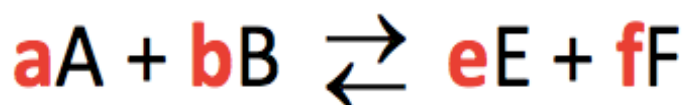


Equilibrium Expressions & Equilibrium Constant

- when a system is at equilibrium, the [reactants] and [products] remains constant
- it is found that the **ratio of [products] to [reactants] is constant at a particular temperature**
- even though the **[reactants] and [products] may change** as a result of a shift in equilibrium, the **ratio remains constant**

For an equilibrium equation with the general form:



experimentally, it is found that:

$$K_{eq} = \frac{[E]^e [F]^f}{[A]^a [B]^b} = \text{a constant}$$

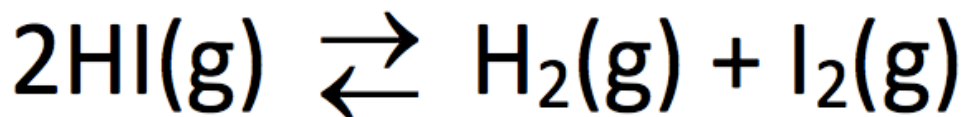
- this expression of concentrations is called the EQUILIBRIUM EXPRESSION and its numerical value K_{eq} is called the EQUILIBRIUM CONSTANT

- the equilibrium constant is the ratio of product concentration terms to reactant concentration terms

$$K_{\text{eq}} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$

- in the K_{eq} expression, the **exponent** to which each of the concentrations is raised is equal to its **coefficient** in the balanced reaction
- the units for K_{eq} vary depending on the number of concentration terms in the numerator as compared to the denominator
- these units do not have any particular importance so **units** for K_{eq} are generally **not shown**

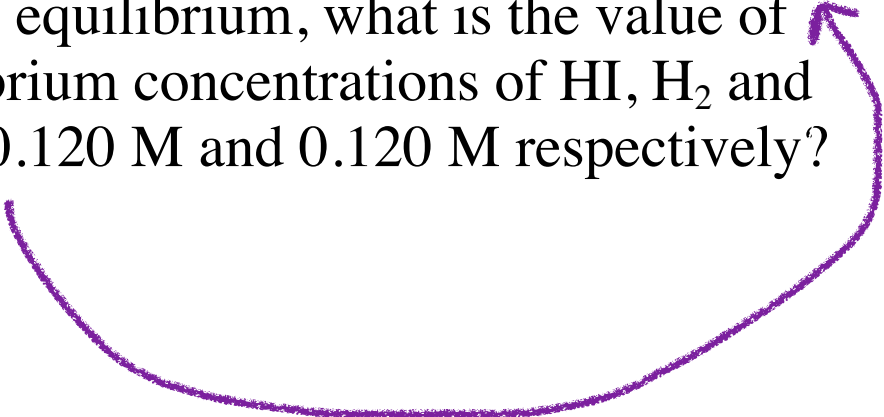
Write the K_{eq} expression for the following equilibrium:



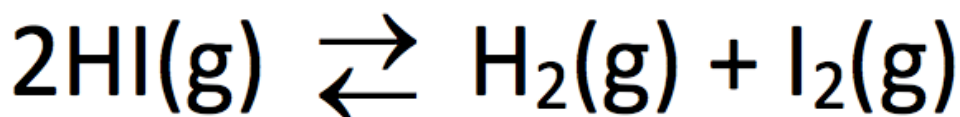
$$K_{eq} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

$$K_{eq} = \frac{(0.120)(0.120)}{(0.250)^2} = 0.230$$

Given the above equilibrium, what is the value of K_{eq} if the equilibrium concentrations of HI, H_2 and I_2 are 0.250 M, 0.120 M and 0.120 M respectively?



Consider the following equilibrium:



If the value of $K_{\text{eq}} = 0.230$ at a particular temperature, what is the equilibrium $[\text{HI}]$ if the $[\text{H}_2] = 0.075 \text{ M}$ and $[\text{I}_2] = 0.320 \text{ M}$?

