A Reaction of Ideal Gasses

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

- Each component:

$$\mu_x(P) = \mu_x^0 + RT\ln(P)$$

- Can write Gibbs Energy as:

$$\Delta G = 2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2}$$

Toward the Equilibrium Constant

- For any reaction involving ideal gasses:

$$aA + bB + \ldots \rightarrow cC + dD + \ldots$$

- We can write the following relationship for Gibbs Energy:

$$\Delta \bar{G} = \Delta \bar{G}^0 + RT \ln \frac{(P_C)^c (P_D)^d \ldots}{(P_A)^a (P_B)^b \ldots}$$

- If we knew $\Delta \bar{G}^0$, we could *calculate* whether a reaction was spontaneous based on P_A, P_B, etc.

What is $\Delta\bar{G}^0$?

- At equilibrium $\Delta\bar{G}$=0, so it must be true that:

$$0 = \Delta\bar{G}^0 + RT\ln\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

$$\Delta\bar{G}^0 = -RT\ln\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = -RT\ln K_{eq}$$

- **This expression allows us to determine $\Delta\bar{G}^0$ if we know partial pressures at equilibrium!!** (This is hugely important!)

Q and K

- Q is the reaction quotient:

$$Q = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

  – Ratio of partial pressures at non-equilibrium conditions

- K_{eq} is the equilibrium constant

$$\mathrm{K}_{eq} = \frac{\left(P_{C,eq}\right)^c \left(P_{D,eq}\right)^d}{\left(P_{A,eq}\right)^a \left(P_{B,eq}\right)^b}$$

  – Ratio of partial pressures *at equilibrium*

Q and K

- For simplicity, we can write:

$$\Delta\bar{G} = -RT\ln K_{eq} + RT\ln Q$$

$$\Delta\bar{G} = RT\ln\frac{Q}{K_{eq}}$$

- Don't confuse K with Q!
  - One is at equilibrium (K), the other is not (Q)

Why Are Ideal Gasses Important?

- **Gaseous behavior:** a way to predict expansion, heats, etc.

- **Equilibrium constants:** based on ideal gas behavior

- **Spontaneous reactions:** predictable based on gaseous chemical potential

Activities

"Not everything is a gas."

- A Great Scientist

- Define a quantity, called the "activity" (a_A) such that:

$$\mu_A = \mu_A^0 + RT \ln a_A$$

- Obviously, this quantity will make μ_A behave *like* an ideal gas, i.e.

$$\mathrm{K}_{eq} = \frac{\left(a_{C,eq}\right)^c \left(a_{D,eq}\right)^d}{\left(a_{A,eq}\right)^a \left(a_{B,eq}\right)^b}$$

Activities

- Activities are *unitless* (just like the units cancel for $\frac{P}{1\text{ atm}}$)

- Activities require a reference (or standard) state, or μ^0

- Activities *define* $\Delta\bar{G}^0$: If I switch activities (or standard states), $\Delta\bar{G}^0$ may change, but $\Delta\bar{G}$ will not

- Activities are generally chosen to simplify calculations

Standard State #1: Ideal Gas

- **Activity:**

$$a_A = \frac{P_A}{1\ \text{atm}}$$

- **Standard State:** Ideal gas with P = 1 atm, as we saw before

Standard State #2: Real Gas

- **Activity:**

$$a_A = \frac{\gamma_A P_A}{1 \text{ atm}}$$

Activity Coefficient
This is **NOT** generally a constant! (Though over a small range of P it may not change much.)

