Dynamic Equilibrium

…going back and forth…

…at the same time…

…at the same rate…

What happens in a reversible reaction?

Consider: $aW + bX \rightleftharpoons cY + dZ$

When the rate of the forward reaction is equal to the rate of the reverse reaction, the system has reached **dynamic equilibrium**

$$Rate_{FWD} = Rate_{REV}$$

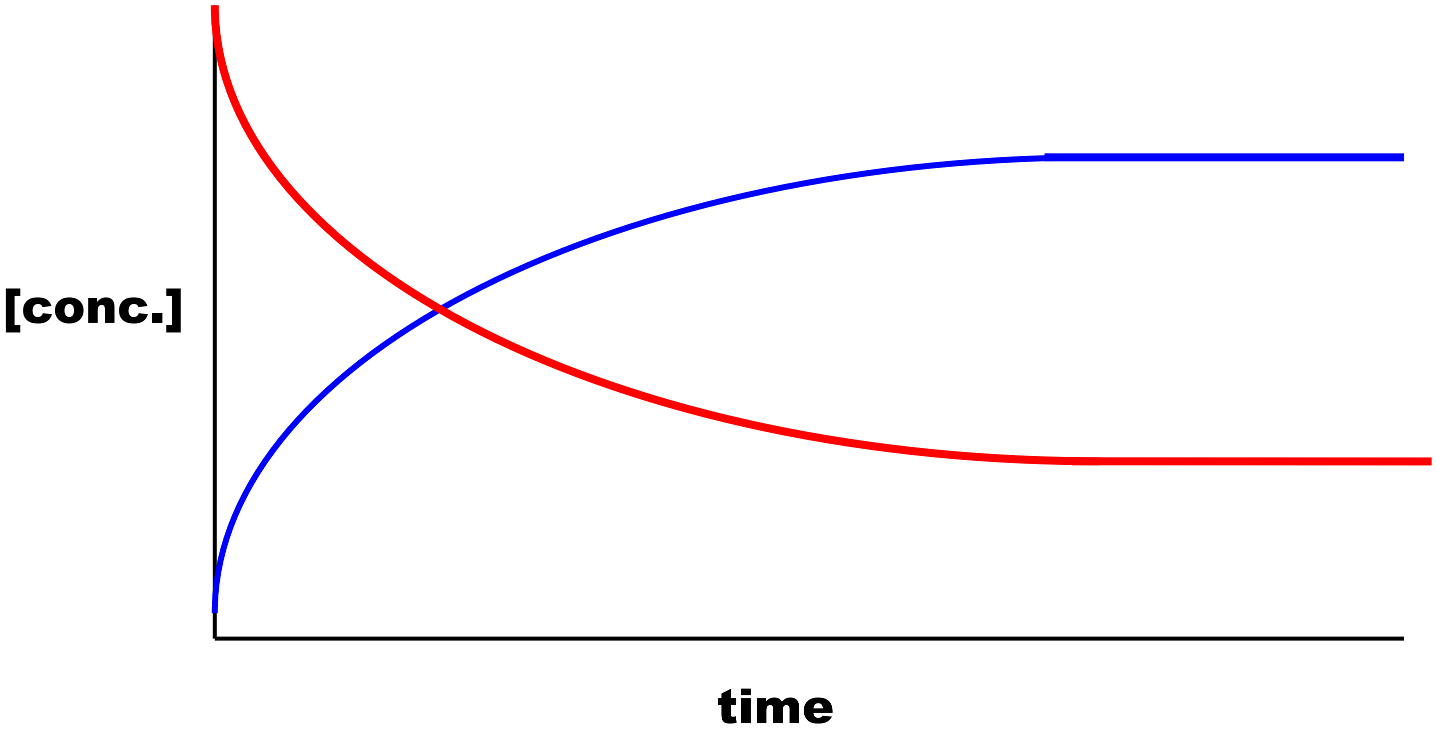
Dynamic Equilibrium

- The reaction does not stop!
  - Products are still being formed
  - Products are still combining to reform the reactants
- *BUT - Nothing* ***appears*** *to be happening*
  - Concentrations stop changing
  - Color changes cease, etc…

Dynamic Equilibrium

- The only thing ***equal*** about equilibrium are the rates of the forward and reverse reactions
- Some reactions reach equilibrium when there is mostly products, others when there is mostly reactants
- a 50/50 mix of both reactants and products is actually rare

