:

Δn_{N} , Δn_{H} , are not independent of each other.

Define a single variable ξ ("xi", pronounced $\bar{x}i$),

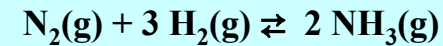
that measures the progress of the reaction.

If $\Delta n_{\text{N}} = -\xi$, then $\Delta n_{\text{H}} = -3\xi$, and $\Delta n_{\text{A}} = +2\xi$

Coefficients come from balanced chemical reaction:

negative for reactants, positive for products.

3



ξ may be positive or negative:

With the above definitions ($\Delta n_{\text{N}} = -\xi$ etc.),

positive ξ means progress towards products.

$n_{\text{N}} = n_{\text{N}}^\circ - \xi$, $n_{\text{H}} = n_{\text{H}}^\circ - 3\xi$, and $n_{\text{A}} = n_{\text{A}}^\circ + 2\xi$.

$$G = \sum n_k \mu_k$$

$$G = \mu_{\text{N}}(n_{\text{N}}^\circ - \xi) + \mu_{\text{H}}(n_{\text{H}}^\circ - 3\xi) + \mu_{\text{A}}(n_{\text{A}}^\circ + 2\xi)$$

$$G = (\mu_{\text{N}} n_{\text{N}}^\circ + \mu_{\text{H}} n_{\text{H}}^\circ + \mu_{\text{A}} n_{\text{A}}^\circ) + \xi (-\mu_{\text{N}} - 3\mu_{\text{H}} + 2\mu_{\text{A}})$$

Equilibrium means that **G is a minimum**

with respect to the progress variable ξ .

The condition for equilibrium is $(\partial G / \partial \xi)_{p,T} = 0$.

$$\text{But } (\partial G / \partial \xi)_{p,T} = (-\mu_{\text{N}} - 3\mu_{\text{H}} + 2\mu_{\text{A}}) = 0$$

4

General reaction: $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$

Stoichiometric coefficients ν_k

$$\text{reactants: } \nu_A = -\alpha \quad \nu_B = -\beta$$

$$\text{products: } \nu_C = +\gamma \quad \nu_D = +\delta$$

Moles of species k as reaction proceeds: $n_k = n_k^\circ + \nu_k \xi$

The change in moles of k is $dn_k = \nu_k d\xi$.

$$\begin{aligned} dG &= V dp - S dT + \sum \mu_k dn_k \\ &= V dp - S dT + \sum \mu_k \nu_k d\xi \\ &= V dp - S dT + (\sum \mu_k \nu_k) d\xi \end{aligned}$$

If we define $\Delta_r G \equiv \sum \nu_k \mu_k$ then

$$dG = V dp - S dT + \Delta_r G d\xi \quad \text{and} \quad (\partial G / \partial \xi)_{T,p} = \Delta_r G$$

5

What is $\Delta_r G$?

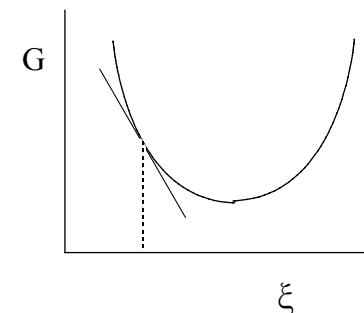
If temperature and pressure are fixed, the only variable during a reaction is ξ .

Picture (on right):

G is a function of ξ :

The **slope** of this plot at any point, $(\partial G / \partial \xi)_{T,p}$, is by definition $\Delta_r G$.

The system comes to equilibrium when $\Delta_r G = 0$: there G is a **minimum**.



6

What is $\Delta_r G$?

Some books give it a special name (chemical affinity or reaction potential) and some give it a special symbol (Atkins does not).

But it should look familiar: you have often calculated $\Delta_r H$ and $\Delta_r G$ values using stoichiometric coefficients.

Actually you have calculated $\Delta_r H^\circ$ and $\Delta_r G^\circ$, a significant distinction, as we shall see.

What this development does is

- (1) shows that the quantity $\Delta_r G \equiv \sum \nu_k \mu_k$ is equal to $(\partial G / \partial \xi)_{T,p}$
- (2) tells you where equilibrium will be in terms of ξ , and
- (3) shows that $\Delta_r G = 0$ at equilibrium.

7

Reactions among ideal gases

For an ideal gas $\mu_{k,g}(p, T, X) = \mu_{k,g}^{\circ*}(T) + RT \ln p_k$

[$^\circ$ means at standard p, i.e. one atm; * means pure;

p_k = **partial** pressure of k]

$\Delta_r G$ for a reaction among ideal gases:

$$\begin{aligned} \Delta_r G &\equiv \sum \nu_k \mu_k = \sum \nu_k (\mu_k^{\circ*} + RT \ln p_k) \\ &= \sum \nu_k \mu_k^{\circ*} + RT \sum \nu_k \ln p_k \\ &= \sum \nu_k \mu_k^{\circ*} + RT \sum \ln p_k^{\nu_k} \end{aligned}$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln \prod p_k^{\nu_k}$$

where $\Delta_r G^\circ \equiv \sum \nu_k \mu_k^{\circ*}$

using the facts that $n \ln x = \ln x^n$ and $\ln x + \ln y = \ln (xy)$.

