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## Chemical Reaction Equilibrium (CRE)

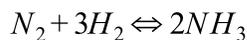
### Chemical Reaction Equilibrium

- Explain the relationship between energy and entropy in reacting systems (i.e., show why the Gibbs Free Energy is still the proper state function for equilibrium)
  - Write balance chemical reaction expressions with associated reaction stoichiometry
  - Relate extent of reaction expressions to the equilibrium constant(s)
  - Use thermochemical data to calculate the equilibrium constant and its dependence on temperature
  - Determine the equilibrium composition for a single-phase, single-reaction system (i.e., calculate the extent of reaction)
    - in vapor phase reactions
    - in liquid phase reactions
  - Determine the equilibrium composition for a multiphase, single-reaction system
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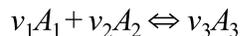
### CRE: Stoichiometry and Extent of Reaction

#### Stoichiometry and Extent of Reaction (Reaction Coordinate)

We know (from years of Chemistry classes) how to balance an equation:



We will write this type of reaction in the following form, replacing each chemical species with a generic  $A_i$  identifier:



where we are using  $v_i$  to denote the stoichiometric coefficients where we would consider  $v_1 = -1$ ,  $v_2 = -3$ , and  $v_3 = +2$  so that, in general, "reactants" would have  $v_i < 0$  and "products" would have  $v_i > 0$ .

#### NOTE:

*We put the reactants and products in quotes since, depending on the initial distribution of chemical species, the reaction can really go in either direction. Here, we will consider "products" to mean chemical species on the right-hand-side.*

Since there is one degree of freedom when determining the  $v_i$  values (that is, you can arbitrarily multiply all of them by any value you like as long as they maintain the same ratios), it is useful to consider changes in the number of moles of each species as ratios, so:

$$\frac{dn_1}{dn_2} = \frac{v_1}{v_2}$$

or that the ratio of the change in moles of any two species is equal to the ratio of their stoichiometric coefficients. Writing one of these expressions for *each* component and then rearranging gives

$$\frac{dn_1}{v_1} = \frac{dn_2}{v_2} = \frac{dn_3}{v_3} = \frac{dn_i}{v_i}$$

## DEFINITION:

We use this expression to define the **extent of reaction or reaction coordinate** as:

$$\frac{dn_i}{v_i} = d\xi$$

Rearranging this and integrating gives a general reactive material balance for any component,  $i$ ,

$$n_i = n_{i_0} + v_i \xi$$

where we need to note that  $n_{i_0}$  is the number of moles of species  $i$  present prior to the reaction occurring.

If we want to calculate a mole fraction, we need to determine the total number of moles, so we sum these up

$$n_{tot} = \sum_i n_i = \sum_i n_{i_0} + \sum_i v_i \xi$$

## NOTE:

*The number of moles is not necessarily a constant. If  $\sum_i v_i \neq 0$  then  $n_{tot}$  changes as the reaction proceeds. Also, we need to note that, when calculating the mole fraction in a multi-phase mixture, we need to use a different material balance in each of the phases.*

Using this we get a vapor and liquid phase mole fraction as

$$y_i = \frac{n_i^v}{n_{tot}^v} = \frac{n_i^v}{\sum_i n_{i_0}^v + \sum_i (v_i \xi)^v}$$

$$x_i = \frac{n_i^L}{n_{tot}^L} = \frac{n_i^L}{\sum_i n_{i_0}^L + \sum_i (v_i \xi)^L}$$

## OUTCOME:

*Write balance chemical reaction expressions with associate reaction stoichiometry*

## TEST YOURSELF:

*Calculate the number of moles and mole fraction as a function of the reaction coordinate for the reaction:*



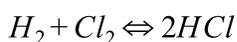
*when we start with 5 moles of  $H_2$  and 2 moles of  $O_2$ . Also, determine the bounds of each variable (that is, what are the maximum and minimum values of  $y_p$ ,  $\xi$ , etc.).*

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CRE: Gibbs Free Energy in Reacting Systems

## Gibbs Free Energy in Reacting Systems

If we consider the following reaction:



We might be tempted to decide that the reaction will proceed until we have minimized the energy of the system. In order to examine that, we consider the bond strengths of each of the bonds:

$$D_{H-H} = 4.5eV, D_{Cl-Cl} = 2.5eV, D_{H-Cl} = 4.5eV$$

so our three species have, respectively

$$H_2 = 4.5eV, Cl_2 = 2.5eV, 2xHCl = 2x4.5eV = 9.0eV$$

In other words, we need to put in  $7eV$  to break the bonds of the "reactants", but regain  $9eV$  when they reform as 2 molecules of  $HCl$ . This would suggest that the reaction would (at equilibrium) proceed completely to the right.

