AP CHEMISTRY

Unit 4:
Acids and Bases

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The Equilibrium Constant

- For a general reaction in the gas phase

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium constant expression is

$$K_{eq} = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

where K_{eq} is the equilibrium constant.

The Equilibrium Constant

- For a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium constant expression for everything in solution is

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where K_{eq} is the equilibrium constant.

$$\mathbf{CH_4\ (g) + 2\ O_2\ (g) \rightleftharpoons CO_2\ (g) + 2\ H_2O\ (g)}$$

1. Write an expression for K_{eq}
2. Calculate K at a given temperature if $[CH_4]$ = 0.020 M, $[O_2]$ = 0.042 M, $[CO_2]$ = 0.012 M, and $[H_2O]$ = 0.030 M at equilibrium. (include units)

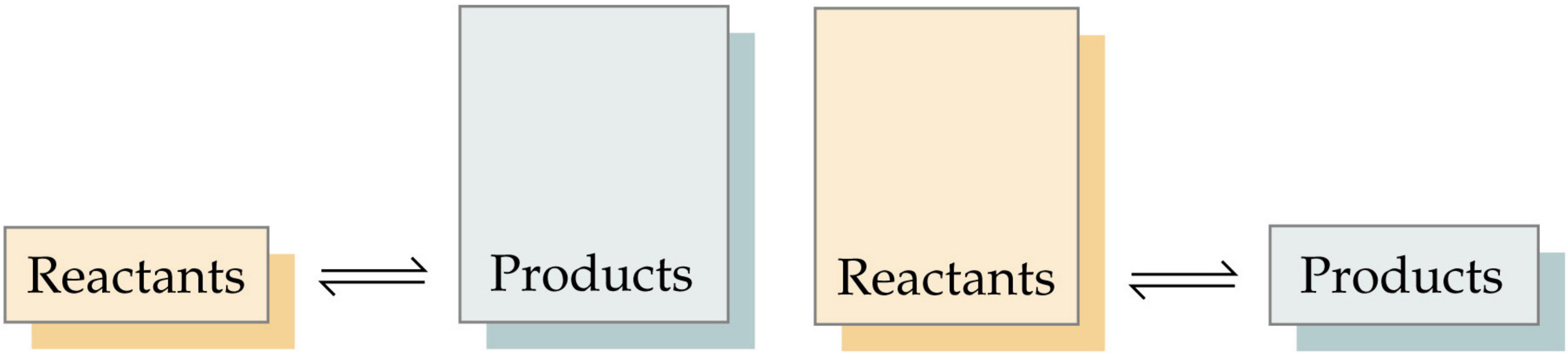
1. $$K_{eq} = \frac{[CO_2][H_2O]^2}{[CH_4][O_2]^2}$$

2. .306

The Magnitude of Equilibrium Constants

- The equilibrium constant, K, is the ratio of products to reactants.
- Therefore, the larger K the more products are present at equilibrium.
- Conversely, the smaller K the more reactants are present at equilibrium.
- If $K >> 1$, then products dominate at equilibrium and equilibrium lies to the right.

- If $K << 1$, then reactants dominate at equilibrium and the equilibrium lies to the left.



(a) $K_{eq} >> 1$

(b) $K_{eq} << 1$

Example – H_2 (g) + I_2 (g) $\rightleftharpoons$ 2 HI (g)

The initial concentration of HI is 0.50 M. The equilibrium concentration of H_2 is 0.10 M. What are the equilibrium concentrations of I_2 and HI? What is the value of K_{eq}?

Example – H_2 (g) + I_2 (g) $\leftrightarrow$ 2 HI (g)

The initial concentration of HI is 0.50 M. The equilibrium concentration of H_2 is 0.10 M. What are the equilibrium concentrations of I_2 and HI? What is the value of K_{eq}?