8

Reactions among ideal gases

$$\Delta_r G = \Delta_r G^\circ + RT \ln \left(\prod p_k^{v_k} \right)$$

$$\text{where } \Delta_r G^\circ \equiv \sum v_k \mu_k^{\circ*}$$

$\Delta_r G^\circ$ can be found from properties of the pure substances at standard pressure; it depends only on T

What is the term $\left(\prod p_k^{v_k} \right)$?

Consider the reaction



$$\prod p_k^{v_k} = p_{\text{N}}^{-1} p_{\text{H}}^{-3} p_{\text{A}}^{+2} = (p_{\text{A}}^2 / p_{\text{N}} p_{\text{H}}^3)$$

$\left(\prod p_k^{v_k} \right)$ is the **reaction quotient Q**.

Define $Q \equiv \prod p_k^{v_k}$, then $\Delta_r G = \Delta_r G^\circ + RT \ln Q$

9

Equilibrium Constants: reactions among ideal gases

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

If the system is at equilibrium, $\Delta_r G = 0$, so

$$\Delta_r G^\circ = -RT \ln K$$

where K is the value of Q at equilibrium.

Q is **arbitrary**: one can prepare a mixture with any Q

If temperature is constant, $\Delta_r G^\circ$ is **constant**,

since it is comprised of **constants** $\mu_k^{\circ*}$.

If the LHS is constant, then the RHS is constant.

Q at equilibrium is not arbitrary: it is **unique**, and called the equilibrium constant K.

10

K for ideal gas reactions

$$\Delta_r G^\circ = -RT \ln K \quad (K = K_{\text{eq}} = K_p)$$

1) K depends on T, but not on p.

$\mu_k^{\circ*}$ are defined at p° , so they are independent of p. If we start with an equilibrium mixture and change p_{tot} , there will be changes (e.g. partial pressures p_k may change), but when equilibrium is restored, K will have returned to its original value.

2) K is dimensionless.

Each p in the expression is actually (p_k/p_k°) , where $p_k^\circ = 1 \text{ atm}$ (or 1 bar), exactly. While this is formally correct, you will often find that chemists and biochemists quote K with units.

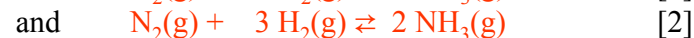
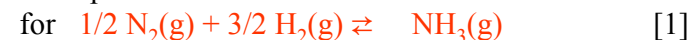
11

K for ideal gas reactions

$$\Delta_r G^\circ = -RT \ln K$$

3) $\Delta_r G$, $\Delta_r G^\circ$, Q, and K all depend on how the chemical equation is balanced.

Example: compare values



$\Delta_r G^\circ$, and K are different for 1 and 2, but they are related.

$$\text{Let } \Delta G_1^\circ = -RT \ln K_1 \text{ and } \Delta G_2^\circ = -RT \ln K_2$$

The v's are twice as large in [2], so since $\Delta_r G^\circ \equiv \sum v_k \mu_k^{\circ*}$:

$$\Delta G_2^\circ = 2 \Delta G_1^\circ = -2 RT \ln K_1 = -RT \ln K_1^2 = -RT \ln K_2.$$

Thus $K_2 = K_1^2$, consistent with the equation $\prod p_k^{v_k}$.

Moral of this story: always include the balanced equation.

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K for ideal gas reactions

$$\Delta_r G^\circ = -RT \ln K$$

- 4) **The value of K has nothing to do with the initial conditions.**

For a given set of initial p's, (p_k^0) there is a **unique** equilibrium set of p's that

- satisfy K, and
- follow the stoichiometry.

We can solve for these equilibrium pressures.

With a different set of p_k^0 values, there will be a different set of equilibrium p's, but the same K.

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K for ideal gas reactions: other concentration units

The equation $\mu_k = \mu_k^{\circ*}(T) + RT \ln p_k$ produces an equilibrium constant in terms of p_k values (K_p).

We can express K's in other units. Example: X_k

partial pressure $p_k = X_k p$, so $K_p = \prod p_k^{v_k}$

$$K_p = \prod (X_k p)^{v_k} = p^{\Delta v} \prod (X_k)^{v_k} \text{ where } \Delta v = \sum v_k.$$

If we define $K_X = \prod X_k^{v_k}$ then $K_p = p^{\Delta v} K_X$.

Conclusion: while K_p (the true thermodynamic K) is independent of pressure,

K_X will depend on pressure, unless $\Delta v = 0$.

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K for ideal gas reactions: other concentration units

K's in other units. Let $c_j = n_j/V$: moles/L

For an ideal gas, $p_j = c_j RT$.

$$K_p = \prod p_k^{v_k} = \prod (c_k RT)^{v_k} = (RT)^{\Delta v} \prod (c_k)^{v_k}$$

If we define $K_c = \prod (c_k)^{v_k}$,

then $K_p = (RT)^{\Delta v} K_c$.

Conclusion: K_c is independent of total p

But it will have a different **numerical value** from K_p , since it is expressed in terms of different units.

15

Using equilibrium constants to determine composition in a reaction mixture



What fraction of O_2 molecules will react to form O_3 at equilibrium when $p = \text{one atm}$ and $T = 25^\circ\text{C}$?

This reaction has a very large positive $\Delta_r G^\circ$:

$$\Delta_r G^\circ = 2(163.2 \text{ kJ/mole}) = 326.4 \text{ kJ/mole.}$$

$$\ln K = -\Delta_r G^\circ/RT = -131.55 \rightarrow K = 6.6 \times 10^{-58}.$$

Let α = fraction of O_2 that reacts.

We know that α will be **very small**.