Graphing R $\rightleftharpoons$ P



Red = reactants

Blue = products

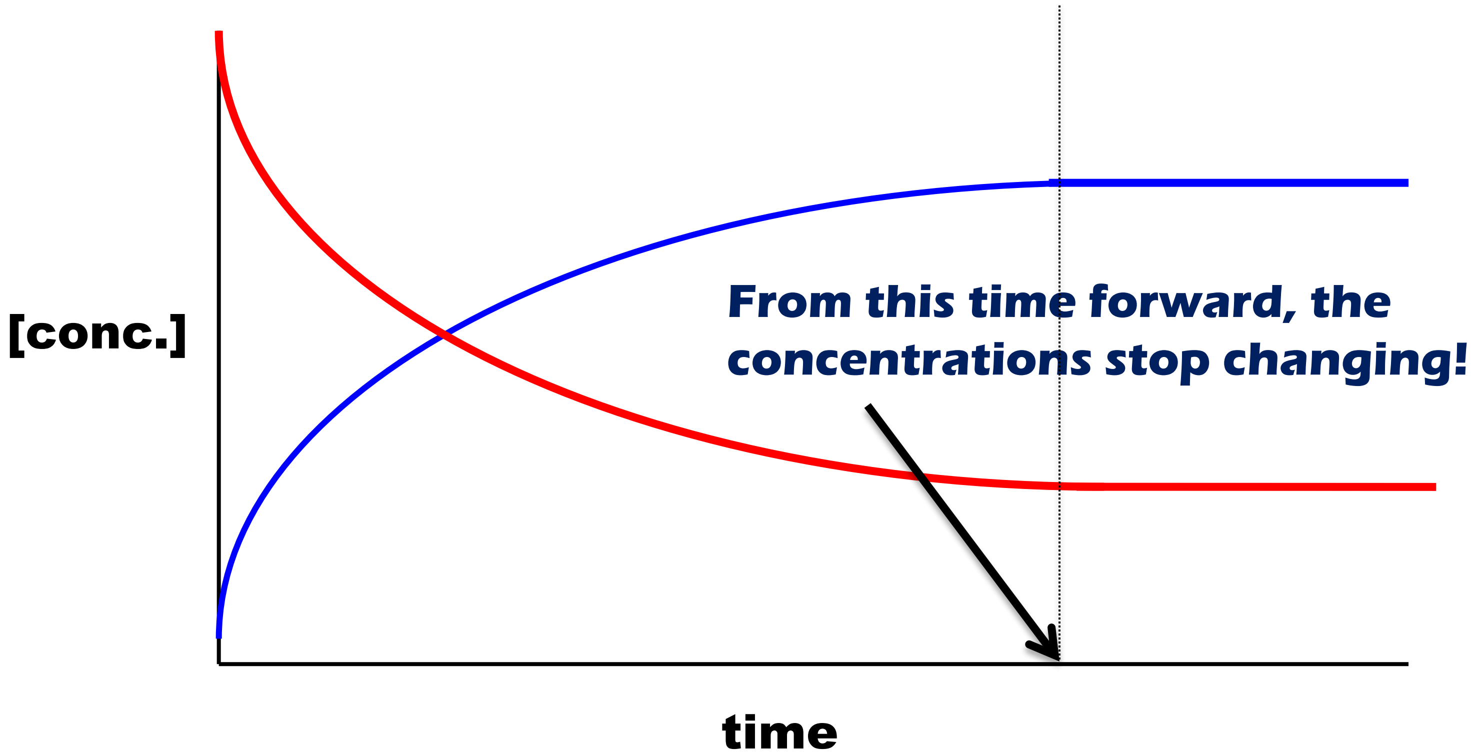
Dynamic Equilibrium

Quantitatively the situation for a reversible reaction can be expressed for <u>"what's in your dish" at that moment</u> using the reactant and product concentrations in the **mass-action expression**

