Factors That Affect Chemical Equilibrium

concentration

pressure

volume

temperature

catalysts have no effect on position of equilibrium

Le Chatelier's Principle

If an external stress is applied to a system at equilibrium, the system adjusts itself in such a way that the stress is partially offset.

Changes in Concentrations

(Le Chatelier's Principle)

Increase the yield of product by

- **increasing concentration of reactant**
- **removing the product from the equilibrium**

Example

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

at equilibrium:

0.683 *M* 8.80 *M* 1.05 *M*

Increase the concentration NH_3 to 3.65 *M*

(Le Chatelier's Principle)

the position of equilibrium shifts to the left

Example

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$

at e

0.683 ... *M*

Increase ... 3.65 *M*

Q is greater than K; the position of equilibrium shifts to the left

$$Q = \frac{[NH_3]^2}{[N_2]\ [H_2]^3} = \frac{(3.65)^2}{(.683)\ (8.80)^3}$$

$$Q = 0.0286$$

What about

$$K_{eq} = [Ba^{2+}][SO_4^{2-}]$$

$$BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq)$$

Add Ba^{2+} (aq)
- $[SO_4^{2-}]$ decreases
- $BaSO_4$ (s) increases

Add SO_4^{2-} (aq)
- $[Ba^{2+}]$ decreases
- $BaSO_4$ (s) increases

Add $BaSO_4$ (s) no change

Changes in Volume and Pressure

Little effect on reactions in solution

Effect can be large on reactions in the gas phase

- **Increase in pressure shifts the equilibrium to the side with the fewer moles of gas**

Practice Exercise

How does the position of equilibrium change as the pressure is increased?

$$2PbS(s) + 5O_2(g) \rightleftharpoons 2PbO(s) + 2SO_4(g)$$

five moles of gaseous reactant → ***two moles of gaseous product***

Increase in pressure causes an increase in products at the expense of reactants

Example

How does the position of equilibrium change as the pressure is increased?

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

one mole of gaseous reactant

two moles of gaseous product

Increase in pressure causes some products to revert to reactants

Practice Exercise

How does the position of equilibrium change as the pressure is increased?

$$H_2\,(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO\,(g)$$

two moles of gaseous reactant

two moles of gaseous product

Increase in pressure leaves the position of equilibrium unchanged

Changes in Temperature

Changes the value of the equilibrium constant

- **A temperature increase favors an endothermic reaction, and a temperature decrease favors an exothermic reaction**

Endothermic reaction

Shifts in the equilibrium position for the reaction:

$$58\ \text{kJ} + N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

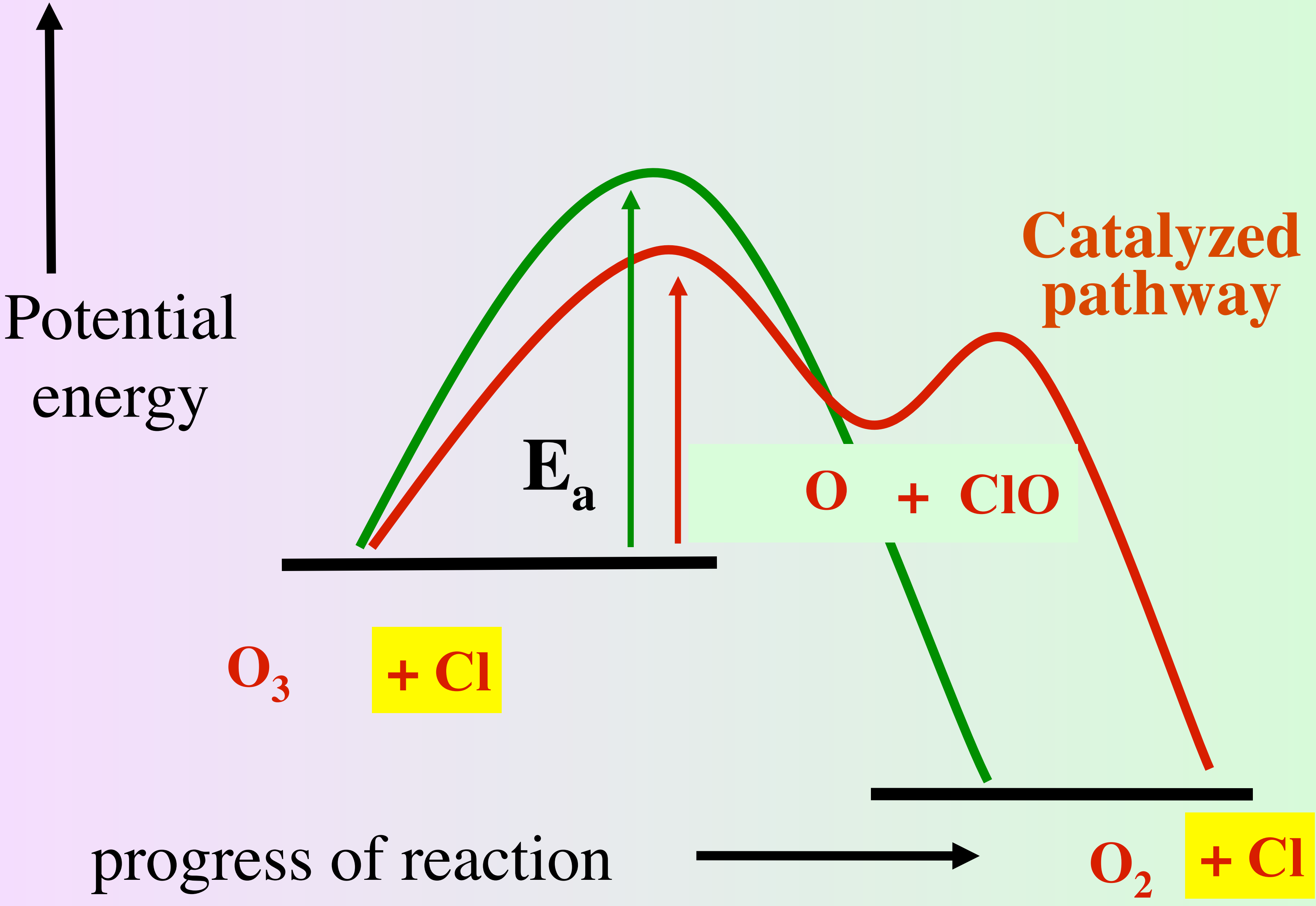
Increase temperature: $\longrightarrow$

The Effect of a Catalyst

Increases rate, but has no effect on position of equilibrium

- **effect of forward and reverse processes is the same**

- **a catalyst increases both the rate of both the forward and reverse reactions**


Potential
energy
Catalyzed
pathway
E$_a$
O + ClO
O_3 + Cl
progress of reaction
O_2 + Cl

The Haber Process

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) + 92.6\text{ kJ}$$

Maximize the yield of ammonia by:

carrying out the reaction at high pressure

$$K_p = \frac{P^2_{NH3}}{P_{N2}\;P^3_{H2}}$$

The Haber Process

$$1N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92.6 \text{ kJ}$$

four moles of gaseous reactant

two moles of gaseous product

Maximize the yield of ammonia by:

carrying out the reaction at high pressure

$$K_p = \frac{P^2_{NH3}}{P_{N2} \; P^3_{H2}}$$

The Haber Process

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g) + 92.6\ kJ$$

$\Delta H^o = -92.6$ kJ/mol

Maximize the yield of ammonia by:

carrying out the reaction at low temperatures

The Haber Process

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) + 92.6\text{ kJ}$$

In practice the reaction is carried out at 500 °C because the rate is too slow at lower temperatures