1. $[I_2] = .1$ M $[HI] = .3$ M

2. $K_{eq} = 9.0$

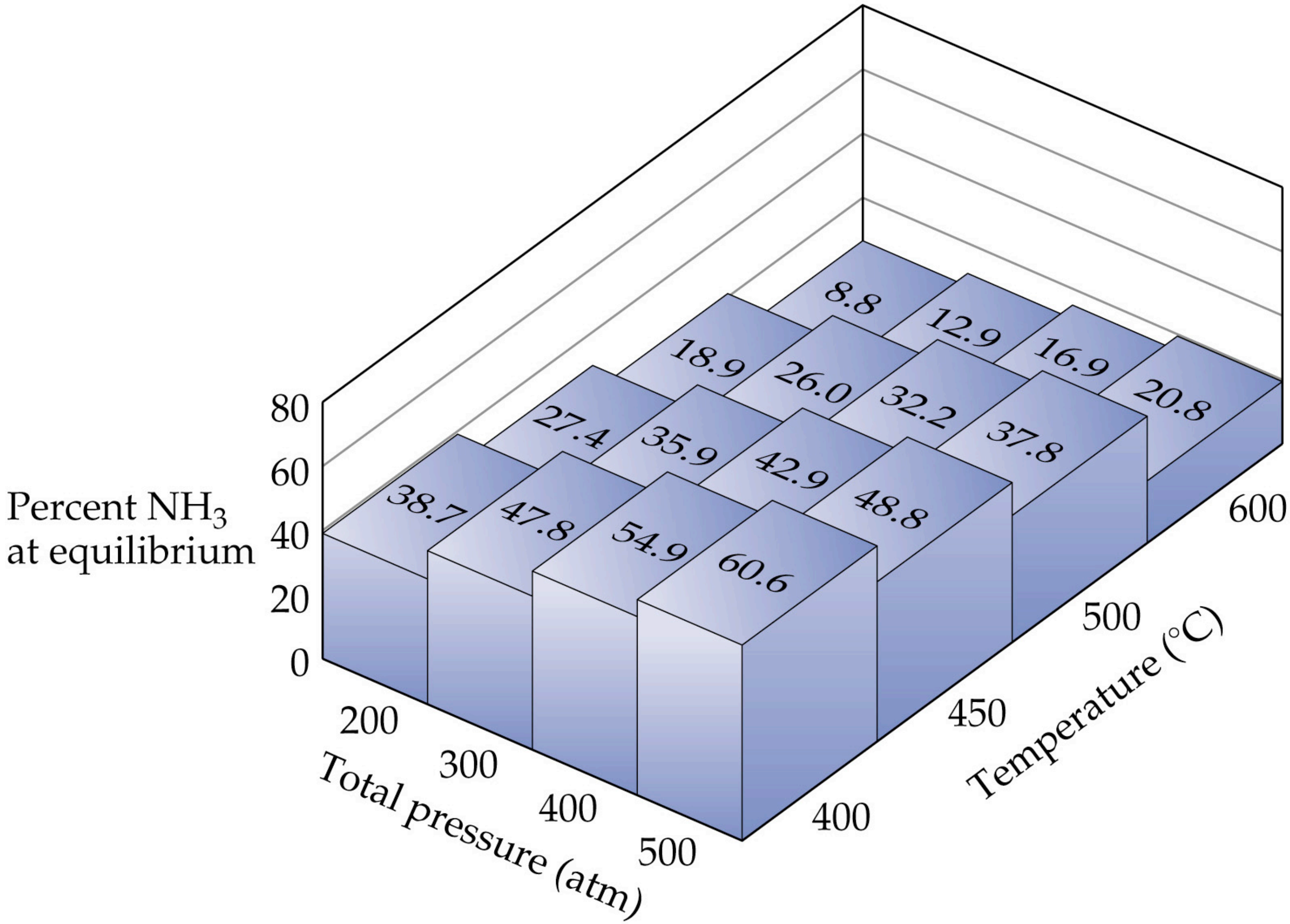
Le Châtelier's Principle

- Consider the production of ammonia

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

- As the pressure increases, the amount of ammonia present at equilibrium increases.
- As the temperature decreases, the amount of ammonia at equilibrium increases.
- Can this be predicted?

- Le Châtelier's Principle: if a system at equilibrium is disturbed, the system will move in such a way as to counteract the disturbance.

