

05

CHEMICAL EQUILIBRIUM

EQUILIBRIUM CONSTANT: IODINE + IODINE \rightleftharpoons TRIIODIDE

CHEMISTRY 136L // FALL 2019

QUANTITY OF INTEREST

Equilibrium Constants

All closed chemical reactions eventually reach their equilibrium state, where the speeds of the *forward* and *reverse* reactions are equal.



So, there is no net change in concentrations at equilibrium.



For a given temperature, the numerical value of the equilibrium constant (K) for a chemical reaction is a **constant that is independent of initial concentrations**.



Equilibrium constants are dimensionless.

QUANTITY OF INTEREST

Equilibrium Constants

If the numerical value of K for a reaction is large, then



equilibrium lies far to the right,
and products dominate over reactants.



Such reactions go to *almost* 100% “completion.”

The vast majority of reactions we have encountered in Chemistry 134L
and 136L thus far fall into this category.

Today, we will study a reaction that does *not* fall in this category.

REACTION OF INTEREST

The triiodide equilibrium

Our focus today is the following equilibrium:



which means the equilibrium constant (K) is

$$K = \frac{[I_3^-]_{eq}}{[I^-]_{eq}[I_2]_{eq}}$$

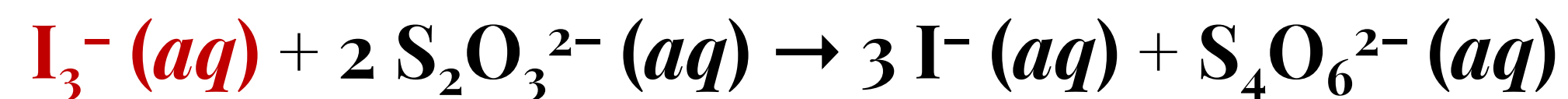
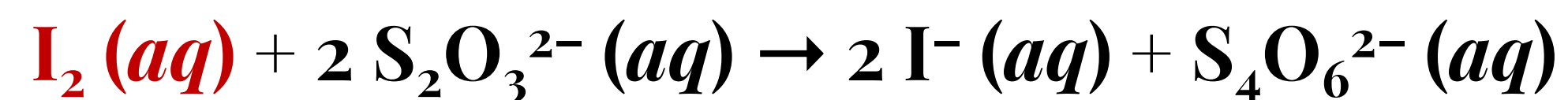
The objective today is to determine the numerical value of K at room temperature.

What are the units for K?

HOW TO DETERMINE VALUE OF K?

We need to know the concentrations of all three species at equilibrium.

Titration would work, but both I_2 and I_3^- are reactive.



If we titrate an aqueous solution containing both I_2 and I_3^- with thiosulfate, we will only be able to calculate the sum

$$\{[I_2]_{eq,aq} + [I_3^-]_{eq,aq}\}$$

HOW TO OVERCOME THE PROBLEM

General Procedure

We can add an immiscible organic solvent, such as *n*-heptane (shake well).

After establishing the following two equilibria:

