- 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:



¥

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



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

 $\star$  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 => 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:

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

- 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!

103

## EQUILIBRIUM CALCULATIONS

- We're often interested in figuring out what happens at equilibrium BEFORE we do an experiment!

- What's the problem? Initially, we know only ... INITIAL concentrations. Since these are NOT equilibrium concentrations, we cannot simply plug them into an equilbrium expression and solve.

- So how do we find out what the concentrations are at equilibrium if we initially know NONE of them?

- To solve an equilibrium problem, write out the equilibrium constant expression. Then, try to RELATE ALL THE EQUILIBRIUM CONCENTRATIONS TO ONE ANOTHER using the chemical equation.

- It helps to assign a variable based on one of the substances in the reaction, then write the concentrations of the other substances based on that variable. How to do this? Take a look at the following examples...

EXAMPLE: Calculate the grams per liter of silver(i) chloride (AgCl) in a solution that is at equilibrium with solid AgCl.

Ag(1 (s) 
$$\rightleftharpoons A_{g}^{+}(a_{4}) + CI^{-}(a_{4})$$
;  $K_{c} = 1.8 \times 10^{-10}$   
 $K_{c} = [A_{g}^{+}][CI^{-}] = 1.8 \times 10^{-10}$   
Assign a variable: 'x' = change in concentration of  
silver ion  
 $A_{g}CI$   
 $A_{g}CI$   
 $A_{g}^{+}$   $O$   $+ X$   $X$   
 $CI^{-}$   $O$   $+ X$   $X$   
 $[A_{g}^{+}][CI^{-}] = 1.8 \times 10^{-10}$  Substitute the variable 'x'  
into the equilibrium expression,  
 $(X) (X) = 1.8 \times 10^{-10}$  then we can solve!  
 $X^{2} = 1.8 \times 10^{-10}$  then we can solve!  
 $X^{2} = 1.8 \times 10^{-10}$  Equivalent to  
 $1.9 \text{ ppm}$   
 $(\text{parts per million, or mg/L})$   
The concentration of dissolved AgCI also equals 'x!  
 $[A_{g}CI]_{dissolved} = [-34 \times 10^{-5} \frac{\text{mol}}{L} \times [\frac{142.3219}{mol} = 0.0019 \text{ g}]_{L}$