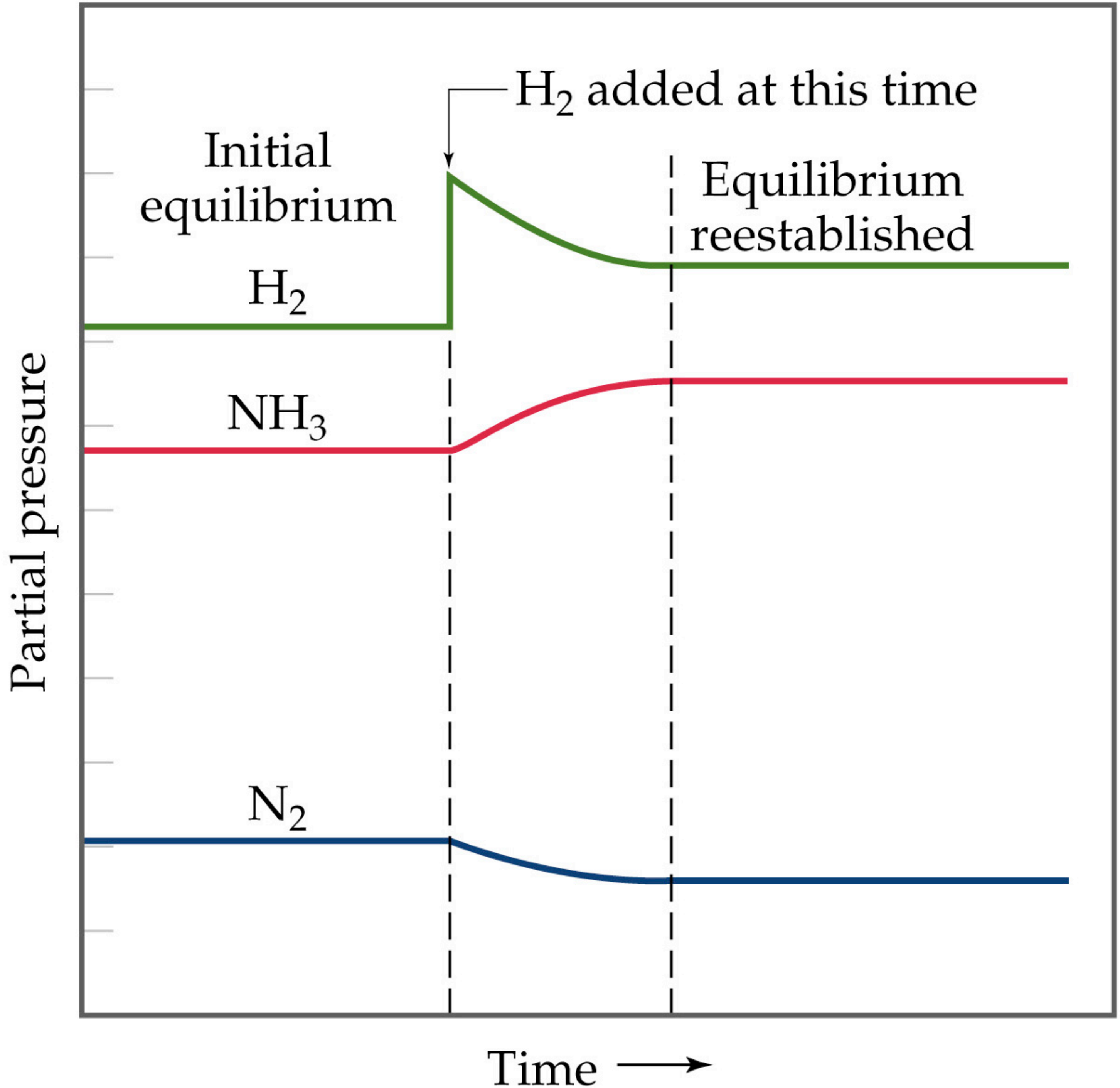


Change in Reactant or Product Concentrations

- Consider the Haber process

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

- If H_2 is added while the system is at equilibrium, the system must respond to counteract the added H_2 (by Le Châtelier).
- The system must consume the H_2 and produce products until a new equilibrium is established.
- So, $[H_2]$ and $[N_2]$ will decrease and $[NH_3]$ increases.


H$_2$ added at this time
Initial equilibrium
Equilibrium reestablished
H$_2$
NH$_3$
N$_2$
Partial pressure
Time

- Adding a reactant or product shifts the equilibrium away from the increase.
- Removing a reactant or product shifts the equilibrium towards the decrease.
- To optimize the amount of product at equilibrium, we need to flood the reaction vessel with reactant and continuously remove product (Le Châtelier).
- We illustrate the concept with the industrial preparation of ammonia.

