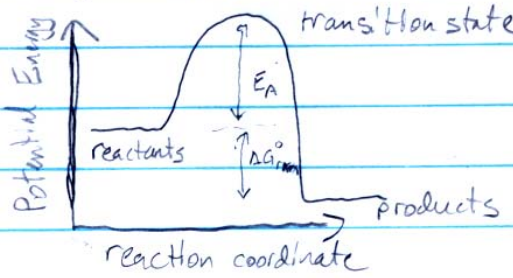
Kinetics Revisited

Last time we looked at kinetics we learned 2 important things:

1. Order of reactions and the equations relating k, $t_{1/2}$, etc.
2. How to interpret a 2-D or 3-D reaction diagram, eg:



Now we'll look at kinetics in more detail.

For the reaction: $X \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2Y$

we have rate $= \frac{d\xi}{dt} = \frac{-1}{1}\frac{d[X]}{dt} = \frac{+1}{2}\frac{d[Y]}{dt}$ for 1 L

or, in general rate = reaction velocity $v = R_f - R_r = \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{V}\frac{1}{\nu_i}\frac{d[Z_i]}{dt}$

where R_f and R_r are the forward and reverse rates (here they would be $k_f[X]$ and $k_r[Y]^2$) and V is volume while ν_i is the stoichiometric coefficient of component Z_i (Usually, we assume $V = 1$ L). Now take the reaction:

$X \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Y$ so $R_f = k_f a_X \xleftarrow{\approx k_f[X]}$ activity

Since $[X] = [X]_0 - \xi$ $R_f = k_f[X] = k_f([X]_0 - \xi)$

Same for $[Y]$, so we get:

$$\frac{d\xi}{dt} = R_f - R_r = k_f([X]_0 - \xi) - k_r([Y]_0 + \xi)$$

this is a differential eq. that we will solve...

To solve the differential eq., simplify: $\frac{d\xi}{dt} = 2k\left[\frac{X_0 - Y_0}{2} - \xi\right]$

where $\underbrace{k_f = k_r = k}_{\text{if } K_{eq}=1}$ and X_0 is short for $[X]_0$ (this − sign is from changing $\xi \Rightarrow z$)

Now set $z = \frac{1}{2}(X_0 - Y_0) - \xi$ so we have $\frac{dz}{dt} = -2kz$

if $z(t) = e^{-2kt}$ then $\frac{dz(t)}{dt} = -2ke^{-2kt} = -2kz$ ✓

So $\xi(t) = \frac{1}{2}(X_0 - Y_0) - z(t) = \frac{X_0 - Y_0}{2} - e^{-2kt}$ or $= \frac{X_0 - Y_0}{2} - \underbrace{\frac{X_0 - Y_0}{2}e^{-2kt}}_{\text{still solves diff eq. and } \xi(0)=0}$

Using the second solution we can write:

$$R_f = k_f(X_0 - \xi) = k_f\left[\frac{2X_0}{2} - \left\{\frac{(X_0 - Y_0)}{2} - \frac{(X_0 - Y_0)}{2}e^{-2kt}\right\}\right] = \frac{k}{2}(X_0 + Y_0) + \frac{k}{2}(X_0 - Y_0)e^{-2kt}$$

and: (these will cancel in $R_f - R_r$)

$$R_r = k_r\left[\frac{2Y_0}{2} + \left\{\frac{(X_0 - Y_0)}{2} - \frac{(X_0 - Y_0)}{2}e^{-2kt}\right\}\right] = \frac{k}{2}(X_0 + Y_0) - \frac{k}{2}(X_0 - Y_0)e^{-2kt}$$

(Internal) Entropy production per volume $= \frac{1}{V}\frac{d_i S}{dt} = \frac{1}{V}\frac{A}{T}\frac{d\xi}{dt} \geq 0$ (A = sum of chem. pot.: $\mu_X - \mu_Y$; rate $= (R_f - R_r)$)

but $\mu_X = \mu_{X_0} + RT\ln a_X$ (activity), same for μ_Y

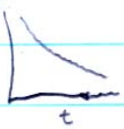
and $\mu_{X_0} - \mu_{Y_0} = -\Delta G^\circ_{rxn} = RT\ln K_{eq}$, so $A = RT\ln K_{eq} + RT\ln\left(\frac{a_X}{a_Y}\right)$

but $K_{eq} = \frac{k_f}{k_r}$ so $A = RT\ln\frac{k_f a_X}{k_r a_Y} = RT\ln\frac{R_f}{R_r}$

so $\frac{1}{V}\frac{d_i S}{dt} = \frac{1}{V}\frac{d\xi}{dt}\cdot\frac{RT\ln\frac{R_f}{R_r}}{T} = (R_f - R_r)R\ln\frac{R_f}{R_r}$ Substituting:

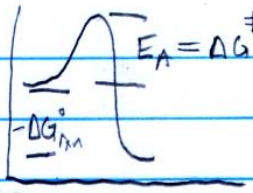
$$= 2\frac{k}{2}(X_0 - Y_0)e^{-2kt}\cdot R\ln\frac{\frac{k}{2}\left(X_0 + Y_0 + [X_0 - Y_0]e^{-2kt}\right)}{\frac{k}{2}\left(X_0 + Y_0 - [X_0 - Y_0]e^{-2kt}\right)}$$

This allows us to plot entropy production vs. time:



9.3

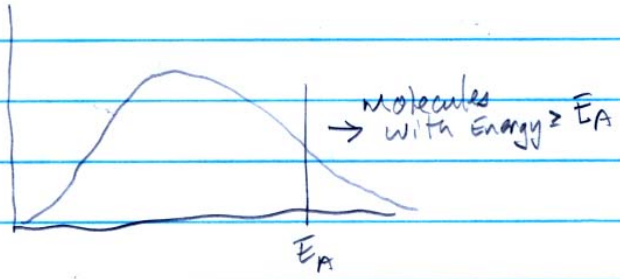
Arrhenius equation, again.



$$k_f = k_0 e^{-E_A/RT} \qquad k_r = k_0 e^{-(E_A - \Delta G^{\circ}_{rxn})/RT}$$

$$K_{eq} = \frac{k_f}{k_r} = \frac{k_0 e^{-E_A/RT}}{k_0 e^{-E_A/RT} e^{\Delta G^{\circ}_{rxn}/RT}} = e^{-\Delta G^{\circ}_{rxn}/RT} \checkmark$$

Not only does this eq flow from $\Delta G^{\circ}_{rxn} = -RT \ln K_{eq}$ but it also relates to the Boltzmann distribution:



What about k_0? Collision Theory says $k_0 \propto \left(\frac{1}{T}\right)^{1/2}$

Transition state theory (TST) says $k_0 \propto \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$ (liquids)

$k_0 \propto \frac{(k_B T)^2}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$ (gases)

$e^{-\frac{\Delta G^{\ddagger}}{RT}} = K_{eq}^{\ddagger}$

The key point of Arrhenius is that rate increases as E_A decreases, which happens due to catalysis.

TST adds the insight that catalysts (enzymes) reduce the energy of the transition state

Thermodynamic's most important eq.

How do we use $\Delta G^\circ_{rxn} = -RT\ln K_{eq}$?

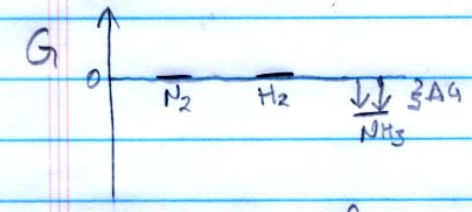
e.g. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$\Delta G^\circ_{rxn} = 2\Delta G^\circ_{f\,NH_3(g)} - \Delta G^\circ_{f\,N_2(g)} - 3\Delta G^\circ_{f\,H_2(g)} = -32.90\ kJ/mol$

($\Delta G^\circ_{f\,NH_3(g)} = -16.45\ kJ/mol$; $\Delta G^\circ_{f\,N_2(g)} = 0$; $\Delta G^\circ_{f\,H_2(g)} = 0$)

@ 25°C $K_{eq} = e^{32{,}900/8.314(298.15)} = 5.80 \times 10^5 = K^\circ = K_p\ (atm^{-2})$

The process of finding ΔG°_{rxn} is like finding ΔH°_{rxn}:



but ΔG°_{rxn} gives K_{eq} so it's more useful than ΔH°_{rxn}

Also, the 2nd most important eq, $\Delta G = \Delta H - T\Delta S$, tells us that $\Delta^\circ G_{rxn}$ and $\Delta^\circ H_{rxn}$ are related to $\Delta^\circ S_{rxn}$:

$$\underbrace{\Delta G^\circ_{rxn}}_{\text{total entropy of universe}} = \underbrace{\Delta H^\circ_{rxn}}_{\text{entropy released to surroundings}} - \overbrace{T\Delta S^\circ_{rxn}}^{\text{depends on T}}$$

