# Chemical Equilibrium in Solution

$I_2(aq) + I^-(aq) = I_3^-(aq)$

For the chemical equilibrium,

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

The thermodynamic Equilibrium constant is defined as;

$$K_a = \frac{a_{I_3^-}}{a_{I_2} a_I} \qquad a_i = \gamma_i c_i$$

and $$K_a = \frac{a_{I_3^-}}{a_{I_2} a_{I^-}} = \frac{\gamma_{I_3^-}}{\gamma_{I_2}\gamma_{I^-}} \frac{[I_3^-]}{[I_2][I^-]} \approx \frac{[I_3^-]}{[I_2][I^-]} = K_c$$

$$K_a \approx K_c$$

implies $\gamma_{I_3^-} = \gamma_{I^-}$; $\gamma_{I_2} = 1$ from the above approximation.

The activity coefficient in general is approximated by

DH Limiting Law; $\log \gamma_i = \dfrac{-509 z_i^2 \sqrt{I}}{1 + \sqrt{I}}$

$$K_a \approx \frac{[I_3^-]}{[I_2][I^-]} = K_c$$

Meaning of [X]:

$[X] = \dfrac{c_X}{c_0}$ where $c_X, c_o$ are concentration of X in mol/L

and concentration of the standard state: 1 mol/L

In effect [X] is the *concentration value of* X, in mol/l *and no unit is involved.*

$$K_a \approx \frac{[I_3^-]}{[I_2][I^-]} = K_c$$

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

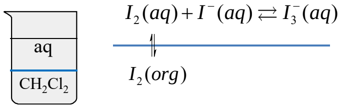
To determine the [I$_2$] one can use the quantitative reaction with the thiosulfate ion.

$$I_2(aq) + 2S_2O_3^{-2}(aq) = 2I^-(aq) + S_4O_6^{-2}(aq)$$

To calculate the concentrations of the three species in aqueous solution direct reaction method is not feasible as it disturbs the reaction equilibrium. Only the *total concentration* [I$_2$(aq) + I$_3^-$(aq)] is easily determinable, not individual values.

The strategy is to establish the reaction equilibrium in the aqueous solution which is in contact with an organic layer.

This establishes a second (partition) equilibrium system in addition to the reaction equilibrium.



$$I_2(aq) + I^-(aq) \rightleftarrows I_3^-(aq)$$

$$\upharpoonleft\downharpoonright$$

$$I_2(org)$$

$$I_2(org) \rightleftarrows I_2(aq)$$

$$k = \frac{I_2(aq)}{I_2(org)}$$

$$I_2(org) \rightleftarrows I_2(aq)$$

$$k = \frac{I_2(aq)}{I_2(org)}$$

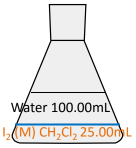
At a given temperature partition coefficient *k* is a constant for a given equilibrium between the two phases.

If *k* is known or established, one can find the I$_2$ concentration in organic layer, and use *k* to find the I$_2$(aq) concentration.

| | -------------- Mix --------------- | | $CH_2Cl_2$ layer titrate 10.00mL | | Aqueous layer titrate 25.00 mL | |
|---|---|---|---|---|---|---|
| Run No. | $CH_2Cl_2$ (25 mL) Molarity I2 | Aqueous Layer (100 mL) Molarity KI | Burette Size, mL | Molarity $S_2O_3^{-2}$ | Burette Size, mL | Molarity $S_2O_3^{-2}$ |
| 1 | 0.080 | 0.0 (DI) | 50 | 0.1 | 10 | 0.01 |
| 2 | 0.040 | 0.0 (DI) | 50 | 0.1 | 10 | 0.01 |
| 3 | 0.020 | 0.0 (DI) | 10 | 0.1 | 10 | 0.01 |
| 4 | 0.080 | 0.15 | 10 | 0.1 | 50 | 0.1 |
| 5 | 0.040 | 0.15 | 10 | 0.1 | 10 | 0.1 |
| 6 | 0.080 | 0.03 | 50 | 0.1 | 10 | 0.1 |

## Determining k

| | | | $CH_2Cl_2$ layer titrate 10.00mL | | Aqueous layer titrate 25.00 mL | |
|---|---|---|---|---|---|---|
| Run No. | CH2Cl2 (25 mL) Molarity $I_2$ | Aqueous Layer (100 mL) Molarity KI | Vol $CH_2Cl_2$ mL | [ $S_2O_3^{-2}$] | Aq. volume mL | [ $S_2O_3^{-2}$] |
| 1 | 0.080 | 0.0 | 10.00 | 0.10 | 25.00 | 0.01 |
| 2 | 0.040 | 0.0 | 10.00 | 0.10 | 25.00 | 0.01 |
| 3 | 0.020 | 0.0 | 10.00 | 0.10 | 25.00 | 0.01 |