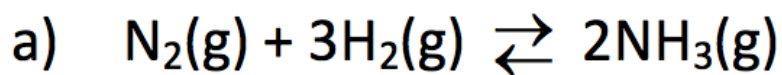
$$K_{\text{eq}} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$
$$[\text{HI}]^2 = \frac{[\text{H}_2][\text{I}_2]}{K_{\text{eq}}}$$
$$= \frac{(0.075)(0.320)}{0.230}$$

$$[\text{HI}] = 0.32 \text{ M}$$

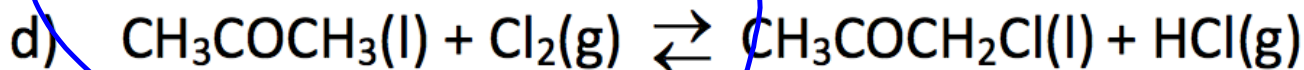
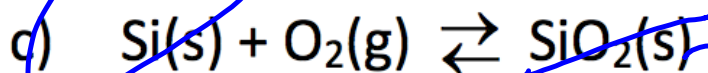
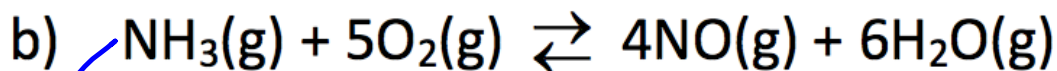
The following substances are not included in the equilibrium expression because their concentrations are essentially constant:

1. **solids** - cannot be compressed and hence their concentrations cannot be changed; concentration determined by **density** of the solid
2. **pure liquids** - cannot be compressed and hence their concentrations cannot be changed; however . . . if there are 2 or more liquids, they may mix and are no longer pure and the concentrations may change due to dilution; **liquids are only pure if there is only one liquid present** in the equilibrium expression

Write the K_{eq} expression for the following equilibrium:



$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$



$$K_{eq} = \frac{[NO]^4 [H_2O]^6}{[NH_3][O_2]^5}$$

$$K_{eq} = \frac{1}{[O_2]}$$

The equilibrium constant, K_{eq} , is a ratio of $\frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$, so numerically, if K_{eq} is large the products are favoured and if K_{eq} is small the reactants are favoured.

$$\text{Large } K_{eq} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$

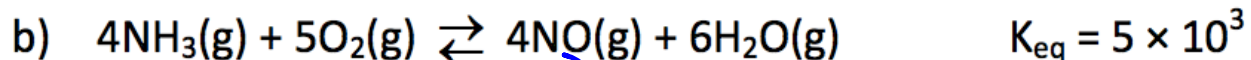
$$\text{Small } K_{eq} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$

$K_{eq} > 1$ then products GREATER THAN reactants

$K_{eq} < 1$ then products LESS THAN reactants

$K_{eq} = 1$ products EQUAL reactants

Predict the relative amount of reactants & products at equilibrium:



R favoured

P favoured

Dependence of K_{eq} on Temperature

- K_{eq} remains constant when concentration, pressure or surface area change
- however . . . changing the temperature affects the value of K_{eq}

Why???

- changing concentration, pressure or surface area **changes the number of reacting molecules per litre**
 - > the equilibrium counteracts these stresses and **shifts to re-establish a new equilibrium**
 - > the ratio of [PRODUCT]/[REACTANT] and the **value of K_{eq} remains the same**
- changing temperature causes a shift in the equilibrium, but the **number of reacting molecules does not change**
 - > therefore the ratio of [PRODUCT]/[REACTANT] changes and the **value of K_{eq} changes**

Varying temperature is the only factor that changes the value of K_{eq} .

Consider the reaction:



- for an **exothermic** reaction, an **increase in temperature** will cause a **shift to the left**
- the [PRODUCTS] decrease while the [REACTANTS] increase . . . and since

$$K_{\text{eq}} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$

the value of K_{eq} decreases

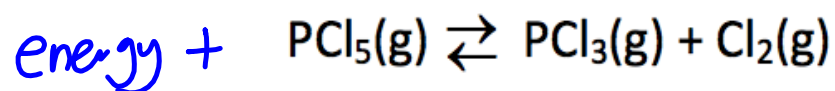
- for an **endothermic** reaction, an **increase in temperature** will cause a **shift to the right**
- the [PRODUCTS] increase while the [REACTANTS] decrease and **the value of K_{eq} would increase**



K_{eq} **increases** when the temperature of an **endothermic** reaction is increased

K_{eq} **decreases** when the temperature of an **exothermic** reaction is increased

Consider the following reaction:



Is the above reaction endothermic or exothermic if K_{eq} is 2.24 at 227°C and 33.3 at 487°C ?

$$\begin{array}{l} K_{\text{eq}} = 2.24 @ 227^\circ\text{C} \\ \uparrow \\ 33.3 @ 487^\circ\text{C} \end{array}$$