16

Using equilibrium constants to determine composition in a reaction mixture



Let α = fraction of O_2 that reacts

	moles O_2	moles O_3	total
initial	n	0	n
change	$-n \alpha$	$(2/3) n \alpha$	
equilibrium	$n(1-\alpha)$	$(2/3) n \alpha$	$n(1-\alpha/3)$

$$p_{\text{O}_2} = (X_{\text{O}_2}) p = p (1-\alpha)/(1-\alpha/3) = 3p (1-\alpha)/(3-\alpha)$$

$$p_{\text{O}_3} = (X_{\text{O}_3}) p = p (2\alpha/3)/(1-\alpha/3) = p (2\alpha)/(3-\alpha)$$

17

Using equilibrium constants to determine composition in a reaction mixture



$$p_{\text{O}_2} = (X_{\text{O}_2}) p = p (1-\alpha)/(1-\alpha/3) = 3p (1-\alpha)/(3-\alpha)$$

$$p_{\text{O}_3} = (X_{\text{O}_3}) p = p (2\alpha/3)/(1-\alpha/3) = p (2\alpha)/(3-\alpha)$$

$$K = p_{\text{O}_3}^2/p_{\text{O}_2}^3 = [p (2\alpha)/(3-\alpha)]^2/[3p (1-\alpha)/(3-\alpha)]^3 \\ = 4\alpha^2(3-\alpha)/[27 p (1-\alpha)^3]$$

$$\text{If } p = 1, \text{ then } K = 4\alpha^2(3-\alpha)/[27(1-\alpha)^3]$$

Since α is small, to a good approximation

$$(1-\alpha) \sim 1 \text{ and } (3-\alpha) \sim 3, \text{ so } K = 4\alpha^2/9$$

$$\alpha = [(9/4) K]^{1/2} = 3.8 \times 10^{-29}$$

18

Using equilibrium constants to determine composition in a reaction mixture



In one million moles (6×10^{29}), 4 molecules react!

Little ozone present when the system is at equilibrium.

General approach: relate K to **one** quantity that measures the extent of reaction, based on the initial values and the stoichiometry.

Think carefully about what you choose as the variable (moles, pressure, fraction, etc.) and spell this out clearly.

Good strategy: make the unknown a **small** quantity to facilitate approximations.

Solve for this quantity (here, α) and determine all equilibrium values from it.

19

Effect of p on equilibria

K is independent of p . Does this mean that changing p has no effect on equilibria? **No!**

K doesn't change, but that often means that **amounts** of reactants and products **do** change; but not always.

There are several different ways in which we can change pressure; each needs to be considered carefully.

Among these are

(1) changing total volume, (2) adding something.

20

Effect of p on equilibrium



$$\Delta_r G^\circ = 2 \Delta_f G^\circ[\text{NO}_2(\text{g})] - 2 \Delta_f G^\circ[\text{NO}(\text{g})]$$

$$= 2(51.31) - 2(86.55) = -70.48 \text{ kJ/mole}$$

$$\ln K = -\Delta_r G^\circ/RT = +28.431 \rightarrow K = 2.2 \times 10^{12}$$

Start with 10 moles of O_2 and 1 mole of NO
at constant $p = \text{one atm}$ and $T = 25^\circ\text{C}$.

What are the amounts present at equilibrium?

Work with moles, and let $x = \text{moles of NO}$

remaining at equilibrium. *Why is this a good choice?*

K is large, and NO is the limiting reagent,
so very little NO remains at equilibrium.

21

Effect of p on equilibrium



Initially: 10 moles of O_2 and 1 mole of NO

$x = \text{moles of NO left at equilibrium}$

moles	NO	O_2	NO_2	total
initially	1	10	0	11
change	$x-1$	$\frac{1}{2}(x-1)$	$-(x-1)$	
final	x	$\frac{1}{2}(x+19)$	$1-x$	$\frac{1}{2}(x+21)$
mole fraction	$2x/(x+21)$	$(x+19)/(x+21)$	$2(1-x)/(x+21)$	

$$K = \frac{p_{\text{NO}_2}^2}{p_{\text{NO}}^2 p_{\text{O}_2}} = \frac{1}{p} \frac{X_{\text{NO}_2}^2}{X_{\text{NO}}^2 X_{\text{O}_2}} = \frac{1}{p} \frac{[2(1-x)]^2 (x+21)}{(2x)^2 (x+19)} = \frac{1}{p} \frac{(1-x)^2 (x+21)}{x^2 (x+19)}$$

22

Effect of p on equilibrium



$$K = \frac{p_{\text{NO}_2}^2}{p_{\text{NO}}^2 p_{\text{O}_2}} = \frac{1}{p} \frac{X_{\text{NO}_2}^2}{X_{\text{NO}}^2 X_{\text{O}_2}} = \frac{1}{p} \frac{[2(1-x)]^2 (x+21)}{(2x)^2 (x+19)} = \frac{1}{p} \frac{(1-x)^2 (x+21)}{x^2 (x+19)}$$

K is constant, but p appears in K ,

so if p changes, then x must change.

Solve assuming that x is small (check at end!):

$$\text{If } x \ll 1, \text{ then } K = 21/(19px^2),$$

$$\text{so } x^2 = 21/(19pK) \rightarrow x = 7.1 \times 10^{-7} \text{ when } p = 1$$

x is small: the approximation is valid

23

Effect of p on equilibrium:



For small x , $x^2 = 21/(19pK)$

$$\rightarrow x = 7.1 \times 10^{-7} \text{ when } p = 1 \text{ atm}$$

Increase p to 10 atm: x decreases by $10^{1/2}$,

$$\rightarrow x = 2.2 \times 10^{-7} \text{ when } p = 10 \text{ atm}$$

When p increases (e.g. make the container smaller)
 x decreases: the reaction shifts toward products.

