**Gaseous Equilibrium Example**

Consider the reaction: \( \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \)

The equilibrium constant is \( K_P(T) = \left( \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}} \right)_{eq} \)

If at the start you have
- one mole of \( \text{PCl}_5(g) \)
- zero moles of \( \text{PCl}_3(g) \)
- zero moles of \( \text{Cl}_2(g) \)

then later you have
- \((1 - \xi)\) moles of \( \text{PCl}_5(g) \)
- \(\xi\) moles of \( \text{PCl}_3(g) \)
- \(\xi\) moles of \( \text{Cl}_2(g) \)

If \( \xi_{eq} \) is the extent at equilibrium,

\[
\begin{align*}
P_{\text{PCl}_3(g)} &= P_{\text{Cl}_2(g)} = \frac{\xi_{eq} P}{1 + \xi_{eq}} \\
P_{\text{PCl}_5(g)} &= \frac{(1 - \xi_{eq}) P}{1 + \xi_{eq}} \\
K_P(T) &= \left( \frac{\xi_{eq}^2}{1 - \xi_{eq}^2} \right) P
\end{align*}
\]

Reaction occurs to an extent \( \xi \)
**$K_P$ 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):

$K_P(T) = \left( \frac{P_Y^V P_Z^V}{P_A^V P_B^V} \right)_{eq}$

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 $\xi_{eq}$ 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.

\[ \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \]

at 200°F

A constant at constant \( T \)

\[ K_p(T) = \frac{\xi_{eq}^2}{1 - \xi_{eq}^2} P \]

As \( P \) increases, \( \xi_{eq} \) must decrease.
\[ dU = \delta q + \delta w \]

Next: Determining Equilibrium Constants