Effects of Volume and Pressure Changes

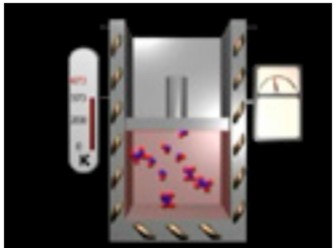
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

- An increase in pressure (by decreasing the volume) favors the formation of colorless N_2O_4.
- The instant the pressure increases, the system is not at equilibrium and the concentration of both gases has increased.
- The system moves to reduce the number moles of gas (i.e. the reverse reaction is favored).
- A new equilibrium is established in which the mixture is lighter because colorless N_2O_4 is favored.

- Increasing total pressure by adding an inert gas has no effect on the partial pressures of reactants and products, therefore it has no effect on the equilibrium.

Effect of Temperature Changes

- The equilibrium constant is temperature dependent.
- For an endothermic reaction, $\Delta H > 0$ and heat can be considered as a reactant.
- For an exothermic reaction, $\Delta H < 0$ and heat can be considered as a product.



- Adding heat (i.e. heating the vessel) favors away from the increase:
  - if $\Delta H > 0$, adding heat favors the forward reaction,
  - if $\Delta H < 0$, adding heat favors the reverse reaction.
- Removing heat (i.e. cooling the vessel), favors towards the decrease:
  - if $\Delta H > 0$, cooling favors the reverse reaction,
  - if $\Delta H < 0$, cooling favors the forward reaction.

Le Châtelier's Principle

The Effect of Catalysis

- A catalyst lowers the activation energy barrier for the reaction.
- Therefore, a catalyst will decrease the time taken to reach equilibrium.
- A catalyst does not effect the composition of the equilibrium mixture.

$$SO_3 (g) \rightleftharpoons SO_2 (g) + {}^{1}/_{2}\, O_2 (g)$$

- $\Delta H = +98.9$ kJ
- Determine the effect of each of the following on the equilibrium (direction of shift)
  - What happens to the concentration of SO_3 after each of the changes?

A) Addition of pure oxygen gas.

B) Compression at Constant Temperature

C) Addition of Argon gas

D) Decrease temperature

E) Remove sulfur dioxide gas

F) Addition of a catalyst

Calculating Equilibrium Concentrations

- The same steps used to calculate equilibrium constants are used.
- K is given.
- Generally, we do not have a number for the change in concentration line.
- Therefore, we need to assume that x mol/L of a species is produced (or used).
- The equilibrium concentrations are given as algebraic expressions.
- We solve for x, and plug it into the equilibrium concentration expressions.

Example – H_2 (g) + FeO (s) $\rightleftharpoons$ H_2O (g) + Fe (s)

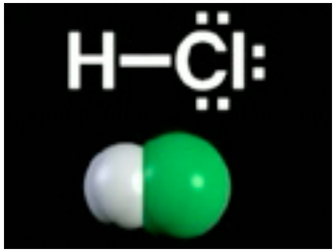
K_c = 5.20

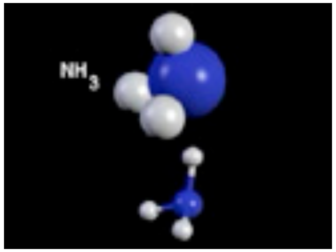
If the initial concentration of H_2 is 0.50 M and the inintial concentration of H_2O is 6.50 M, what will the equilibrium concentrations be?

If the initial concentration of H_2 is 1.00 M (no H_2O present), what will the equilibrium concentrations be?

Acids and Bases: A Brief Review

- Acids: taste sour and cause dyes to change color.
- Bases: taste bitter and feel soapy.
- Arrhenius: acids increase $[H^+]$, bases increase $[OH^-]$ in solution.
- Arrhenius: acid + base $\rightarrow$ salt + water.
- Problem: the definition confines us to aqueous solution.