This follows [LeChatelier's](#) principle: if p increases, the equilibrium shifts in the direction to offset the change. There are fewer moles of gas on the RHS, so moving towards products decreases pressure.

24

Effect of p on equilibrium:



What if we had increased p by adding an inert gas to the equilibrium mixture at fixed volume?

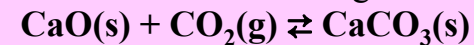
Assuming ideal gas behavior, the gases don't interact, so the partial pressures of reactants and products are not changed.

Since total pressure goes up, mole fractions go down.

But if the partial pressures don't change, the system remains at equilibrium, so there is no shift!

25

Reactants other than gases:



Gas and one or more **pure condensed phases**
(several distinct solids can exist together),

For pure solids: $\mu = \mu^\circ$

$$\mu_{\text{CaO}} = \mu^\circ_{\text{CaO}} \quad \text{and} \quad \mu_{\text{CaCO}_3} = \mu^\circ_{\text{CaCO}_3}$$

For the gas: $\mu_{\text{CO}_2} = \mu^\circ_{\text{CO}_2} + RT \ln p_{\text{CO}_2}$

$$\Delta_r G \equiv \sum v_k \mu_k$$

$$\Delta_r G = \mu^\circ_{\text{CaCO}_3} - \mu^\circ_{\text{CaO}} - [\mu^\circ_{\text{CO}_2} + RT \ln p_{\text{CO}_2}]$$

$$\Delta_r G = [\mu^\circ_{\text{CaCO}_3} - \mu^\circ_{\text{CaO}} - \mu^\circ_{\text{CO}_2}] - RT \ln p_{\text{CO}_2}$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln (1/p_{\text{CO}_2})$$

26



$\text{CaCO}_3(\text{s})$ (**limestone**)

heated at 900°C forms

CaO (**quicklime**).

CaO reacts very exothermically
with water to form

$\text{Ca}(\text{OH})_2$ (**slaked lime**)

used since antiquity in construction;
(also used to dissolve bodies!)

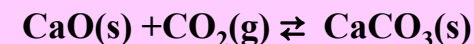
Slaked lime can react with CO_2 to
regenerate CaCO_3 .



interesting video:

<http://www.cee.princeton.edu/scherer/Slaking%20lime.html>

Gases with pure solids or liquids:



$$\Delta_r G = \Delta_r G^\circ + RT \ln (1/p_{\text{CO}_2})$$

Chemical potentials of the pure condensed phases
contribute to $\Delta_r G^\circ$, but these substances
do not appear in the equilibrium constant.

When writing equilibrium constants,
include gases (partial pressures in atmospheres),
but omit solids and pure liquids.

A "rule" in general chemistry; now you know why!

Because the composition of pure phases does
not vary, there are no logarithmic terms in
the chemical potential to contribute to K.

28

Equilibria involving ideal solutions

$$\mu_A(p, T, X) = \mu_A^*(p, T) + RT \ln X_A$$

$$\Delta_r G \equiv \sum v_k \mu_k = \sum v_k (\mu_k^* + RT \ln X_k)$$

$$\Delta_r G = \sum v_k \mu_k^* + RT \sum v_k \ln X_k$$

$$\Delta_r G = \sum v_k \mu_k^* + RT \sum \ln X_k^{v_k}$$

$$\Delta_r G = \sum v_k \mu_k^* + RT \ln \prod X_k^{v_k}$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

where $\Delta_r G^\circ = \sum v_k \mu_k^*$ and $Q = \prod X_k^{v_k}$

Conclusion: similar equation as for ideal gases, with subtle difference in meaning of $\Delta_r G^\circ$:

now it is a function of T and p,

since μ_k^* depends on T and p.

29

Equilibria involving ideal solutions.

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

where $\Delta_r G^\circ = \sum v_k \mu_k^*$ and $Q = \prod X_k^{v_k}$

Other concentration units:

suppose $[A] = g_A X_A$, where g_A is some constant.

Then $X_A = [A]/g_A$

$$\mu_A = \mu_A^* + RT \ln [A]/g_A = \mu_A^* - RT \ln g_A + RT \ln [A]$$

Define $\mu_A^\circ \equiv \mu_A^* - RT \ln g_A$

(LHS: properties of pure substance, constant at fixed T)

then $\mu_A = \mu_A^\circ + RT \ln [A]$

Plug this into the equation $\Delta_r G \equiv \sum v_k \mu_k$:

$$\Delta_r G = \Delta_r G^\circ + RT \ln \prod [k]^{v_k}$$

30

Equilibria involving ideal solutions

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

where $\Delta_r G^\circ = \sum v_k \mu_k^\circ$, $Q = \prod [k]^{v_k}$

$$\mu_A^\circ = \mu_A^* - RT \ln g_A, \text{ and } [A] = g_A X_A$$

The same equation, but we have tucked the conversion factor from mole fraction to molarity into the definition of μ_A° .

$$\mu_A = \mu_A^\circ + RT \ln [A]$$

μ_A° is now the chemical potential of A in a solution in which the molarity of A is exactly one (the reference or standard state).