- **Standard State:**
  - At low pressures, $\gamma_A \approx 1$
  - Actual γ_A may be far from 1 at 1 atm, but μ is extrapolated from low pressures
  - This is a *hypothetical* standard state

Standard State #3: Pure Substance

- **Activity:**

$$a_A = 1 \text{ (at 1 atm)}$$

- **Standard State:**
  - Stays roughly constant near "regular" pressures
  - Need high pressures? Remember that:

$$G(P_2) - G(P_1) = \int_{P_1}^{P_2} V dP, \text{ or}$$

$$\mu(P_2) - \mu(P_1) = \int_{P_1}^{P_2} \bar{V} dP$$

Standard State #4: Solvent

- **Activity:**

$$a_A = \gamma_A X_A$$

  - X_A is mole fraction, which for solvent is normally close to 1
  - γ_A approaches 1 for pure solvent, it *is* 1 for ideal solvent

- **Standard State:**
  - Same as pure substance ($a_A = 1$)
  - For non-dilute solutions, may deviate from 1
  - **Example:** Water in most chemical reactions

Standard State #5: Solute

- **Activity:**

$$a_A = \gamma_A C_A$$

  - C_A is concentration in molar units
  - γ_A approaches 1 for dilute solutions (in the limit of infinite dilution, as $C_A \rightarrow 0$), for ideal solutes it *is* one

- **Standard State:**
  - Extrapolated from infinite dilution so that $a_A = 1$ at 1M concentration
  - Actual activity at 1 M may be much different

Biochemist's Standard State

- **Activity:**

$$a_{\text{weak acid}} = \sum A^- + HA + H_2A^+ + \cdots$$

$$a_{H^+} = 1 \text{ (protons at pH 7)}$$
$$a_A = \gamma_A C_A \text{ (for others)}$$

- **Standard State:**
  - Similar to solution standard state, with some simplifications for buffers
  - Because of differences, uses $\Delta\bar{G}^{0\prime}$ (note prime)

Equilibrium Using Activities

- When standard state is established, it is possible to calculate $\Delta\bar{G}$ as before

- At equilibrium:

$$\Delta\bar{G}^0 = -RT\ln\frac{a_C^c a_D^d}{a_A^a a_B^b} = -RT\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

  – Second expression applies for **ideal solutes**
  – This assumption is often applied without rigor, but it's frequently close enough

Activities of Ionic Species

- Ions will repel and attract each other; e.g., negative cloud around positive ion will "screen" electric charge
  - High concentrations will lower activity coefficient

- Debye-Huckel: Develop a simple theory for charge screening

- Result (approximate; applies at low concentrations c_i):

$$\log \gamma_i = -0.509 Z_i^2 I^{1/2}$$

$$I = \frac{1}{2} \sum_i c_i Z_i^2$$

Ionic Strength → I

Charge of species i → Z_i

Example: Ionic Activity

- Calculate activity for Mg^{2+} in a 50 mM solution of $MgCl_2$

$$I = \frac{1}{2}[(0.050)(2)^2 + (0.100)(-1)^2] = 0.15 \text{ M}$$

$$\log \gamma_{\text{Mg}^{2+}} = -0.509(2)^2(0.15)^{\frac{1}{2}} = -0.789$$

$$\gamma_{\text{Mg}^{2+}} = 0.16$$

$$a_{\text{Mg}^{2+}} = (0.16)(0.050) = 8.1 \times 10^{-3} \text{ (no units!)}$$

Can We Mix Standard States?

- **Absolutely!** Pick what makes the most sense for each compound
  - Solvent standard state for water
  - Biochemist's standard state for weak acids at pH 7
  - Solute standard state for others

- $\Delta\bar{G}^0$ will change, but if we are consistent in our definitions, $\Delta\bar{G}$ will not change, *even if we switch standard states*

A(*aq.*) + B(*g.*) → C(*aq.*)

- Lookup table:
  - $\Delta \bar{G}^0$ for B, using real gas standard state
  - $\Delta \bar{G}^0$ for A, C using solute standard state
  - $\Delta \bar{G}^0_{rxn} = \Delta \bar{G}_{products} - \Delta \bar{G}_{reactants}$
- As long as we use the framework above, we can write $Q = \frac{a_C}{a_A a_B}$ and use $\Delta \bar{G}^0_{rxn} = -RT \ln K_{eq}$
- $\Delta \bar{G}^0$ is relative and will change with different standard states; $\Delta \bar{G}$ represents a *real quantity* (non-PV work) and *cannot* change with standard state.