

Kinetics and Equilibria

By definition, **kinetic processes** are not **equilibrium processes**.
In fact, we may think of kinetic processes as the mechanism that nature uses to reach the equilibrium state.

Binary Collision rate
in forward direction.

Binary Collision rate
in reverse direction.

has 2 rate constants, we can write,
assuming these are **ELEMENTARY** reaction steps:

(Equilibrium condition)

Where $[A]_e$ etc. are the equilibrium concentrations
of $[A]$ etc.

Using the Arrhenius form for the rate constants k_f and k_r

$$k_f = A_f e^{-E_{Af}/RT} \quad k_r = A_r e^{-E_{Ar}/RT}$$

But later we will learn (or you already know from high school):

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\ln[K_{eq}] = -\Delta G^0/RT$$

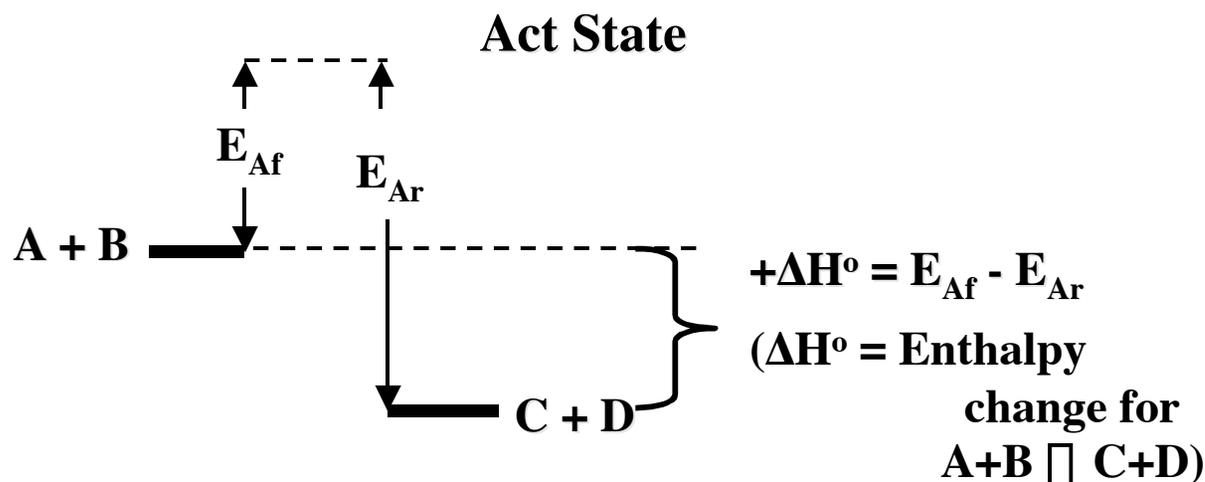
Where ΔH^0 is the enthalpy change for the reaction and ΔS^0 is the entropy change for the reaction. ΔG^0 is called the Free Energy

Equating these two forms for the equilibrium constant allows us to connect thermodynamics and kinetics!

↑ Kinetic form of K_{eq}

↑ Thermodynamic form of K_{eq}

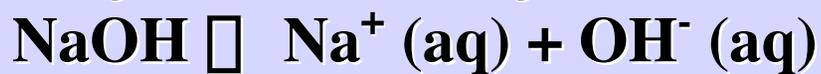
“Identify” A_f / A_r with $\{e^{(\Delta S^\circ/R)}\}$ (T “independent” assuming ΔS° indep of T).



Acid-Base Equilibria

Several ways to define acid, base:

1)



Oversimplified:

$\text{H}^+ \sim 10^{-13}$ cm in diameter because is a free proton
(unique in + charged species)

Evidence exists for presence of H_3O^+ in solution. Small size of H^+ allows it to be incorporated into the structure of the solvent.

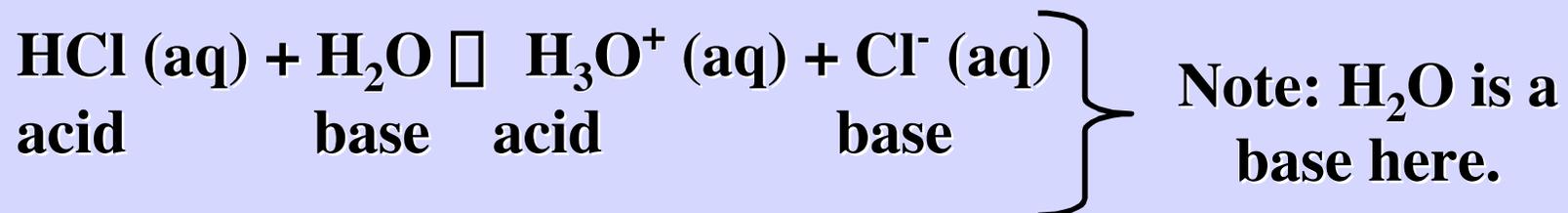
**H_3O^+ is called the hydronium ion-is particularly stable.
Less evidence for species like H_9O_4^+ ($4\text{H}_2\text{O}+\text{H}^+$)**

More accurate view:

Some non- OH^- species can neutralize acids:



2)





Conjugate pairs: CO_3^{2-} , HCO_3^- and H_2O , OH^-

Strengths of Acids and Bases:

Equate to tendency to transfer a proton to H_2O



Need a **quantitative** measure of acidity or H^+ donating power.