When comparing equations for μ_k , the definition of the standard state changes, but the working equations are the same!

31

Equilibria involving real (non-ideal) solutions

$\mu_k = \mu_k^\circ + RT \ln a_k$ where $a_k = \text{activity}$ of k
 μ_k° is the chemical potential of k in a solution in which the activity of k is exactly one. From this we obtain (as before)

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

where $\Delta_r G^\circ = \sum v_k \mu_k^\circ$ and $Q = \prod a_k^{v_k}$

The differences are (1) definition of standard state μ_k° , and (2) the quantity that appears in Q (p_k , $[k]$, a_k).

But the beauty is that $\Delta_r G^\circ = -RT \ln K$ can be used widely: ideal gases, condensed phases, solutions (real and ideal).

You must know the standard state used for $\Delta_r G^\circ$ since the quantities that appear in K must have corresponding units.

32

Effect of Temperature on Equilibrium

$\Delta_r G^\circ = -RT \ln K$ is totally general.

Gibbs-Helmholtz equation (many weeks ago):

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -H/T^2$$

add Δ_r and $^\circ$: $[\partial(\Delta_r G^\circ/T)/\partial T]_p = -\Delta_r H^\circ/T^2$

$$[\partial(-R \ln K)/\partial T]_p = -\Delta_r H^\circ/T^2$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \Delta_r H^\circ/RT^2 \quad \text{The Van't Hoff equation}$$

Useful if you have an equation for $\ln K$ vs. T .

Alternate form: $[\partial(\ln K)/\partial(1/T)]_p = -\Delta_r H^\circ/R$

Van't Hoff plot: $\ln K$ vs. $1/T$, slope = $-\Delta_r H^\circ/R$

33

The Van't Hoff Equation

Differential forms:

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \Delta_r H^\circ/RT^2 \quad \text{or}$$

$$[\partial(\ln K)/\partial(1/T)]_p = -\Delta_r H^\circ/R$$

Integrated form (assuming $\Delta_r H^\circ$ constant):

$$\ln(K_2/K_1) = (-\Delta_r H^\circ/R) [(1/T_2 - 1/T_1)]$$

Use: solve for $\Delta_r H^\circ$ when K 's known at two T 's

or predict $K_2(T_2)$ from $\Delta_r H^\circ$ and $K_1(T_1)$

Integrated Clausius-Clapeyron equation is a special case

$$\ln(p_2/p_1) = (-\Delta_{\text{vap}}H^\circ/R) [(1/T_2 - 1/T_1)]$$

for the "reaction" $\mathbf{A(l)} \rightleftharpoons \mathbf{A(g)}$ where $K_{\text{eq}} = p_A$

34

Standard (or reference) States

For an ideal gas, the standard state is $p_i = \text{one atm}$

p_i in atm appears in K_{eq} K_{eq} is independent of p

For a pure solid or liquid, the standard state is

the pure solid or liquid at standard pressure

and the pure substance does not appear in K_{eq}

For an ideal solute, the most common standard state is

a one molar solution of the solute

and the molarity of that solute appears in K_{eq}

For a non-ideal solute, the most common standard state

is solution at unit activity for that solute

and the activity of that solute appears in K_{eq}

35

Biochemical Standard States

For ideal solutes, the most common standard state is

a one molar solution of the solute.

Many biochemical reactions involve $[H^+]$,

this standard state is very acidic: $\text{pH} = 0$

Biochemists often choose a different standard state:

$a_{H^+} = (1.0 \times 10^{-7} \text{ M})$ or $\text{pH} = 7$. This changes $\Delta_r G^\circ$ and K

Some distinguish with notation ($\Delta_r G^\circ$) but many do not:
[the table headings convey the information](#)

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Standard States:
Example using **Chemical** Convention



Does this reaction proceed? To what extent? Lots or little?

Calculate ΔG° , using **chemical** $\Delta_f G^{\circ}$ values:

$$\begin{aligned} \Delta G^{\circ} &= \Delta_f G^{\circ} \{ \text{HCOO}^{\text{-}}(\text{aq}) \} + \Delta_f G^{\circ} \{ \text{H}^{\text{+}}(\text{aq}) \} \\ &\quad - \Delta_f G^{\circ} \{ \text{HCOOH}(\text{aq}) \} \\ &= (-351.9) + (0) - (-372.2) = +21.3 \text{ kJ/mole} \end{aligned}$$

$K = 1.9 \times 10^{-4} = K_a$ for formic acid, $pK_a = 3.72$.

$\Delta G^{\circ} > 0$ so **starting at the chemical standard state (all three species at 1 M) reaction proceeds towards reactants.**

This makes sense: formic acid is a weak acid.

At the standard state $Q = 1$, so $Q > K$.

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Standard States: Biochemical Convention



What is ΔG° at the **biochemical** standard state, $\text{pH} = 7$?

Call this $\Delta G^{\circ'}$:

$$\begin{aligned} \Delta G^{\circ'} &= \Delta G^{\circ} + RT \ln [\text{H}^{\text{+}}][\text{HCOO}^{\text{-}}][\text{HCOOH}] \\ &= \Delta G^{\circ} + RT \ln 10^{-7} \\ &= \Delta G^{\circ} - 7 \{ 2.303 RT \} = \Delta G^{\circ} - 39.96 \text{ kJ/mole} \end{aligned}$$

ΔG° and $\Delta G^{\circ'}$ differ by $\sim 40 \text{ kJ/mole}$.