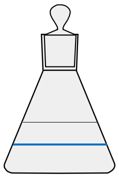
| | $CH_2Cl_2$ layer titrate 10.00mL | | Aqueous layer titrate 25.00 mL | | |
|---|---|---|---|---|---|
| Run No. | Vol (mL) 0.1M $S_2O_3^{-2}$ | [$I_2$ org] | Vol (mL) 0.01M $S_2O_3^{-2}$ | [$I_2$ aq] | k |
| 1 | | | | | |
| 2 | | | | | |
| 3 | | | | | |
| | | | | mean k = | |

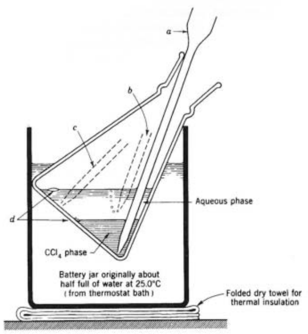
## Determining $K_c$

| | | | $CH_2Cl_2$ layer titrate 10.00mL | | Aqueous layer titrate 25.00 mL | |
|---|---|---|---|---|---|---|
| Run No. | CH2Cl2 (25 mL) Molarity $I_2$ | Aqueous Layer (100 mL) Molarity KI | Vol $CH_2Cl_2$ mL | [ $S_2O_3^{-2}$] M | Aq. volume mL | [ $S_2O_3^{-2}$] M |
| **4** | 0.080 | 0.15 | 10.00 | 0.10 | 25.00 | 0.10 |
| **5** | 0.040 | 0.15 | 10.00 | 0.10 | 25.00 | 0.10 |
| **6** | 0.080 | 0.03 | 10.00 | 0.10 | 25.00 | 0.10 |

| | $CH_2Cl_2$ layer (use -10mL pipette) | | Aqueous layer (use 25-mL pipette) | | | | |
|---|---|---|---|---|---|---|---|
| Run No. | Vol (mL) 0.1M $S_2O_3^{-2}$ | [$I_2$ org] | Vol (mL) 0.01M $S_2O_3^{-2}$ | [$I_2$ aq]$_{Total}$ | [$I_3^{-1}$ aq] | [$I^{-1}$ aq] | $K_c$ |
| **4** | | | | | | | |
| **5** | | | | | | | |
| **6** | | | | | | | |

$$\left[I^-(aq)\right]=\left[I^-(aq)\right]_0-\left[I_3^-(aq)\right]$$





## Titration Reaction

$$I_2+2S_2O_3^{-2}=2I^-+S_4O_6^{-2}$$

*or*

$$I_3^-+2S_2O_3^{-2}=3I^-+S_4O_6^{-2}$$

$$@\ \text{'endpoint'}\quad \frac{mol\ I_2}{mol\ S_2O_3^{-2}}=\frac{1}{2}$$

$$[I_2]V_{I_2}=\frac{1}{2}\left[S_2O_3^{-2}\right]V_{S_2O_3^{-2}}$$

$$[I_2]=\frac{1}{2}\left[S_2O_3^{-2}\right]\frac{V_{S_2O_3^{-2}}}{V_{I_2}}$$

Titration of the aqueous layer of the reaction mixture:

$\Rightarrow [I_2(aq)]+[I_3^-(aq)]$ of the equilibrium system

## Determining $K_c$

| | | | $CH_2Cl_2$ layer titrate 10.00mL | | Aqueous layer titrate 25.00 mL | |
|---|---|---|---|---|---|---|
| Run No. | CH2Cl2 (25 mL) Molarity $I_2$ | Aqueous Layer (100 mL) Molarity KI | Vol $CH_2Cl_2$ mL | [ $S_2O_3^{-2}$] M | Aq. volume mL | [ $S_2O_3^{-2}$] M |
| 4 | 0.080 | 0.15 | 10.00 | 0.10 | 25.00 | 0.10 |
| 5 | 0.040 | 0.15 | 10.00 | 0.10 | 25.00 | 0.10 |
| 6 | 0.080 | 0.03 | 10.00 | 0.10 | 25.00 | 0.10 |

$$K_c=\frac{[I_3^-]_{aq}}{[I_2]_{aq}[I^-]_{aq}}$$

| | $CH_2Cl_2$ layer (use -10mL pipette) | | Aqueous layer (use 25-mL pipette) | | | | |
|---|---|---|---|---|---|---|---|
| Run No. | Vol (mL) 0.1M $S_2O_3^{-2}$ | [$I_2$ org] | Vol (mL) 0.01M $S_2O_3^{-2}$ | [$I_2$ aq] total | [$I_2$ aq] | [$I_3^{-1}$ aq] | [$I^{-1}$ aq] |
| 4 | | | | | | | |
| 5 | | | | | | | |
| 6 | | | | | | | |

$$\left[I^-(aq)\right]=[I^-(aq)]_0-\left[I_3^-(aq)\right]$$