Note that large K is associated with strong acid since it means numerator is large compared to denominator. Large $K \rightleftharpoons$ HA is a good proton donor to H_2O .

If acid is strong, e.g., HCl, then conjugate base is weak (Cl^-)
Will prove this latter in a quantitative fashion.

3) Lewis Concept (most general): Acid is any substance that can accept electrons and a base is any substance that can donate electrons.

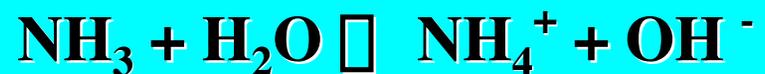
Acid-Base Equilibria Considerations

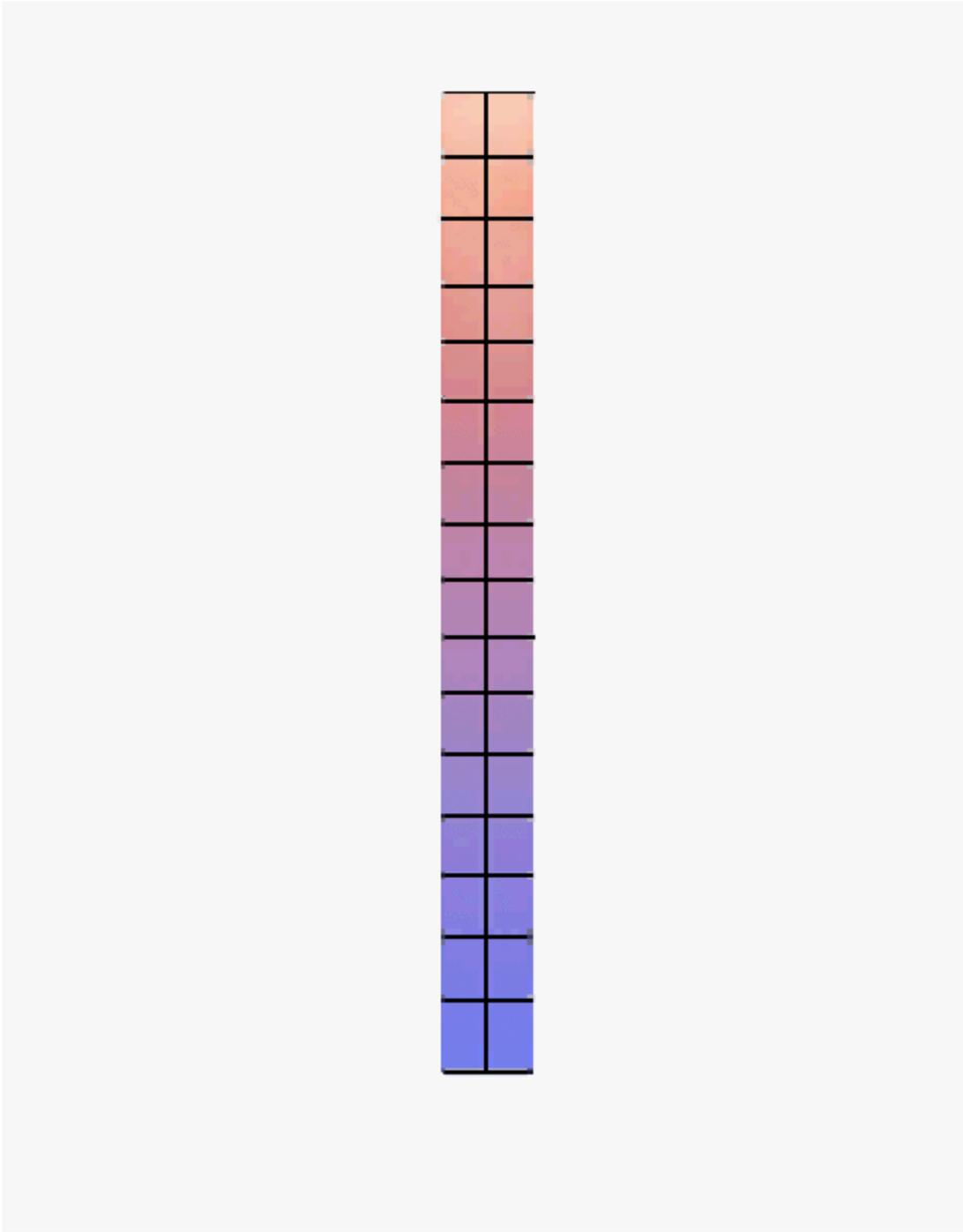
$$K' = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-][\text{H}_2\text{O}]} \quad (\text{K}' \text{ is a true equilibrium constant})$$

$$K'[\text{H}_2\text{O}] = K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

Acid ionization constant

K_a is called the acid ionization constant





pH=
 $-\log_{10}[\text{H}_3\text{O}^+]$

Bonus * Bonus * Bonus * Bonus * Bonus * Bonus

Suppose you have $[\text{H}_3\text{O}^+]$ from added $\text{HCl} = 0.1 \text{ M} = 10^{-1} \text{ M}$

Then $[10^{-1}][\text{OH}^-] = 10^{-14}$

In pure H_2O , $[\text{OH}^-] = [\text{H}_3\text{O}^+] = 10^{-7}$, **but**

Weak Acids and Bases

Add acetic acid to H_2O :

$$K = K_a$$

What are $[\text{CH}_3\text{COOH}]$, $[\text{H}_3\text{O}^+]$, $[\text{CH}_3\text{COO}^-]$?