This is a big shift! $\Delta G^{\circ'} = 21.3 - 39.96 = -18.7 \text{ kJ/mole}$

Starting at the biochemical standard state,

pH 7, with $[\text{HCOOH}]$ and $[\text{HCOO}^{\text{-}}] = 1 \text{ M}$, reaction proceeds towards products (solution is acidic)

If $[\text{HA}] = [\text{A}^{\text{-}}]$, this is a buffer, so $\text{pH} = pK_a$ at equilibrium

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Biochemical Standard States: *not just pH*

Many biochemical species exhibit a range of protonation.

Example: in a **phosphate buffer** at pH near 7: lots of $\text{H}_2\text{PO}_4^{\text{-}}$, and $\text{HPO}_4^{\text{2-}}$; very little H_3PO_4 and $\text{PO}_4^{\text{3-}}$.

In the chemists' standard state, each concentration is unity.

Such a solution is not stable, and cannot exist.

The chemists' standard state is very far from reality!

The biochemists choose a state such that **the sum is unity**:

$$[\text{P}_i] \equiv [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^{\text{-}}] + [\text{HPO}_4^{\text{2-}}] + [\text{PO}_4^{\text{3-}}] = 1$$

while **the relative amounts are those at pH 7.**

By doing this, they can write K_{eq} 's including $[\text{P}_i]$ only, and not have to pay attention to where the protons are!

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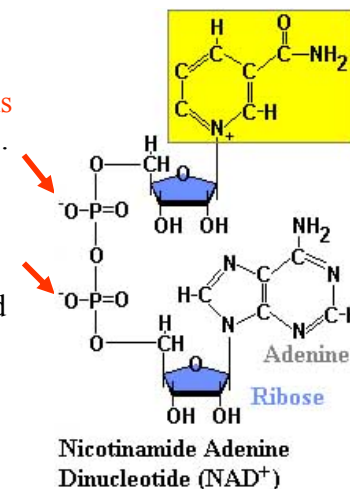
Biochemical Standard States

Molecule at right: label says $\text{NAD}^{\text{+}}$ but the charge is -1 .

The charge would be $+1$ if **protons** were added at the two phosphates. A better generic label would be $(\text{NAD})_{\text{ox}}$, the oxidized form.

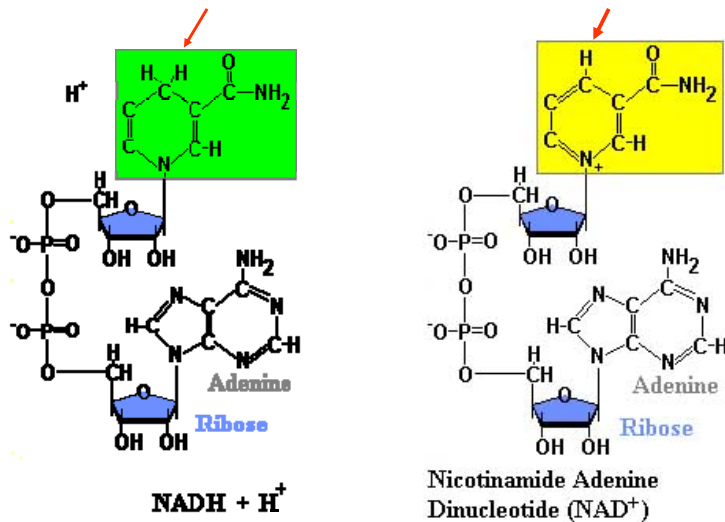
At $\text{pH} = 7$, the -1 charge shown dominates, but $(\text{NAD}^{\text{+}}$, NAD , and $\text{NAD}^{\text{-}}$) are all present.

The biochemist's standard state combines these.



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Reduced and oxidized forms



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Biochemical Standard States

Values for $\Delta_f H^\circ$, S° , and $\Delta_f G^\circ$ for dissolved species that involve H^+ (including water) are often very different in a biochemistry book from those in a chemistry book.

While generating tables of data for the biochemical standard state may be quite complicated, **using it is not.**

But the rules change: if using biochemical $\Delta_f H^\circ$ and S° or $\Delta_f G^\circ$ (read the headings!), then when writing K_{eq} :

[H⁺] is written as [H⁺]/10⁻⁷ (it can be omitted if pH = 7!)

For species that can gain or lose protons (examples):

[P_i] instead of individual phosphate species

[NAD]_{ox} instead of [NAD⁻], [NAD] and [NAD⁺]

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Standard States

One could use the chemists' standard state throughout.

The fact that a solution in which all phosphate species are one molar is *impossible* does not render the use of such solution as the standard state useless or *wrong*.

But it does say that the chemists' $\Delta_f G$ and $\Delta_f G^\circ$ are often quite different: **any real solution** is very different from **the standard one**.

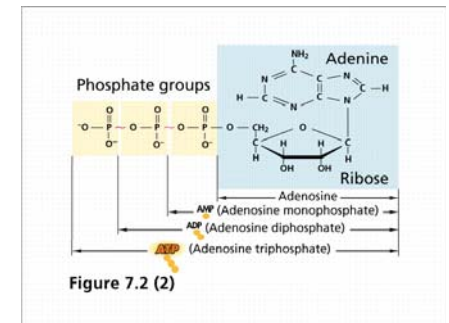
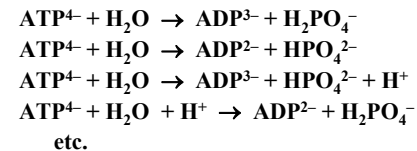
By using standard states **close to the actual solutions**, **biochemists'** $\Delta_f G$ and $\Delta_f G^\circ$ are closer to each other.

