13.4 Colligative Properties

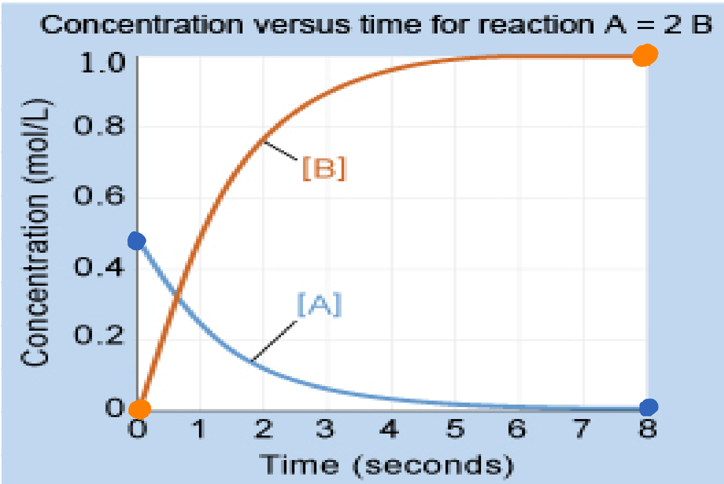
Vapor Pressure Lowering – van't Hoff Factor?

Which of the following solutions would have the **lowest freezing point**?

a)	**0.15m** CuI_2	$Cu^{2+} + 2I^-$	: $i = 3$	$3 \times 0.15 = 0.45$
b) ✓	**0.17m** $Zn(CH_3COO)_2$	$Zn^{2+} + 2\,CH_3COO^-$	: $i = 3$	$3 \times 0.17 = 0.51$ ✓
c)	**0.14m** CoI_2	$Co^{2+} + 2I^-$	: $i = 3$	$3 \times 0.14 = 0.42$
d)	**0.47m** Urea (nonelectrolyte)		: $i = 1$	$1 \times 0.47 = 0.47$

14.2 Expressing the Rate of a Reaction

Average Rate and Reaction Stoichiometry



A = 2B

Timed from 0 to 8 seconds

$$\text{Rate} = \frac{\Delta[B]}{\Delta t} = \frac{[B]_8 - [B]_0}{t_8 - t_0} = \text{Rate of Formation of B}$$

$$\text{Rate} = \frac{\Delta[A]}{\Delta t} = \frac{[A]_8 - [A_0]}{t_8 - t_0} = \text{Rate of Dissapearance of A}$$

For B :

$$\text{Rate} = \frac{1M - 0M}{8s - 0s} = 0.125\ M.s^{-1}$$

For A :

$$\text{Rate} = \frac{0M - 0.5M}{8s - 0s} = -0.0625\ M.s^{-1}$$

No surprise, A = 2B, that the average rate of formation of B is twice the average rate of Dissapearance of A.

14.2 Expressing the Rate of a Reaction

Average Rate and Reaction Stoichiometry

$$A = 2B$$

$$\text{Average Rate of Reaction} = \frac{1}{2}\frac{\Delta[B]}{\Delta t} = -\frac{1}{1}\frac{\Delta[A]}{\Delta t}$$

$$= \tfrac{1}{2}(0.125\ M.s^{-1})^{*} = -(-0.0625\ M.s^{-1})^{*}$$

$$= 0.0625\ M.s^{-1} = 0.0625\ M.s^{-1}$$

* See previous slide to see where these numbers come from.

Generalization: $aA + bB = cC + dD$

$$\text{Average Rate of Reaction} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

14.2 Expressing the Rate of a Reaction

Average Rate and Reaction Stoichiometry

For the decomposition of hydrogen peroxide in dilute sodium hydroxide at 20 °C,

$$2\,H_2O_2(aq) \rightarrow 2\,H_2O(\ell) + O_2(g)$$

the **average rate of disappearance** of H_2O_2 over the period from t = 0 to t = 516 min is found to be **8.08×10^{-5} M/min**.

What is the **average rate of appearance of O_2** over the same period?

What is the **average rate of the reaction**?

$$\text{Average Rate of Reaction} = -\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{1}{1}\frac{\Delta[O_2]}{\Delta t}$$