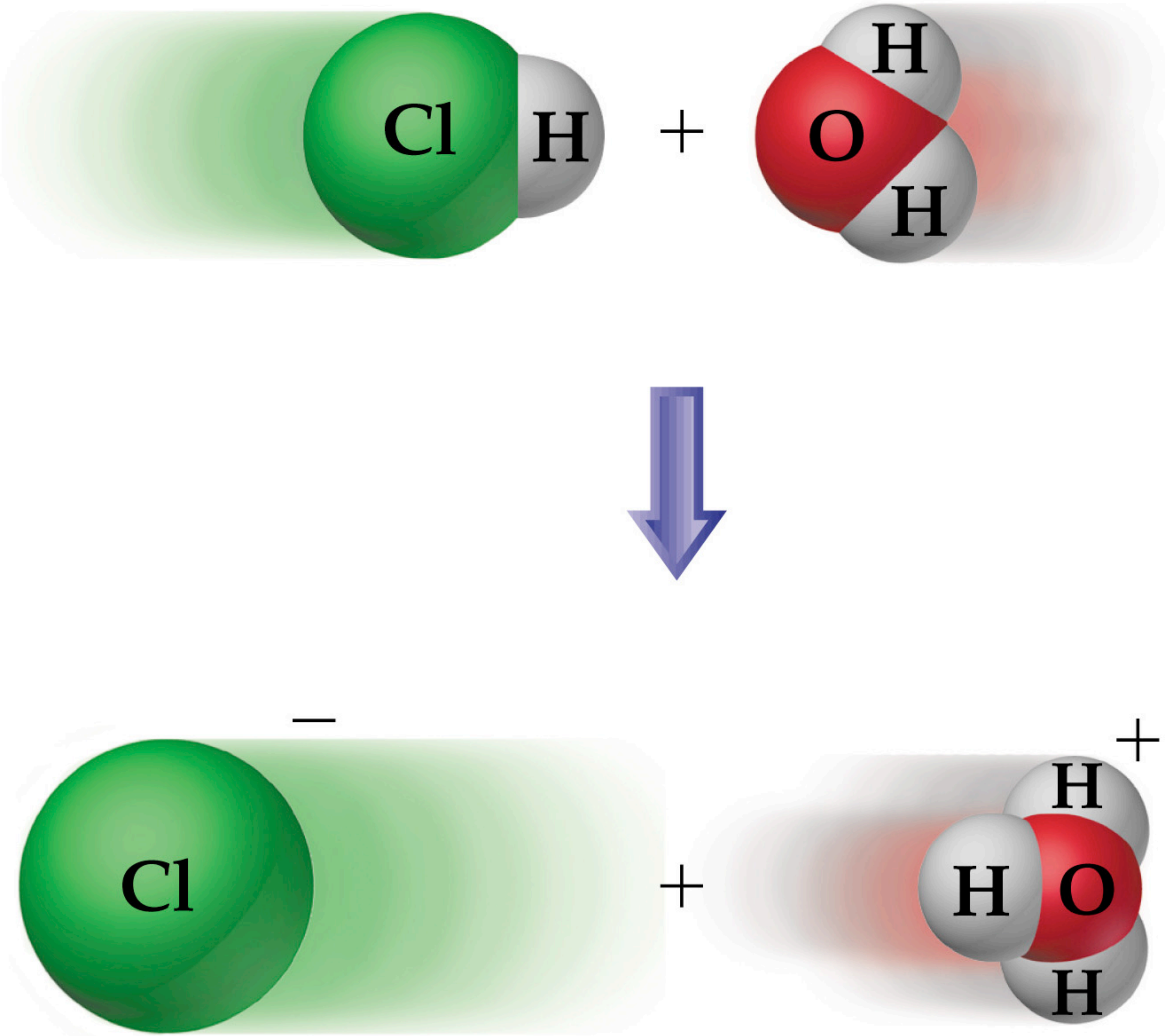
Brønsted-Lowry Acids and Bases

The H^+ Ion in Water

- The $H^+(aq)$ ion is simply a proton with no electrons. (H has one proton, one electron, and no neutrons.)
- In water, the $H^+(aq)$ joins a water molecule to become $H_3O^+(aq)$.
- Generally we use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably.

Proton Transfer Reactions

- Focus on the $H^+(aq)$.
- Brønsted-Lowry: acid donates H^+ and base accepts H^+.
- Brønsted-Lowry base does not need to contain OH^-.
- Consider $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$:
  - HCl donates a proton to water. Therefore, HCl is an acid.
  - H_2O accepts a proton from HCl. Therefore, H_2O is a base.
- Water can behave as either an acid or a base.
- Amphoteric substances can behave as acids and bases.



Cl
H
+
H
O
H
−
Cl
+
+
H
H
O
H