Statistical Molecular Thermodynamics

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Video 12.3

Noxious Equilibrium Example

Gaseous Equilibrium Example

Consider the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

The equilibrium constant is $K_P(T) = \left(\dfrac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}}\right)_{eq}$

If at the start you have

one mole of $PCl_5(g)$
zero moles of $PCl_3(g)$
zero moles of $Cl_2(g)$

Reaction occurs to an extent ξ

then later you have

$(1-\xi)$ moles of $PCl_5(g)$
ξ moles of $PCl_3(g)$
ξ moles of $Cl_2(g)$

$\text{total} = (1-\xi) + 2\xi = 1+\xi$

If ξ_{eq} is the extent at equilibrium,

$$P_{PCl_3(g)} = P_{Cl_2(g)} = \frac{\xi_{eq} P}{1+\xi_{eq}}$$

$$P_{PCl_5(g)} = \frac{(1-\xi_{eq})P}{1+\xi_{eq}}$$

partial pressures

P = *total* pressure

$$K_P(T) = \frac{\xi_{eq}^2}{1-\xi_{eq}^2} P$$

K_P Is a Function Only of T

$$K_P(T) = \frac{\xi_{eq}^2}{1-\xi_{eq}^2} P$$

So this *looks* like K_P depends not only on T, but also on the total pressure, P…

But we've already derived that K_P depends only on T (cf. video 12.2):

$$K_P(T) = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{eq}$$

Evidently, since K_P is a constant at a fixed temperature, if one has a change in the total pressure, P, then there must be some concomitant change in ξ_{eq} to maintain the same value of K_P.

Self-assessment

What is the name of the principle that states that the position of an equilibrium will shift in response to a change in the reaction conditions, e.g., a change in pressure?

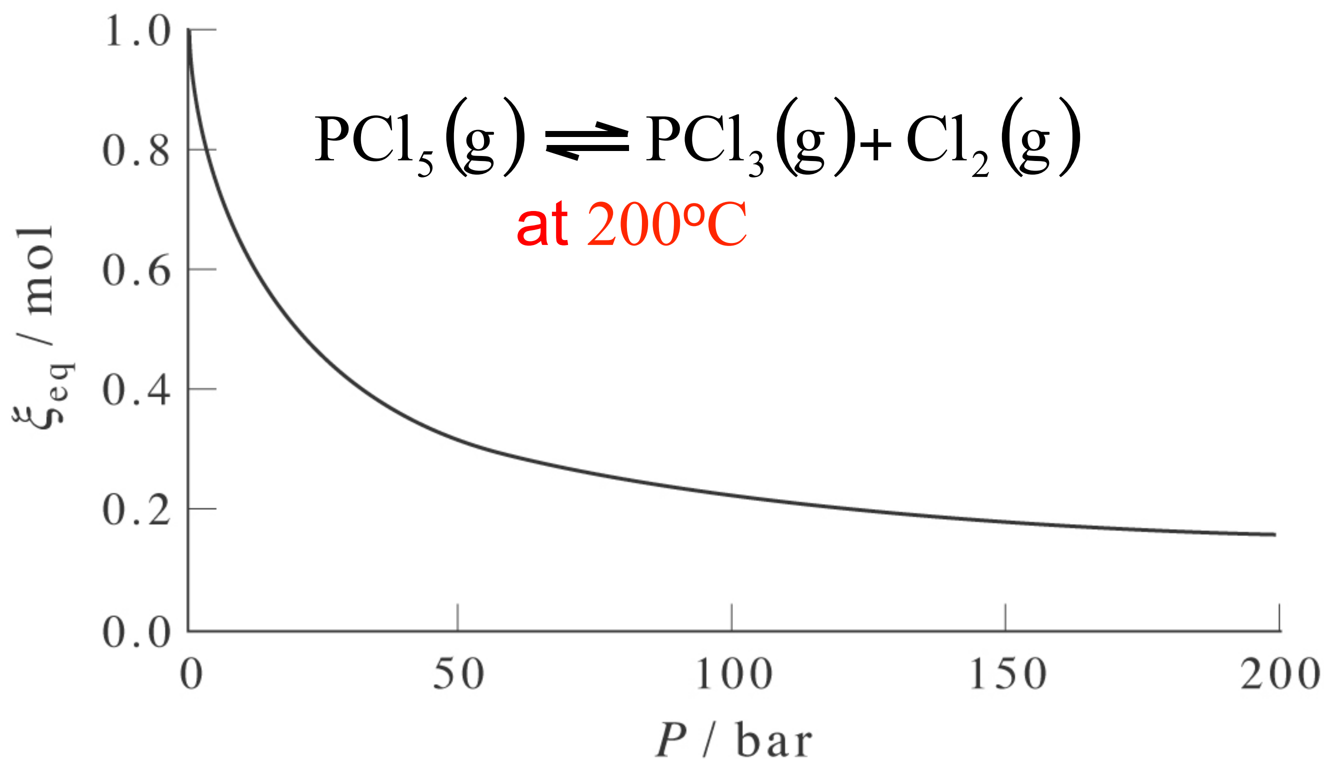
Self-assessment Explained

What is the name of the principle that states that the position of an equilibrium will shift in response to a change in the reaction conditions, e.g., a change in pressure?

Le Châtelier's Principle

Shift in Equilibrium with Pressure

Having a change in pressure change the position of equilibrium is an example of ***Le Châtelier's principle***. Following a change in conditions that displaces equilibrium, a reaction will adjust to the new equilibrium state.



A constant at constant T

$$K_P(T) = \frac{\xi_{eq}^2}{1-\xi_{eq}^2} P$$

As P increases ξ_{eq} must decrease

Next: Determining Equilibrium Constants