For the reaction: aW + bX ⇌ cY + dZ

$$Q = \frac{[Y]^c [Z]^d}{[W]^a [X]^b}$$

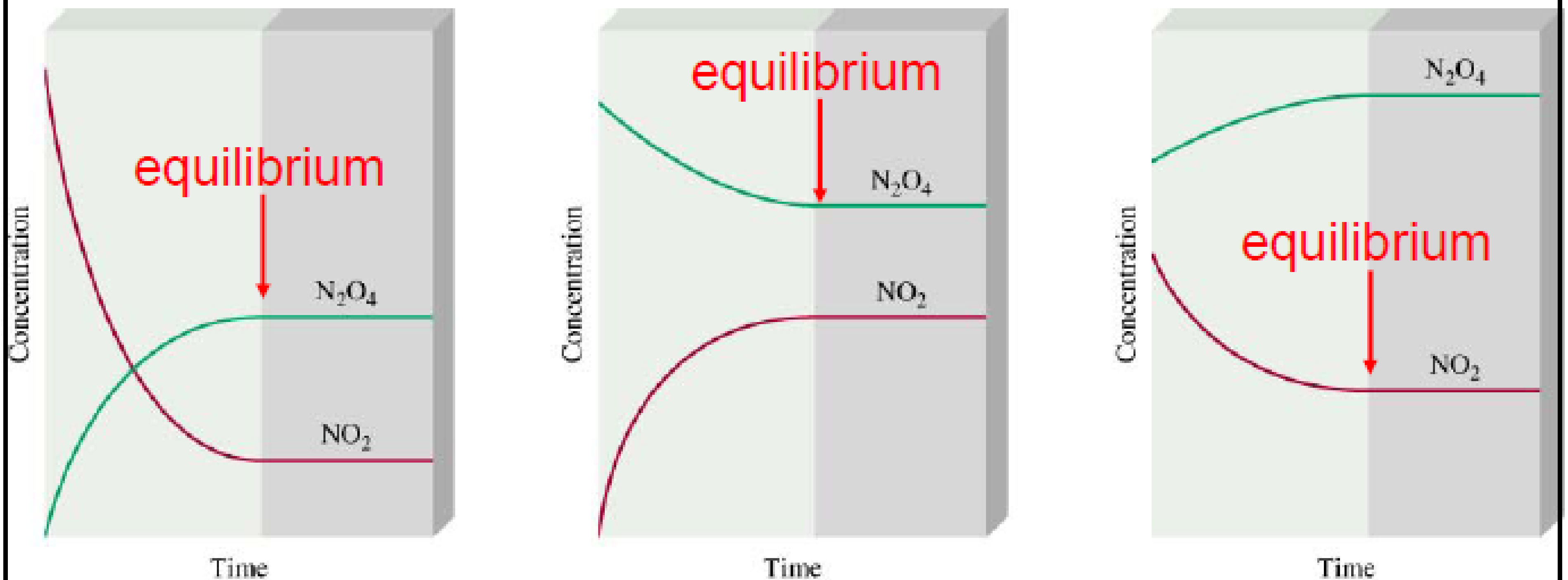
Graphing R ⇌ P



Red = reactants

Blue = products

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$



Start with NO_2 | Start with N_2O_4 | Start with NO_2 & N_2O_4

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

constant

Table 14.1 The NO_2–N_2O_4 System at 25°C

Initial Concentrations (*M*)		Equilibrium Concentrations (*M*)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

constant

Ratio of Concentrations at Equilibrium	
$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.0851	4.65×10^{-3}
0.102	4.66×10^{-3}
0.0967	4.60×10^{-3}
0.0880	4.60×10^{-3}
0.227	4.63×10^{-3}

Dynamic Equilibrium

Consider: aW + bX ⇌ cY + dZ

At equilibrium, because the **concentrations** stop changing, **Q** becomes constant and is replaced by **K** – the equilibrium constant.

$$K = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

Dynamic Equilibrium

$$K = \frac{[Y]^c [Z]^d}{[W]^a [X]^b}$$

Note :

1) [products] on top and [reactants] on bottom
2) Coefficients become exponents

Dynamic Equilibrium

$$K = \frac{[Y]^c [Z]^d}{[W]^a [X]^b}$$

K = the equilibrium constant

- K is unitless

K is temperature dependent

as long as the temperature is constant, so is K for a reversible reaction

Dynamic Equilibrium

Note : $aW_{(aq)}$ + $\mathbf{bX_{(s)}}$ ⇌ $cY_{(aq)}$ + $\mathbf{dZ_{(l)}}$

Pure substances (*solids*, *liquids*) do not have a changeable [molarity] and so drop out of the equilibrium expression

$$K = \frac{[Y]^c}{[W]^a}$$

What's in your dish at equilibrium?

Consider: $aW + bX \rightleftharpoons cY + dZ$

Which of the chemicals are "in your dish" at equilibrium?

There MUST be some of EACH of them to be at equilibrium

The size of K indicates what there is "more of" once equilibrium is reached.

-called the "*equilibrium position*"

K – the equilibrium constant

- The size of K tells us something about the <u>equilibrium position</u>
  - i.e. what are the concentrations of the reactants and products at equilibrium?

- Because the products are in the numerator, *the larger the K value*, the *more products* that are present at equilibrium and the *fewer reactants* that remain.

K – the equilibrium constant

General rule: $K < 10^{-4}$

- the equilibrium mixture is mostly reactants
- The reaction does not “proceed” very far forward in order to reach equilibrium
- The smaller K is, the fewer products formed

K – the equilibrium constant

General rule: $10^{-4} < K < 10^{4}$

- the equilibrium mixture has significant amounts of reactants and products
  - Not necessarily a “50/50” mix, but reasonably similar amounts of reactants and products

K – the equilibrium constant

General rule: $K > 10^4$

- the equilibrium mixture is mostly products
- The larger K gets, the more the forward reaction “goes to completion”

Dynamic Equilibrium

…going back and forth…

…at the same time…

…at the same rate…