However, having two moles of *differing* material (or better yet, all three!) gives us higher entropy than if we make a system of pure  $HCl$ .

### NOTE:

*This entropic argument becomes particularly powerful when we either gain (higher entropy) or lose (lower entropy) moles as the reaction proceeds (i.e.,  $\sum_i \nu_i \neq 0$ ).*

In reality, we need to *balance* our change in energy with the change in entropy (trying to minimize energy, while maximizing entropy), in much the same way that we did with phase equilibrium.

Mathematically, we can see this by considering the Gibbs Free Energy of the system (which is a mixture!):

$$G = \sum_i n_i \bar{G}_i = \sum_i n_i \mu_i$$

we recall that we need a reference state for  $\bar{G}_i$  or  $\mu_i$ .

### NOTE:

*We will use the **standard state** as our reference point, which is chosen to be the  $T$  of interest in our problem and a pressure of 1 bar.*

this gives us a  $\mu_i$  expression of

$$\mu_i = g_i^o + RT \ln \left[ \frac{\hat{f}_i}{f_i^o} \right]$$

For simplicity, let's use an ideal gas for this example, so we reduce our expression to:

$$\mu_i = g_i^o + RT \ln \left[ \frac{p_i}{1bar} \right] = g_i^o + RT \ln \left[ \frac{y_i P_{tot}}{1bar} \right]$$

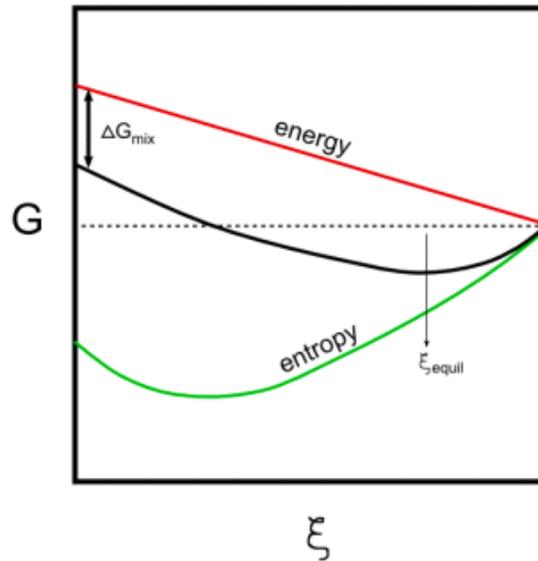
Plugging this into our total  $G$  expression, we can expand each of the  $\ln$  terms and make use of the  $\ln$  product rule to get

$$G = \sum_i n_i g_i^o + RT \sum_i n_i \ln[P_{tot}] + RT \sum_i n_i \ln[y_i]$$

where we can note that:

- all terms depend on  $\zeta$  through the  $n_i$  variable
- the first term otherwise depends only on the bond energies
- the second term otherwise is constant
- the third term looks like the  $\Delta G_{mix}$

If we plot this for the reaction in question, we get



**NOTE:**

The minimum Gibbs Free Energy balances the entropy gained through diversifying the material present with the energy gained by changing the bond energies. We note that the **minimum** free energy as a function of  $\xi$  is found where  $\frac{dG}{d\xi} = 0$ .

**OUTCOME:**

Explain the relationship between energy and entropy in reacting systems

CRE: Equilibrium Constants and the Gibbs Free Energy

**Equilibrium Constants and  $\Delta g_{rxn}^o$**

For reactive equilibrium, we then require that:

$$\frac{dG}{d\xi} = 0$$

which we can write as

$$\frac{dG}{d\xi} = 0 = \frac{d}{d\xi} \left( \sum_i n_i \mu_i \right) = \sum_i \mu_i \frac{dn_i}{d\xi} = \sum_i \mu_i \frac{d(n_{i0} + v_i \xi)}{d\xi} = \sum_i \mu_i v_i$$

so our criterion for reactive equilibrium is

$$0 = \sum_i v_i \mu_i$$

recalling that  $\mu_i$  is given by (at standard state):

$$\mu_i = g_i^o + RT \ln \left[ \frac{\hat{f}_i}{f_i^o} \right]$$

we can combine these expressions to get:

$$0 = \sum_i v_i \left[ g_i^o + RT \ln \left[ \frac{\hat{f}_i}{f_i^o} \right] \right]$$

Rearranging we get:

$$-\frac{\sum_i \nu_i g_i^o}{RT} = \sum_i \nu_i \ln \left[ \frac{\hat{f}_i}{f_i^o} \right]$$