They can often look at $\Delta_f G^\circ$ to predict whether a reaction will be extensive, rather than having to calculate $\Delta_f G$

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Biochemical Energetics

ATP



Written together (not specifying where H's are present) as



$$\begin{aligned} \Delta G^\circ (\text{ATP} \rightarrow \text{ADP}) &= \Delta G_f^\circ \{\text{ADP}\} + \Delta G_f^\circ \{\text{P}_i\} - \Delta G_f^\circ \{\text{ATP}\} - \Delta G_f^\circ \{\text{water}\} \\ &= (-1230.12) + (-1059.49) - (-2097.89) - (-155.66) = \mathbf{-36.06 \text{ kJ/mole}} \end{aligned}$$

This free energy is used to drive many biochemical reactions

The net reaction is the **combination of many individual ones**, weighted by the appropriate relative concentrations at pH 7

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Biochemical Energetics

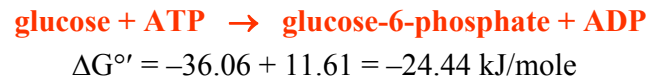


Consider the phosphorylation of glucose:



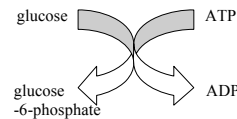
At standard conditions, this is **not** favored ($\Delta G^{\circ'} > 0$).

But it is favored if **combined** with $\text{ATP} \rightarrow \text{ADP}$:



Mechanisms for coupling?

here: **common species** P_i
sometimes via enzyme



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Good reference about biochemical standard states

“Calculation of Standard Transformed Gibbs Energies and Standard Transformed Enthalpies of Biochemical Reactants” by **Robert A. Alberty**

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

ARCHIVES OF BIOCHEMISTRY AND BIOPHYSICS
Vol. 353, No. 1, May 1, pp. 116–130, 1998

PDF version available on course webpage (Alberty.pdf)

The good news is that someone else has done the hard work, so you can generally use these tables without knowing the details.

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ROBERT A. ALBERTY

TABLE II

Standard Transformed Gibbs Energies of Formation and Standard Transformed Enthalpies of Formation of Reactants at 298.15 K, 1 Bar, pH 7, and Three Ionic Strengths

Reactant	I(M)	$\Delta_f G^{\circ'}/\text{kJ mol}^{-1}$			$\Delta_f H^{\circ'}/\text{kJ mol}^{-1}$		
		0	0.1	0.25	0	0.1	0.25
ATP		-2098.00	-2097.55	-2097.89	-2992.93	-2995.32	-2995.59
ADP		-1234.36	-1230.97	-1230.12	-2001.89	-2005.22	-2005.92
AMP		-367.50	-361.99	-360.29	-1012.19	-1015.86	-1016.88
Adenosine		519.43	527.39	529.96	-0.01	-4.04	-5.34
P_i		-1058.56	-1059.17	-1059.49	-1301.24	-1299.91	-1299.39
Glucose 6-phosphate		-1325.00	-1320.37	-1318.92	-2276.06	-2278.56	-2279.30
Glucose		-436.42	-429.08	-426.71	-1262.19	-1265.91	-1267.11
H_2O		-157.28	-156.05	-155.66	-285.83	-286.45	-286.65
NAD_{ox}		1038.86	1054.17	1059.11	0	-7.76	-10.26
NAD_{red}		1101.47	1115.55	1120.09	-31.94	-39.08	-41.38
NADP_{ox}		998.91	1008.70	1011.86	0	-4.96	-6.57
NADP_{red}		1064.85	1070.97	1072.95	-29.18	-32.28	-33.28
Acetaldehyde		20.83	23.27	24.06	-212.33	-213.57	-213.97
Acetate		-249.44	-248.22	-247.82	-486.01	-486.63	-486.83
Alanine		-91.31	-87.02	-85.64	-554.80	-556.97	-557.67
Ammonia		80.52	82.35	82.94	-132.51	-133.44	-133.74
Ethanol		58.10	61.77	62.96	-288.30	-290.16	-290.76
Pyruvate		-352.40	-351.18	-350.78	-596.22	-596.84	-597.04
Formate		-311.04	-311.04	-311.04	-426.55	-426.55	-426.55

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Ionic strength

Alberty (and others) often tabulate thermodynamic values at various values of **ionic strength**.

Ionic strength: $I = \frac{1}{2} \sum c_i z_i^2$ **sum over all ions in solution**

Non-ideal effects for ionic species are typically the same when **I** is the same (example follows).

Using data for an **I** close to that of the solution of interest incorporates well most corrections for non-ideal effects.

