



# EXPERIMENT 6

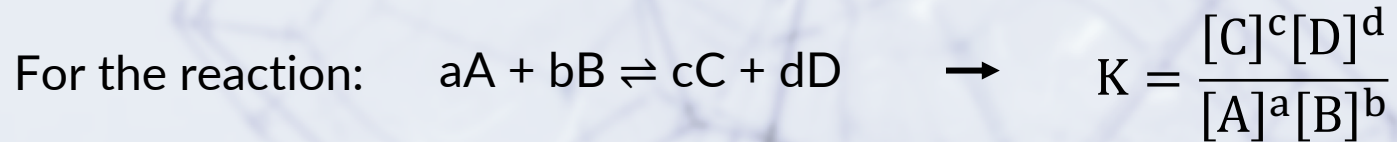
## The Triiodide Equilibrium

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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 independent of initial concentrations.**



**Equilibrium constants are dimensionless.**

If the numerical value of  $K$  for a reaction is large



Equilibrium lies far to the right  
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 in this category.

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

## THE TRIIODIDE EQUILIBRIUM



$$K = \frac{[\text{I}_3^-]_{\text{eq}}}{[\text{I}_2]_{\text{eq}}[\text{I}^-]_{\text{eq}}}$$

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

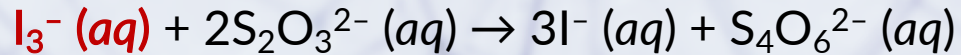
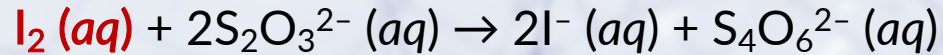
*What are the units of K?*



To determine the numerical value of K,  
we need to know the concentration of three species when equilibrium prevails.



We can titrate or use spectrophotometry, but there is a problem.



If we titrate an aqueous solution containing both  $\text{I}_2$  and  $\text{I}_3^-$  with thiosulfate,  
we will be able to calculate only the sum of  $\{[\text{I}_2]_{\text{eq,aq}} + [\text{I}_3^-]_{\text{eq,aq}}\}$ .



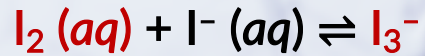
But this is not enough to figure out K!

To overcome the problem:

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



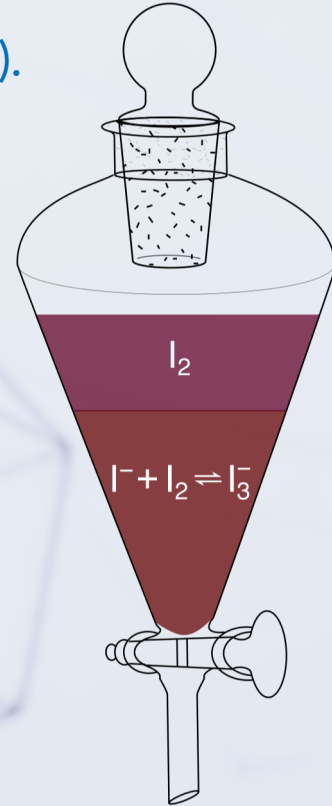
After establishing the following two equilibria:



Separate the two layers.



Titrate each layer separately  
(thiosulfate in buret & starch as indicator)



For the second equilibrium:



$$K' = \frac{[I_2]_{n\text{-heptane}}}{[I_2]_{aq}} = 41.8$$



If we know the numerical value of  $K'$ , we can figure out  $[I_2]_{eq,aq}$

$$[I_2]_{eq,aq} = \frac{[I_2]_{n\text{-heptane}}}{K'}$$

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

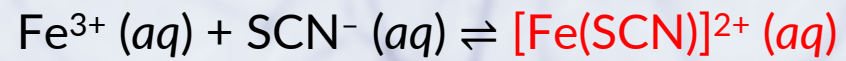
They are available in the chemical literature.

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

$$[I_3^-]_{eq,aq} = \underbrace{\{[I_2]_{eq,aq} + [I_3^-]_{eq,aq}\}}_{\text{AQUEOUS LAYER TITRATION}} - \underbrace{[I_2]_{eq,aq}}_{\text{ORGANIC LAYER TITRATION}}$$

$$[I^-]_{eq,aq} = [I^-]_0 - [I_3^-]_{eq,aq} \quad (\text{DUE TO STOICHIOMETRY})$$

## The Fe(III)-thiocyanate Equilibrium



## NOTES

1. Organic layer titration: shake well by hand and vent.
2. Must do three aqueous layer titrations and three n-heptane layer titrations.
3. Accuracy of your experimental value of K will be graded.
4. In part E, to measure 23 mL water and 2 mL solution, use your 10 mL measuring cylinder.

