HOW TO TELL IF A REACTION IS AT EQUILIBRIUM?

- Use REACTION QUOTIENT (Q)

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Reaction quotient = equilbrium expression using NON-EQUILIBRIUM concentrations.

- If Q = Kc, then reaction is at equiilibrium.
- If Q < Kc, then reaction is NOT at equilibrium and proceeds to the right, forming more products.
- If Q > Kc, then reaction is NOT at equilibrium and proceeds to the left, forming more reactants.

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g) \;;\; K_c = 3.07 \times 10^{-4}$$

$[NOBr] = 0.0720\ \underline{M}$, $[NO] = 0.0162\ \underline{M}$, $[Br_2] = 0.0123\ \underline{M}$

Is mix at equilibrium? If not, which direction will reaction proceed?

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = 3.07 \times 10^{-4}$$

$$Q = \frac{(0.0162)^2(0.0123)}{(0.0720)^2} = 6.33 \times 10^{-4}$$

$$6.33 \times 10^{-4} > 3.07 \times 10^{-4}$$

$$Q > K_c$$

Since Q > Kc, the reaction is NOT at equilibrium and will proceed to the LEFT, forming more NOBr at the expense of the two products.

MODIFYING EQUILIBRIUM

- Remember, at equilibrium the reaction has not actually STOPPED. Both forward and reverse processes are still happening - just at the same rate so there's no overall concetration change.

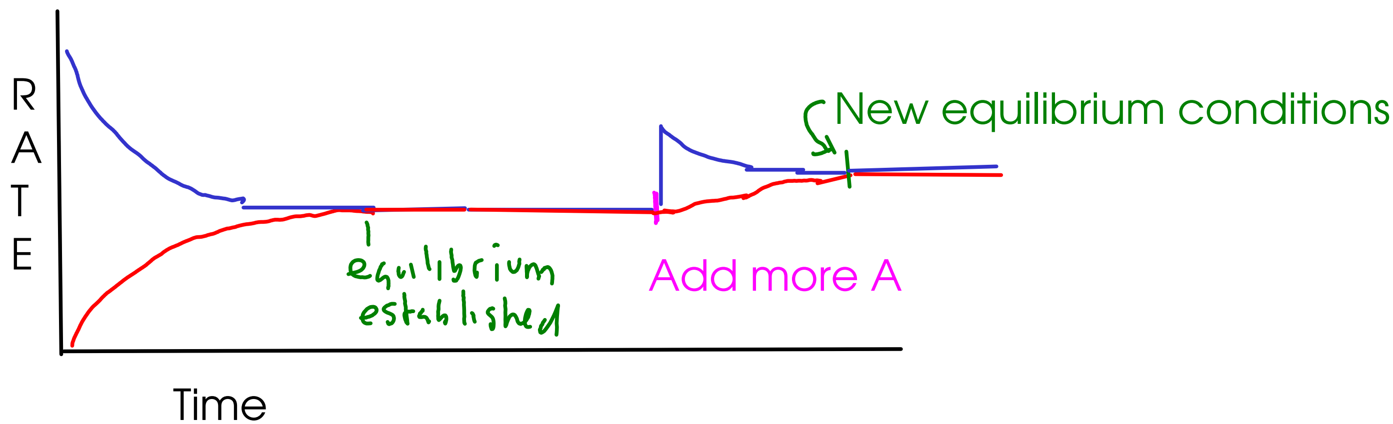
- If you do something to the reaction mixture that changes the rates of the forward or the reverse reaction (or sometimes BOTH), the mixture will no longer be at equilibrium.

Simplest case is to add or remove a substance, changing its concentration.

$$A + B \rightleftharpoons C + D$$

$$Rate_{,fwd} = k_f[A][B]$$

$$Rate_{,rev} = k_r[C][D]$$



- After adding A, the rate of the forward reaction increased. As more C and D were produced by the (faster) forward reaction, the forward reaction and reverse reaction came back to equilibrium, but at a new set of conditions.

- The addition of A caused our equilibrium to SHIFT towards the RIGHT - consuming some of the extra A to form more products (C and D).

99 - LE CHATELEIR'S PRINCIPLE states that if an equilbrium is disturbed, it will SHIFT in such a way as to counteract the disturbance and restore equilibrium.

For concentrations:

* Increasing the concentration of a REACTANT will cause the equilibrium to shift to the RIGHT, making more products.
* Decreasing the concentration of a REACTANT will cause the equilibrium to shift to the LEFT, making more reactants.

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* Increasing the concentration of a PRODUCT will cause the equilibrium to shift to the LEFT, making more reactants.
* Decreasing the concentration of a PRODUCT will cause the equilibrium to shift to the RIGHT, making more products.

This one can be used to DRIVE a reaction to produce product, even if the Kc value is NOT favorable.

- TEMPERATURE can also cause equilibrium shifts. These temperature-caused shifts can be easily illustrated with Le Chaleleir's principle.

endothermic reaction:

$$A + B + heat \rightleftarrows C + D$$

- Heat, here, is represented as if it's a reactant!
- If temperature INCREASES, the equilibrium shifts to the RIGHT, making more products.
- If temperature DECREASES, the equilibrium shifts to the LEFT, making more reactants.

exothermic reactions:

$$A + B \rightleftarrows C + D + heat$$

- In the exothermic case, heat is a product!
- If temperature INCREASES, then the equilibrium shifts to the LEFT, making more reactants.
- If temperature DECREASES, then the equilibrium shifts to the RIGHT, making more products.

- Optimization:
* For ENDOTHERMIC reactions, run as hot as possible. You make MORE products FASTER.
* For EXOTHERMIC reactions, you want to run the reaction cooler (for more products), but not so cool as to make the reaction slow!