### DEFINITION:

We define the **Gibbs Free Energy change of reaction** ( $\Delta g_{rxn}^o$ ) in a manner similar to  $\Delta h_{rxn}^o$  (from Hess's Law) so that it is:

$$\Delta g_{rxn}^o = \sum_i \nu_i g_i^o$$

Using this definition and two ln rules (the first is that  $a \ln[x] = \ln[x^a]$ , while the second is the inverse of the product rule), we get:

$$-\frac{\Delta g_{rxn}^o}{RT} = \ln \left( \prod_i \left[ \frac{\hat{f}_i}{f_i^o} \right]^{\nu_i} \right)$$

### NOTE:

The  $\prod_i$  operator denotes the **product** of all  $i$  components (much like  $\sum_i$  denotes the **sum** of components  $i$ ).

Because  $\Delta g_{rxn}^o$  is at standard state, it is a function only of  $T$ . For simplicity, we then define:

### DEFINITION:

The **Reaction Equilibrium Constant** ( $K$ ) is also a function only of temperature and is defined as:

$$\ln K = -\frac{\Delta g_{rxn}^o}{RT}$$

Combining this definition with our equation thus far we get:

$$K = \prod_i \left[ \frac{\hat{f}_i}{f_i^o} \right]^{\nu_i}$$

### NOTE:

This is essentially what we are used to as a typical equilibrium expression (from Freshman Chemistry, for example), except that now we are explicitly accounting for species and mixing non-idealities (by using fugacities).

### OUTCOME:

Use thermochemical data to calculate the equilibrium constant and its dependence on temperature

### TEST YOURSELF:

Use tabulated values of  $\Delta g_{rxn}^o$  to determine the equilibrium constant at 25C for the following reaction:



CRE: Vapor-Phase Reaction Equilibrium

## Reaction Equilibrium in the Vapor Phase

In general, we have determined that for reactive equilibrium we have:

$$K = \prod_i \left[ \frac{\hat{f}_i}{f_i^o} \right]^{v_i}$$

where  $f_i^o$  is the fugacity of species  $i$  at the reference pressure of 1 bar.

For a vapor-phase reaction, we will assume that the vapor **at the reference state** behaves ideally, so that the value of  $f_i^o = 1$  bar.

**NOTE:**

*Just because the reference state behaves ideally, does **not** mean that the material itself behaves ideally under the reaction conditions.*

with this in mind, we can write our general expression for vapor phase reaction as

$$K = \prod_i [\hat{f}_i[\text{bar}]]^{v_i} = \prod_i [y_i \hat{\phi}_i P_{tot}[\text{bar}]]^{v_i}$$

where  $\hat{f}_i^o$  and  $P_{tot}$  are in units of bar.

**NOTE:**

*This means that there will be an explicit pressure dependence of the equilibrium whenever the  $v_i$  do not cancel!*

Recall that, for the special case of an ideal gas mixture, the term  $\hat{\phi}_i = 1$ .

**OUTCOME:**

*Determine the equilibrium composition for a single-phase, single-reaction system in vapor phase reactions*

**OUTCOME:**

*Relate extent of reaction expressions to the equilibrium constant(s)*

**TEST YOURSELF:**

*Write an expression for the equilibrium constant in terms of the initial composition and the reaction coordinate, for the following vapor-phase reaction (assuming ideal gas behavior):*



CRE: Temperature Dependence of the Equilibrium Constant

**The Equilibrium Constant as a Function of Temperature**

Since the equilibrium constant is a function of  $T$  only (we already saw how changes in  $P$  affect equilibrium), we would like to determine:

$$\frac{d \ln[K]}{dT} = \frac{d}{dT} \left[ \frac{-\Delta g_{rxn}^o}{RT} \right]$$

taking the derivative of the quotient on the right gives

$$\frac{d \ln[K]}{dT} = \frac{-1}{RT} \frac{d[\Delta g_{rxn}^o]}{dT} + \frac{\Delta g_{rxn}^o}{RT^2}$$