ΔS°_{rxn}: entropy of system

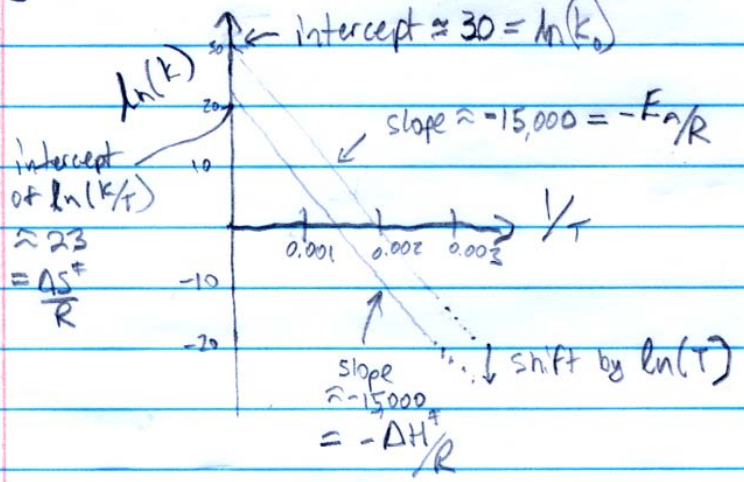
} All 3 terms are T-independent

Take home message: The reason these 2 eqns are so important is because they tell us whether products are favored in <u>any</u> reaction based on constants that can be found in a table, and the tell us <u>why</u> products are favored (heat released, internal entropy or both).

Van't Hoff and Arrhenius plots

Problem 9.3 (due next week) illustrates how these two plots are used:

given temperatures and rate constants plot:



this plot shows an Arrhenius plot gives E_A and k_0, but a Van't Hoff plot gives ΔH and ΔS, or in this case* $\Delta H^\ddagger$ and $\Delta S^\ddagger$

(* we plotted $\ln\left(\frac{k}{T}\right)$ instead of $\ln(K_{eq})$, but the result of TST is $k \propto \left(k_B T/h\right) e^{-\Delta G^\ddagger/RT}$ or $k/T \propto \left(k_B/h\right) K_{eq}^\ddagger$ (rate constant) so we were really plotting $\ln\left(\frac{k_B}{h} K_{eq}^\ddagger\right)$, which has the form of a van't Hoff plot)

final note about activity, fugacity, etc

the definition: $a_i = \gamma_i x_i$ would indicate that the activity of an ideal gas or solution ($\gamma_i = 1$) would range from $0 \to 1$.

However, there are 2 other definitions:

$$a_i = \gamma_i P_i / P^\circ \quad \leftarrow P_i: \text{partial pressure}; \; P^\circ \leftarrow 1 \text{ bar}$$

and

$$a_i = \gamma_i C_i / C^\circ \quad \leftarrow C_i: \text{concentration}; \; C^\circ \leftarrow 1M \text{ or } 1m$$

in these cases, a_i can range from $0 \to \infty$ (or $0 \to 55$ M, e.g. ← maximum conc. in H_2O)

Fugacity, $f_i = \gamma_i \Phi_i P_i$ ← Φ_i: fugacity coeff. ($\Phi_i = 1$ for $P_i \to 0$); P_i: partial pressure

So, fugacity has units of pressure and corrects for deviations due to mixing (γ_i) and Pressure (Φ_i)
we can separate these two corrections, e.g.:

$$\mu_i(T, P, \text{mix}) = \mu_i(T, P^\circ, \text{pure}) + RT \ln f_{i(\text{pure})} + RT \ln a_i$$

in general, we correct for pressure using $f_{i(\text{pure})} = \Phi_i P_i$
and mixing using $a_i = \gamma_i x_i$

we correct for T using $\dfrac{\mu_i(T)}{T} = \dfrac{\mu_i(T_0)}{T_0} + \displaystyle\int_{T_0}^{T} \frac{-\overline{H}_i(T')}{T'^2} dT'$

where T' is a place-holder for the integral from $T_0 \to T$