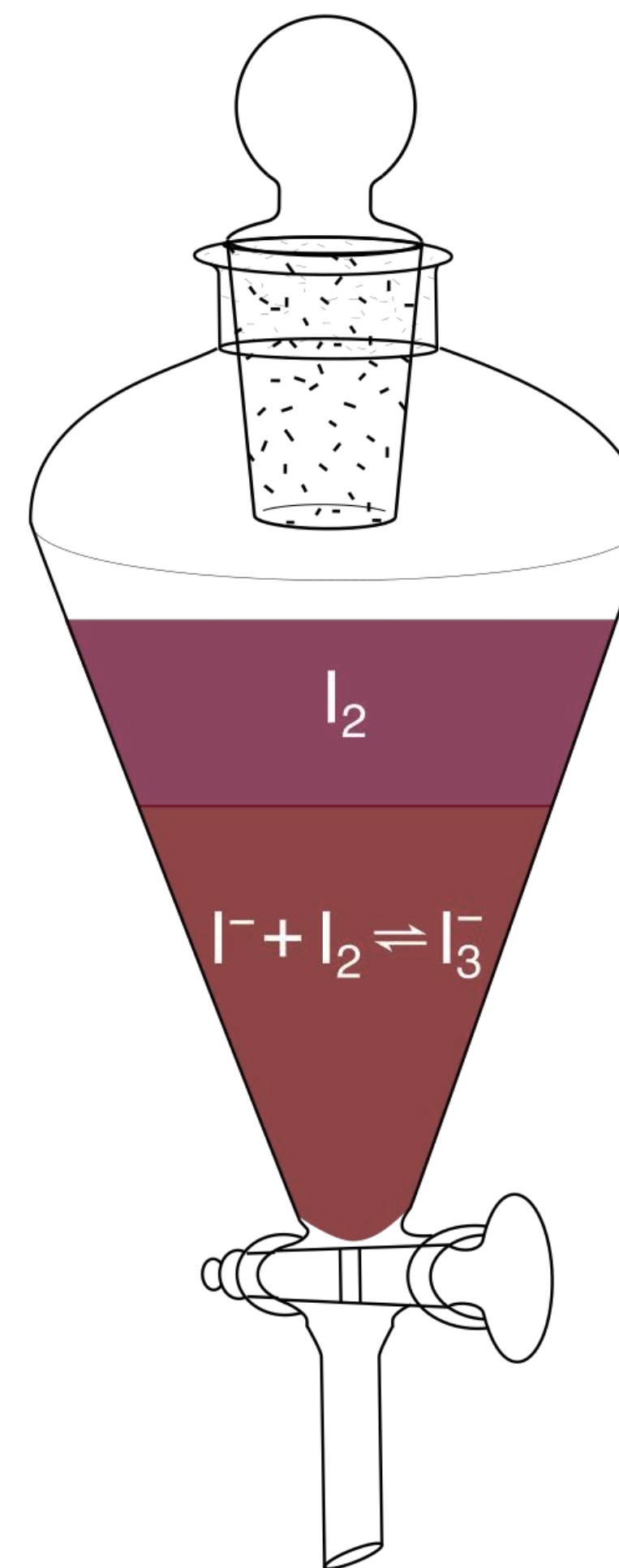


Separate the two layers.

Titrate each layer separately.

Titrant: thiosulfate ($S_2O_3^{2-}$)

Indicator: starch



SECOND EQUILIBRIUM

General Procedure



We have:

$$K' = \frac{[\text{I}_2]_{\text{n-heptane}}}{[\text{I}_2]_{\text{aqueous}}}$$

If we know the value of K' , we can figure out $[\text{I}_2]_{\text{eq,aq}}$

$$[\text{I}_2]_{\text{eq,aq}} = \frac{[\text{I}_2]_{\text{n-heptane}}}{K'}$$

The numerical value of K' for the distribution of I_2 between water and several other *immiscible* liquids can be determine independently.

They are available in the chemical literature.

FINALLY

General Procedure

How do we determine $[I_3^-]_{\text{eq,aq}}$ and $[I^-]_{\text{eq,aq}}$?

$$[I_3^-]_{\text{eq,aq}} = \underbrace{\{[I_2]_{\text{eq,aq}} + [I_3^-]_{\text{eq,aq}}\}}_{\substack{\text{Aqueous} \\ \text{Layer} \\ \text{Titration}}} - \underbrace{[I_2]_{\text{eq,aq}}}_{\substack{\text{Organic} \\ \text{Layer} \\ \text{Titration}}}$$

$$[I^-]_{\text{eq,aq}} = [I^-]_0 - [I_3^-]_{\text{eq,aq}} \quad \text{Material balance \& Stoichiometry}$$

Fe(III)-thiocyanate Equilibrium