$$-\frac{\Delta[H_2O_2]}{\Delta t} = 8.08\times10^{-5}\ M.min^{-1}$$

$$\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t}$$

$$= \frac{1}{2}\left(-\frac{\Delta[H_2O_2]}{\Delta t}\right)$$

$$= 1/2\,(8.08\times10^{-5}\ M.min^{-1})$$

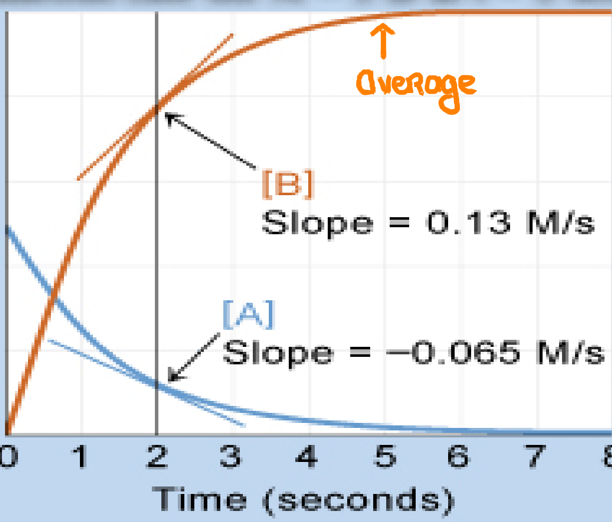
$$= 4.04\times10^{-5}\ M.min^{-1}$$

$$\text{Average Rate of Reaction} = \frac{\Delta[O_2]}{\Delta t}$$

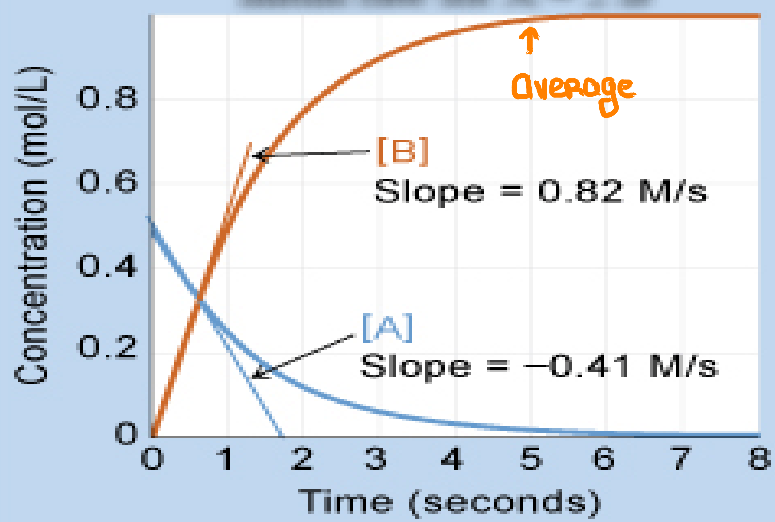
$$= 4.04\times10^{-5}\ M.min^{-1}$$

Instantaneous and Initial Rates

Instantaneous rate for A = 2 B at t = 2 seconds



Initial rate for A = 2 B



Initial Rate : Is where the Rate of Formation and the Rate of Disappearance is linear and thus becomes our region of choice.

14.3 Rate Laws

Concentration and Reaction Rate

It should come as no surprise that the Rate of Formation or Dissapearance is directly proportional to the concentration.

$$aA + bB = cC + dD$$

$$\text{Initial Reaction Rate} = k[A]^x[B]^y$$

x : is referred to as the order with respect to A.

y : is referred to as the order with respect to B.

$x + y$: is the overall order of the reaction.

k : is the rate constant.

Note 1: x and y are not necessarily equal to a and b. In fact x and y can only be determined experimentally

Note 2: Our discussion will initially be confined to orders, 0, 1 and 2.

For A:

Zero Order : Initial Rate $= k[A]^0$

First Order : Initial Rate $= k[A]^1$

Second Order : Initial Rate $= k[A]^2$

14.3 Rate Laws

Determining Rate Law Using the Method of Initial Rates

$NO + O_3 = NO_2 + O_2$

a) What is the rate law?

b) What is the rate constant?

Exp	$[NO]_o$, M	$[O_3]_o$, M	Initial Rate, Ms^{-1}
1	0.139	0.0436	0.527
2	0.139	0.0872	1.05
3	0.278	0.0436	1.05
4	0.278	0.0872	2.11

Exp 1: $Rate_1 = k[NO]_1^x[O_3]_1^y$

$0.527 = k(0.139)^x(0.0436)^y$

Exp 2: $Rate_2 = k[NO]_2^x[O_3]_2^y$

$1.05 = k(0.139)^x(0.0872)^y$

$$\frac{Rate_2}{Rate_1}: \quad \frac{1.05}{0.527} = \frac{k(0.139)^x(0.0872)^y}{k(0.139)^x(0.0436)^y}$$

$1.99 = 2^y$

$y = 1$

Exp 1: $0.527 = k(0.139)^x(0.0436)^y$

Exp 3: $Rate_3 = k[NO]_3^x[O_3]_3^y$

$1.05 = k(0.278)^x(0.0436)^y$

$$\frac{Rate_3}{Rate_1}: \quad \frac{1.05}{0.527} = \frac{k(0.278)^x(0.0436)^y}{k(0.139)^x(0.0436)^y}$$

$1.99 = 2^x$

$x = 1$

Initial Rate $= k[NO][O_3]$

Exp 1: $0.527 = k(0.139)(0.0436)$

$$k = \frac{0.527}{(0.139)(0.0436)} = 86.9\ M^{-1}s^{-1}$$