 

[TP] For the reaction 2 $NO_2(g) \rightarrow N_2O_4(g)$, what temperature range will result in the greatest amount of products?

25% 1. Very low $T$
25% 2. Very high $T$
25% 3. The amount will be the same at all $T$
25% 4. More information needed

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# Lecture 36 CH102 A1 (MWF 9:05 am)

Friday, April 28, 2017

- Complete: Effect of temperature on equilibrium

Begin ch18: How long does a reaction take to reach equilibrium?
- [...] versus time $\rightarrow K = k_{for} / k_{rev}$
- Definition of "rate"

Next lecture: Rate versus [...] from experiment. Making sense of rate versus [...]: Reaction mechanism. Making sense of rate constants: the Arrhenius relation, Effect of temperature on reaction rate: activation energy. Putting it all together: first Law, second Law, equilibrium, and kinetics.

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[TP] The reaction 2 $NO_2(g) \rightarrow N_2O_4(g)$ is exothermic. What temperature range will result in the greatest amount of products?

25% 1. Very low $T$
25% 2. Very high $T$
25% 3. The amount will be the same at all $T$
25% 4. More information needed

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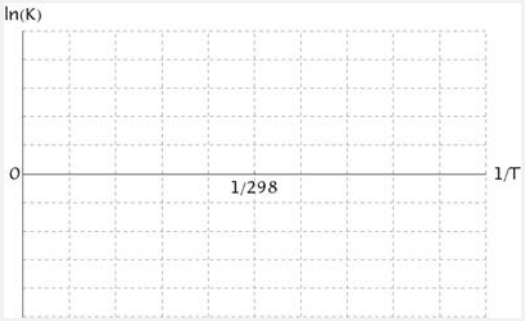
## Using $\ln(K) = -(\Delta H^o / R)(1/T) + \Delta S^o/R$

Sketch $\ln(K)$ versus $1/T$ for the exothermic reaction $2\ NO_2(g) \rightarrow N_2O_4(g)$

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## The goal of kinetics: How long?

What direction are we going?

$$-T\,\Delta S_{tot} = \Delta G = R\,T\ln(Q/K)$$

How far will we go?

$$-T\,\Delta S^\circ_{tot} = \Delta G^\circ = -R\,T\ln(K) = \Delta H^\circ - T\,\Delta S^\circ$$

How long to get there?

Chemical Kinetics!

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[Quiz] The exothermic reaction $2\ NO_2(g) \rightarrow N_2O_4(g)$ has the greatest amount of products at very low $T$. The reason for this is that ...

17% 1. $\Delta_r S^o < 0$
17% 2. heat is a "product" so removing heat (decreasing $T$) shifts equilibrium to products
17% 3. $\Delta_r H^o < 0$ and so $K$ increases as $T$ is decreased.
17% 4. 1, 2 and 3
17% 5. 1 and 3
17% 6. Something else

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## [...] versus time $\rightarrow K = k_{for}/k_{rev}$

Consider the reaction A ⇄ B. Assume initially [A] = 1 M but [B] = 0.
How do you expect [A] to change with time?

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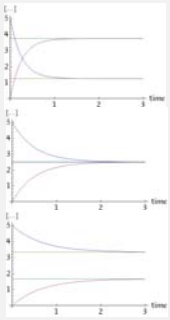
[TP] Consider three different chemical reactions,
reactants ⇄ products
For each reaction, initially [reactant] = 5 and [product] = 0.
Initially, which reaction consumes reactant fastest?

33% 1. Top
33% 2. Middle
33% 3. Bottom



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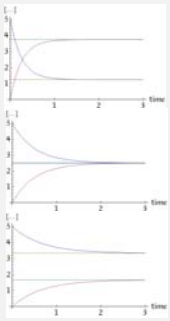
[TP] Consider three different chemical reactions,
reactants ⇄ products
For each reaction, initially [reactant] = 5 and [product] = 0.
Initially, which reaction consumes reactant slowest?

33% 1. Top
33% 2. Middle
33% 3. Bottom



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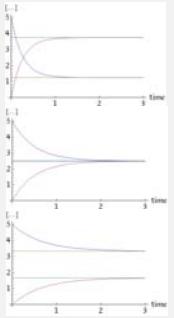
[Quiz] Consider three different chemical reactions,
reactants ⇄ products
For each reaction, initially [reactant] = 5 and [product] = 0,
and yet reactant is consumed at different rates.
This means that ...

33% 1. Rate depends only on [...]
33% 2. Rate is constant but different for each reaction.
33% 3. Rate depends on [...] and something else.



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## What does [...] versus time depend on?

