

# A Reaction of Ideal Gasses



- Each component:

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

- Can write Gibbs Energy as:

$$\Delta G = 2\mu_{\text{NH}_3} - \mu_{\text{N}_2} - 3\mu_{\text{H}_2}$$

# Toward the Equilibrium Constant

- For any reaction involving ideal gasses:



- We can write the following relationship for Gibbs Energy:

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

- 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

$$K_{eq} = \frac{(P_{C,eq})^c (P_{D,eq})^d}{(P_{A,eq})^a (P_{B,eq})^b}$$

– 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  $\mu_A$  behave *like* an ideal gas, i.e.

$$K_{eq} = \frac{(a_{C,eq})^c (a_{D,eq})^d}{(a_{A,eq})^a (a_{B,eq})^b}$$

# Activities

- Activities are *unitless* (just like the units cancel for  $\frac{P}{1 \text{ atm}}$ )
- Activities require a reference (or standard) state, or  $\mu^0$
- 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

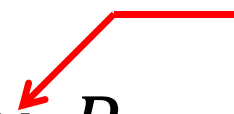
- **Activity:**

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

- **Standard State:** Ideal gas with  $P = 1 \text{ atm}$ , 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  $\gamma_A$  may be far from 1 at 1 atm, but  $\mu$  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
- $\gamma_A$  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
- $\gamma_A$  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:**

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

$$a_{H^+} = 1 \text{ (protons at pH 7)}$$

$$a_A = \gamma_A C_A \text{ (for others)}$$

- **Standard State:**

- Similar to solution standard state, with some simplifications for buffers
- Because of differences, uses  $\Delta\bar{G}^{0'}$  (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  Charge of species  $i$  



# Example: Ionic Activity

- Calculate activity for  $\text{Mg}^{2+}$  in a 50 mM solution of  $\text{MgCl}_2$

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

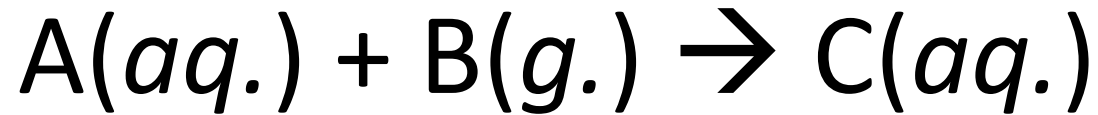
$$\log \gamma_{\text{Mg}^{2+}} = -0.509(2)^2(0.15)^{\frac{1}{2}} = -0.789$$

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

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

# 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*



- Lookup table:
  - $\Delta\bar{G}^0$  for B, using real gas standard state
  - $\Delta\bar{G}^0$  for A, C using solute standard state
  - $\Delta\bar{G}_{rxn}^0 = \Delta\bar{G}_{products} - \Delta\bar{G}_{reactants}$
- As long as we use the framework above, we can write  $Q = \frac{a_C}{a_A a_B}$  and use  $\Delta\bar{G}_{rxn}^0 = -RT \ln K_{eq}$
- $\Delta\bar{G}^0$  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.