Using the fundamental property relations, we have shown that

$$\left( \frac{\partial g}{\partial T} \right)_P = -s \text{ so } \left( \frac{\partial \Delta g_{rxn}^o}{\partial T} \right)_P = -\Delta s_{rxn}^o$$

combining these expressions yields

$$\frac{d \ln[K]}{dT} = \frac{\Delta s_{rxn}^o}{RT} + \frac{\Delta g_{rxn}^o}{RT^2}$$

which, using the definition of  $g \equiv h - Ts$  can be simplified to

$$\frac{d \ln[K]}{dT} = \frac{\Delta h_{rxn}^o}{RT^2}$$

whereupon integration gives

$$\ln[K] = \int \frac{\Delta h_{rxn}^o}{RT^2} dT$$

**When**  $\Delta h_{rxn}^o \neq f(T)$

When the heat of reaction is independent of temperature, we can pull it out of the integral and evaluate the indefinite integral to give

$$\ln[K] = -\frac{\Delta h_{rxn}^o}{RT} + C$$

As with the Clausius-Clapeyron equation, we can eliminate the integration constant by using a reference value (typically at 298K) and write

$$\ln\left[\frac{K}{K_o}\right] = -\frac{\Delta h_{rxn}^o}{R} \left[\frac{1}{T} - \frac{1}{T_o}\right]$$

**NOTE:**

*When we have an exothermic reaction ( $\Delta h_{rxn}^o < 0$ ) this means that  $K$  will decrease with increasing  $T$ . Alternatively, when we have an endothermic reaction ( $\Delta h_{rxn}^o > 0$ )  $K$  will increase with increasing  $T$ .*

**When**  $\Delta h_{rxn}^o = f(T)$

When the heat of reaction is **not** independent of temperature, we need to formally account for the temperature dependence inside the integral.

This is done by recalling that:

$$\Delta h_{rxn}^o = \sum_i \nu_i \Delta h_{f_i}^o$$

Since  $\Delta h_{f_i}^o$  data is typically available at 298K, we can write

$$\Delta h_{rxn}^o = \sum_i \nu_i \left[ \Delta h_{f_i, 298K}^o + \int_{298K}^T c_{p_i} dT \right]$$

and plugging the resultant function of temperature into the  $\ln[K]$  integral.

**OUTCOME:**

*Use thermochemical data to calculate the equilibrium constant and its dependence on temperature*

**TEST YOURSELF:**

*Calculate the equilibrium constant for the following vapor-phase reaction occurring at 250C:*



CRE: Liquid and Solid Phase Reaction Equilibrium

### Reaction Equilibrium in the Solid and Liquid Phases

Again, we start with the general expression for reactive equilibrium:

$$K = \prod_i \left[ \frac{\hat{f}_i}{f_i^o} \right]^{\nu_i}$$

Here, the  $f_i^o$  value is the fugacity of species  $i$  at the reference pressure of 1 bar.

As with liquids and solids in the phase equilibrium sections of the course, we will consider this reference value to be the *pure species fugacity* ( $f_i$ ), but now it will be specifically at the reference pressure of 1 bar ( $f_i^o$ ).

If we expand our expression for the mixture fugacity (numerator) in terms of activity coefficients, we get:

$$K = \prod_i \left[ \frac{\hat{f}_i}{f_i^o} \right]^{v_i} = \prod_i \left[ \gamma_i x_i \frac{f_i}{f_i^o} \right]^{v_i}$$

**NOTE:**

*Since liquids and solids are essentially incompressible, the pure species fugacity at any pressure is typically very close to the same as the pure species fugacity at 1 bar. This is why we would typically choose the **saturation fugacity** ( $f_i = P_i^{sat}$ ) to be the "correct" value of pure species fugacity.*

**DEFINITION:**

*If we have very high pressure reactions, we must use the **Poynting correction** that states:*

$$\frac{f_i}{f_i^o} = \exp \left[ \frac{1}{RT} \int_{P^o}^P v_i dP \right]$$

For most problems, we can still assume the liquid/solid to be incompressible (so  $v_i$  is constant), so that this reduces to

$$\frac{f_i}{f_i^o} = \exp \left[ \frac{v_i}{RT} (P - P^o) \right]$$

Combining these we get:

$$K = \prod_i \left[ \gamma_i x_i \exp \left[ \frac{v_i}{RT} (P - P^o) \right] \right]^{v_i}$$

which at low pressures gives us:

$$K = \prod_i [\gamma_i x_i]^{v_i}$$

which at low pressures and for an ideal solution gives us:

$$K = \prod_i [x_i]^{v_i}$$

**NOTE:**

*This last form is what you may be familiar with from Chemistry classes and is typically called the **law of mass action**. Remember that it assumes that the fugacity is independent of pressure and that the solution is ideal!*

**OUTCOME:**

*Determine the equilibrium composition for a single-phase, single-reaction system in liquid phase reactions*

## Multi-Phase Reaction Equilibrium

The most important point to make regarding multi-phase reaction equilibrium is that now you must satisfy both the phase equilibrium criteria and the reaction equilibrium criterion. That is, the fugacity of each species is equal in each phase (so for species  $i$  in a three phase ( $\alpha, \beta, \gamma$  phases):

