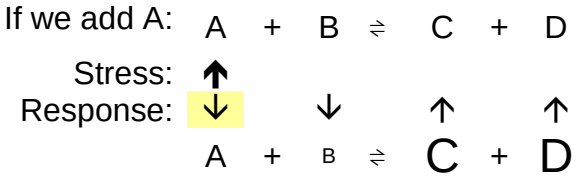
Le Châtelier's Principle

Le Châtelier's Principle states that if a system at equilibrium is disturbed, the system will change to relieve or diminish the effect of the disturbance.

Some types of disturbances are:

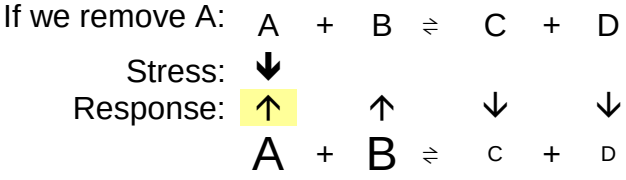
[1] **Concentration Changes**: The position of equilibrium shifts away from a substance that is being added, or toward a substance that is being removed. This is a two-step process: first there is a stress to the chemical system, and then the system responds to the stress.

If we add A:



…the equilibrium shifts to the right.

If we remove A:



…the equilibrium shifts to the left.

[2] **Temperature Changes**: If heat is added, the system will undergo a shift to use up the heat energy. You can treat heat as one of the "products" or "reactants" of the formula.

[3] **Pressure/Volume Changes**: [a] Increased pressure (decreased volume) is relieved by a shift to the side having fewer gas molecules. [b] Decreased pressure (increased volume) is relieved by a shift to the side with more gas molecules. [c] If a chemical system has no gases, pressure changes will have virtually no effect on the position of equilibrium.

These are not disturbances:

[1] Addition of Inert (Non-reacting) Gas: It will have no effect on the equilibrium, provided there isn't also a pressure change in the reacting gases to go with it.

[2] Addition of Catalyst: A catalyst will only make the reaction go faster. It will not change where the equilibrium is.

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EXERCISES

A. Consider the reaction:

$$N_{2\,(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)} + \text{heat}$$

Determine the effects of the following stresses on the equilibrium. Will the equilibrium shift to the left, to the right, or not at all:

1) increase $[N_2]$
2) decrease $[NH_3]$
3) decrease $[H_2]$
4) increase temperature
5) decrease the total pressure
6) decrease the volume
7) add helium at constant volume so that total pressure is increased
8) add helium with total pressure constant

B. Consider the reaction:

$$CH_{4\,(g)} + C\ell_{2\,(g)} \rightleftharpoons CH_3C\ell_{\,(g)} + HC\ell_{\,(g)} + 110\ \text{kJ}$$

Determine the effects of the following stresses on the equilibrium. Will the equilibrium shift to the left, to the right, or not at all:

1) increase $[CH_4]$
2) decrease $[CH_3C\ell]$
3) decrease temperature
4) decrease total pressure
5) add a catalyst
6) spray water to form hydrochloric acid

C. Consider the solution of barium sulphate, which has low solubility:

$$BaSO_{4\,(s)} \rightleftharpoons Ba^{2+}_{\,(aq)} + SO_4^{2-}{}_{(aq)}$$

Determine the effects of the following stresses on the equilibrium. Will the equilibrium shift to the left, to the right, or not at all:

1) add Ba^{2+} ions
2) remove SO_4^{2-}
3) add $BaSO_{4\,(s)}$
4) increase temperature

SOLUTIONS

A. (1) right (2) right (3) left (4) left (5) left (6) right (7) no effect: the partial pressures of the gases in the reaction will stay the same. (8) left, since the partial pressures must be decreasing (and volume must be increasing)

B. (1) right (2) right (3) right (4) no effect, since both sides have the same numbers of molecules (5) no effect (6) right

C. (1) left (2) right (3) no effect, since the solid is already in excess (4) right, more solids dissolve at higher temperatures

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