Salt	type	c_+	c_-	z_+	z_-	I
KCl	1:1	c	c	1	-1	c
K_2SO_4	1:2	2c	c	1	-2	3c
CaCl_2	2:1	c	2c	2	-1	3c
MgSO_4	2:2	c	c	2	-2	4c
$\text{Al}(\text{NO}_3)_3$	3:1	c	3c	3	-1	6c
$\text{Ca}_3(\text{PO}_4)_2$	2:3	3c	2c	2	-3	15c

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Ionic solutions: non ideal behavior

Consider the water solubility of Thallium iodate, $\text{TlIO}_3(\text{s})$:



If ideal, $K = K_{\text{sp}} = [\text{Tl}^+][\text{IO}_3^-]$ is constant

Measure s , the molar solubility of TlIO_3 in water and in solutions of KCl and K_2SO_4 $s = [\text{Tl}^+] = [\text{IO}_3^-]$

Calculate $K_{\text{sp}} = s^2$

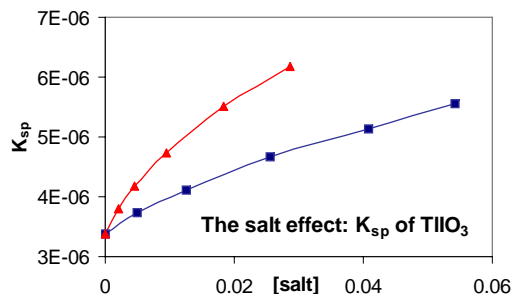
Not constant!

The Salt Effect

Solubility & K increase; effect bigger with K_2SO_4

Why?

Coulombs law!



Ionic solutions: non ideal behavior



To account for non-ideality, use **activities**: $K_{\text{sp}} = (a_{\text{Tl}^+})(a_{\text{IO}_3^-})$

But $a_k = \gamma_k[k]$, so $K_{\text{sp}} = (\gamma_{\text{Tl}^+}) [\text{Tl}^+] (\gamma_{\text{IO}_3^-}) [\text{IO}_3^-]$

$K_{\text{sp}} = (\gamma_{\text{Tl}^+})(\gamma_{\text{IO}_3^-}) K_{\text{sp}}'$ where $K_{\text{sp}}' = [\text{Tl}^+][\text{IO}_3^-]$

K_{sp} is the true (thermodynamic) constant

K_{sp}' is the **apparent** or **concentration constant** (which varies).

In the ideal limit (approached at infinite dilution) $K_{\text{sp}} = K_{\text{sp}}'$

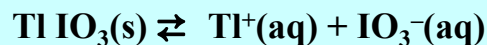
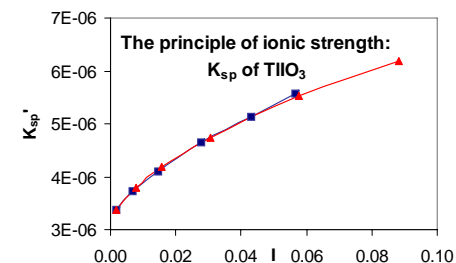
Previous data, now **plotted vs.**

ionic strength

(due to both TlIO_3 and KX)

Data superimpose!

Why ionic strength is useful.

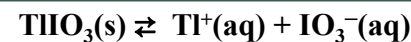


Solubility of $\text{TlIO}_3(\text{s})$ in the presence of salts

[KCl]	s	I	Ksp'
0	0.001838	0.001838	3.378E-06
0.0049	0.001930	0.006830	3.725E-06
0.01257	0.002025	0.014595	4.101E-06
0.02565	0.002158	0.027808	4.657E-06
0.04081	0.002266	0.043076	5.135E-06
0.05422	0.002359	0.056579	5.565E-06

[K ₂ SO ₄]	s	I	Ksp'
0	0.001838	0.001838	3.378E-06
0.00198	0.001948	0.007888	3.795E-06
0.00453	0.002044	0.015634	4.178E-06
0.00952	0.002177	0.030737	4.739E-06
0.01844	0.002349	0.057669	5.518E-06
0.02861	0.002486	0.088316	6.180E-06

Ionic solutions: non ideal behavior



Same data: now plot $\log K'$ vs. **square root** of ionic strength

Curve becomes straight line

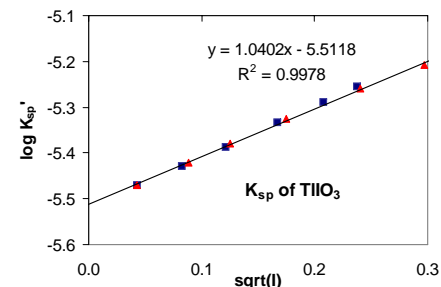
Intercept (at $I = 0$) is $\log K_{\text{sp}}$

$K_{\text{sp}} = 10^{-5.51} = 3.1 \times 10^{-6}$

Empirical (and theoretical)

equations for ionic γ_k :

$\log \gamma_k$ proportional to $I^{1/2}$
for dilute solutions



example: **Debye-Huckel** equation: $\log \gamma_k = -0.51 z_k^2 I^{1/2}$

$K_{\text{sp}} = (\gamma_{\text{Tl}^+})(\gamma_{\text{IO}_3^-}) K_{\text{sp}}' \rightarrow \log K_{\text{sp}}' = \log K_{\text{sp}} - \log (\gamma_{\text{Tl}^+}) - \log (\gamma_{\text{IO}_3^-})$

TD values tabulated at various I values incorporate this!

The bottom line:

- Non-ideal effects can be very large in **ionic solutions**.
- Accounting for them explicitly, using activity coefficients for each ion, is possible using various empirical equations, but this can be tedious.
- To an excellent approximation, these effects depend on one parameter: **the ionic strength of the solution**.
- The true thermodynamic equilibrium constant K is the value at infinite dilution ($I = 0$)
- Apparent equilibrium constants K' and the corresponding thermodynamic values ($\Delta_r G^\circ$, $\Delta_r H^\circ$, $\Delta_r S^\circ$) **at specified values of ionic strength** can be defined using standard equations.
- Using them obviates need for activity coefficients: they are built in! **Alberty table an important example**.