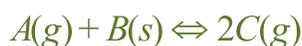
$$\hat{f}_i^\alpha = \hat{f}_i^\beta = \hat{f}_i^\gamma$$

In addition, the reaction equilibrium condition still holds:

$$K = \prod_i \left[ \frac{\hat{f}_i}{f_i^o} \right]^{v_i}$$

### EXAMPLE:

*If we had the following reaction:*



*we would write:*

$$K = \frac{\left[ \frac{\hat{f}_{Cg}}{f_{Cg}^o} \right]^2}{\left( \frac{\hat{f}_{Ag}}{f_{Ag}^o} \right) \left( \frac{\hat{f}_{Bs}}{f_{Bs}^o} \right)}$$

*We would take the gas phase as our reference for both A and C, so that each of those would give  $\hat{f}_i = y_i \hat{\phi}_i P_{tot}(\text{bar})$ . We would take the solid phase as reference for materials B. If no A or C dissolves in the solid, this expression becomes very simple since  $x_B = 1$  so  $\gamma_B = 1$  and we then simply need to worry about using the Poynting correction for the term  $f_B / f_B^o$  (note no "hat" since it is pure), which is often equal to 1 anyway.*

*Making all of these simplifications gives us:*

$$K = \frac{(y_C \hat{\phi}_C P_{tot})^2}{(y_A \hat{\phi}_A P_{tot})(x_B)}$$

*Note that  $x_B = 1$  and is only shown here to highlight the fact that this expression includes mole fractions **by phase** where necessary. Also, we took the Poynting correction for B to be 1.*

It is useful to discuss further the choice of  $f_i^o$ .

On the one hand, your choice of  $f_i^o$  must match your **value** of  $K$ . In other words, your reference phase for each species must match the state of aggregation that is used to calculate  $\Delta g_{rxn}^o$  in the expression:

$$K = \exp\left[-\frac{\Delta g_{rxn}^o}{RT}\right]$$

On the other hand, it is relatively easy to use a different  $\Delta g_{f_i}^o$  in order to enable whatever reference phase you want.

## NOTE:

If there is immiscibility between any of the phases (that is, if any of the phases remain pure because nothing mixes into it ... as with a solid, for example), it is useful to choose the pure species as a reference for that material since the  $f_i / f_i^o$  term would depend only on pressure and any mole fractions, activity coefficients, or fugacity coefficients would be equal to 1 (since the material is pure).

## OUTCOME:

Determine the equilibrium composition for a multiphase, single-reaction system

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CRE: Gibbs Phase Rule for Reactive Systems

### Gibbs Phase Rule for Reactive Systems

It is useful to recap the origins of Gibbs Phase Rule in order to see how the existence of reactions impacts the overall number of degrees of freedom available.

Recall that, we get adjustable intensive variables from (that is, we can independently set values for each of these intensive variables):

- $T$  and  $P$  (the state postulate says we only get two)
- $N-1$  compositions (since for a mixture  $\sum_i x_i = 1$  must also be satisfied) **for each phase** ( $\pi$ ), so we can fix  $(N-1)\pi$  compositions
- Total:  $2 + (N-1)\pi$

We then have Thermodynamic relations that relate these intensive variables (that is, they reduce our degrees of freedom):

- For multi-phase systems (with  $\pi$  phases), we have  $(\pi-1)$  equilibrium relations  $\hat{f}_i^\alpha = \hat{f}_i^\beta$  for each of the  $N$  components  $i$  (for example for a 2 component, 2 phase system that satisfies Raoult's Law, we can write both  $x_1 P_1^{sat} = y_1 P_{tot}$  and  $x_2 P_2^{sat} = y_2 P_{tot}$ )
- Total:  $(\pi-1)N$

Combining these two arguments, we get the non-reactive Gibbs Phase Rule that the number of degrees of freedom,  $D$  is:

$$D = (2 + N\pi - \pi) - (N\pi - N) = 2 + N - \pi$$

If we now include a number of reactions ( $r$ ), each must satisfy an equilibrium expression, so

- For each  $j$  of the  $r$  reactions we can write  $K_j = \prod_i \left[ \frac{\hat{f}_i}{f_i^o} \right]^{v_{ij}}$

Adding these "extra" Thermodynamic relations to our existing rule yields the reactive Gibbs Phase Rule where  $D$  is now:

$$D = 2 + N - \pi - r$$

## OUTCOME:

Calculate the degrees of freedom using Gibbs Phase Rule (for reactive systems)