The initial rate of a reaction like X → Y is ...

rate = $k_{for}$ [X]

The initial rate of its reverse reaction Y → X is ...

rate = $k_{rev}$ [Y]

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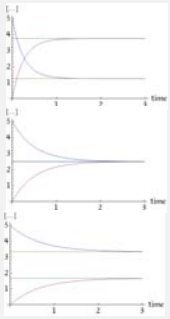
[TP] Consider three different chemical reactions,

reactants ⇄ products

For each reaction, eventually concentrations stop changing.
This means …

33% 1. Reactant is used up.
33% 2. Conversion of reactant to product stops.
33% 3. Something else.



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## What does [...] versus time depend on?

The initial rate of a reaction like $X \rightarrow Y$ is

$$\text{rate}_{for} = k_{for}[X]$$

The initial rate of its reverse reaction $Y \rightarrow X$ is

$$\text{rate}_{rev} = k_{rev}[Y]$$

Concentrations stop changing when the rate of the forward and rate of the reverse reaction balance each other …

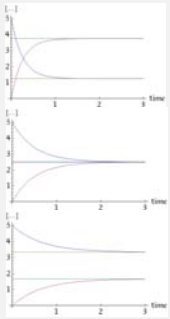
$$\text{rate}_{for} = \text{rate}_{rev}$$





[TP] For $X \rightarrow Y$, eventually concentrations stop changing.
This means that $rate_{for} = rate_{rev}$ and so that always …

20% 1. $k_{for} = k_{rev}$
20% 2. $[X] = [Y]$
20% 3. $k_{for}[X] = k_{rev}[Y]$
20% 4. $k_{for}[X]_e = k_{rev}[Y]_e$
20% 5. None of these



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## What does [...] versus time depend on?

Concentrations stop changing when the rate of the forward and rate of the reverse reaction balance each other …

$$\text{rate}_{for} = \text{rate}_{rev}$$

Rates match at equilibrium, so then concentrations have their equilibrium values, and so at equilibrium …

$$k_{for}[X]_e = k_{rev}[Y]_e$$

## What does [...] versus time depend on?

Rates match at equilibrium, so then concentrations have their equilibrium values, and so at equilibrium

$$k_{for}[X]_e = k_{rev}[Y]_e$$

Express the equilibrium constant for X → Y in terms of its equilibrium concentrations ...

$$K = [Y]_e / [X]_e$$



Definition of rate



## What does [...] versus time depend on?

Rates match at equilibrium, so then concentrations have their equilibrium values, and so at equilibrium

$$k_{for}[X]_e = k_{rev}[Y]_e$$

Express the equilibrium constant for X → Y in terms of its forward and reverse rate constants ...

$$K = k_{for} / k_{rev}$$



## Definition of rate

"rate" is defined as ...

change in concentration per unit time,
rate = Δ[...]/ Δtime

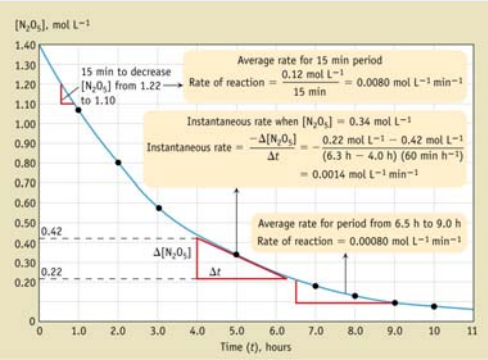
Think of the analogous quantity "speed" ...

change in distance per unit time,
speed = Δdistance / Δtime



$2\ N_2O_5(aq) \rightarrow 4\ NO_2(aq) + O_2(g)$








[TP] For the reaction

$3\ A + 4\ B \rightarrow 2\ D$

at a certain time, [B] is decreasing at 0.012 M/s.
What is the rate of the reaction?

33% 1. 0.012 M/s
33% 2. −0.012 M/s
33% 3. Something else

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## Definition of rate of reaction

$a\ A + b\ B \rightarrow c\ C \ldots$

rate ...

$= -(1/a)\ d[A] / dt$

$= -(1/b)\ d[B] / dt$

$= +(1/c)\ d[C] / dt$

Rate of reaction = always positive

Rate always has units M/s





[TP] In the chemical reaction

$2\ A + 3\ B \rightarrow C$

the initial rate of consumption of B is 0.15 M/s.
This means that the rate of the reaction is ...

20% 1. −0.15 M/s
20% 2. +0.15 M/s
20% 3. −0.10 M/s
20% 4. +0.050 M/s
20% 5. None of these

Response Counter

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