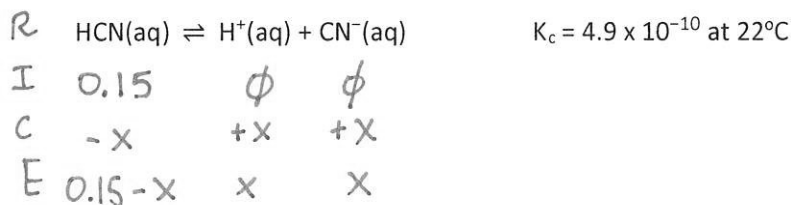


RICE Approximations: Simplifying the Math

Sometimes RICE math can get complicated. Let's try an example!

1. What are the equilibrium concentrations of each chemical species in a 0.15 M solution of HCN at 22°C?



$$K_c = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{x^2}{0.15-x} = 4.9 \times 10^{-10}$$

$$x^2 = (0.15-x)4.9 \times 10^{-10}$$

$$x^2 = 7.35 \times 10^{-11} - 4.9 \times 10^{-10}x$$

$$\Rightarrow x^2 + 4.9 \times 10^{-10}x - 7.35 \times 10^{-11} = 0 \quad \left. \begin{array}{l} \text{Need the quadratic} \\ \text{eq'n to solve!} \end{array} \right\}$$

$$a = 1$$

$$b = 4.9 \times 10^{-10}$$

$$c = -7.35 \times 10^{-11}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-4.9 \times 10^{-10} \pm \sqrt{(4.9 \times 10^{-10})^2 + 4(1)(+7.35 \times 10^{-11})}}{2(1)} \Rightarrow x = \pm 8.57 \times 10^{-6} \text{ but...}$$

x can't be negative!

$$\Rightarrow x = 8.57 \times 10^{-6} \text{ M}$$

$$\Rightarrow [\text{HCN}]_{\text{eq}} = 0.15 - 8.57 \times 10^{-6} \text{ (b/c it's a concentration)}$$

$$[\text{H}^+]_{\text{eq}} = [\text{CN}^-]_{\text{eq}} = 8.6 \times 10^{-6} \text{ M}$$

Check:

$$K_c = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{(8.6 \times 10^{-6})^2}{0.15} = 4.9 \times 10^{-10} \quad \checkmark$$

But wait! You should never actually have to use the quadratic equation on the AP Chemistry test. (Mastering Chem, however, is a different story... ;D)

But how can we solve a problem of this type without doing piles of math?

(from previous page)
 $[HCN]_{eq} = 0.15 - 0.0000086$
 $\approx 0.15 M$ negligible!

The "X is Negligible" Approximation

↳ aka too tiny to affect

addition or subtraction

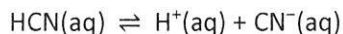
There are two common problem types where this approximation is valid:

- Very small K values (where $K < 10^{-5}$ or Initial Molarity $\geq 1000 \times K$) when starting from reactants: in this case, barely any products will be made. *want $K \ll [reactants]_{initial}$*
- Very large K values (where $K > 10^5$) when starting from products: in this case, barely any reactants will be made. *want $K \gg [products]_{initial}$*

Note: The assumption about x being negligible only works when x is less than 5% of the initial concentration, so you can check the validity of your assumption after solving for x!

Let's try that first problem again, this time using the "x is negligible" approximation.

- What are the equilibrium concentrations of each chemical species in a 0.15 M solution of HCN at 22°C?



0.15	ϕ	ϕ
$-x$	$+x$	$+x$
<hr style="width: 100%;"/>	x	x
0.15-x		

$$K_c = 4.9 \times 10^{-10} \text{ at } 22^\circ\text{C}$$

check assumption:
 $\frac{8.6E-6}{0.15} \times 100 = 0.0057\%$
 ($\ll 5\%$)

$$K_c = \frac{[H^+][CN^-]}{[HCN]} = \frac{x^2}{0.15-x} \approx \frac{x^2}{0.15} = 4.9E-10$$

$$K_c \ll 0.15$$

⇒ x negligible!

Yes, you MUST justify for FRQ credit!

$$\Rightarrow x = \sqrt{(0.15)(4.9E-10)}$$

$$= 8.6E-6 M \text{ (just like when using quadratic!)}$$

$$\Rightarrow [HCN]_{eq} = 0.15 - x \approx 0.15 M$$

$$[H^+]_{eq} = [CN^-]_{eq} = 8.6 \times 10^{-6} M$$

- For the reaction $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$, which of the following conditions allows you to conclude that the change in concentration, x, is negligible? (Multiple correct answers!)

a. At a constant temperature, $[NO_2] = 1.0 M$ and $K_c = 4.0 \times 10^{-7}$.

b. At a constant temperature, $[N_2O_4] = 1.0 M$ and $K_c = 4.0 \times 10^{-7}$.

c. At a constant temperature, $[N_2O_4] = 1.0 M$ and $K_c = 4.0 \times 10^6$.

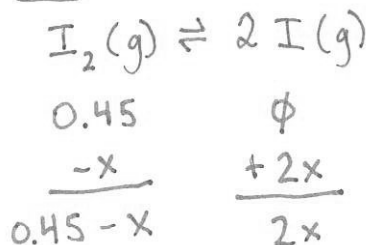
d. At a constant temperature, $[NO_2] = 1.0 M$ and $K_c = 4.0 \times 10^6$.

↳ starting w/ reactants and $K_c \ll 1.0$

↳ starting w/ products and $K_c \gg 1.0$

$$\frac{1.58 \text{ mol}}{3.5 \text{ L}} = 0.45 \text{ M}$$

3. Consider the equilibrium reaction: $\text{I}_2(\text{g}) \rightleftharpoons 2 \text{I}(\text{g})$, where $K_c = 5.6 \times 10^{-12}$. If 1.58 moles of $\text{I}_2(\text{g})$ are placed into a 3.5 L reaction vessel, what are the equilibrium concentrations of the reactant and the product?



$$K_c = \frac{[\text{I}]^2}{[\text{I}_2]} = \frac{(2x)^2}{0.45-x} \approx \frac{4x^2}{0.45} = 5.6 \times 10^{-12}$$

$$K_c \ll 0.45 \\ \Rightarrow x \text{ negligible}$$

$$x = \sqrt{\frac{(0.45)(5.6 \times 10^{-12})}{4}}$$

$$= 7.94 \times 10^{-7} \text{ M}$$

$$[\text{I}_2]_{\text{eq}} = 0.45 - x \approx 0.45 \text{ M}$$

$$[\text{I}]_{\text{eq}} = 2x = 2(7.94 \times 10^{-7}) = 1.6 \times 10^{-6} \text{ M}$$

Check K:

$$\frac{(1.6 \times 10^{-6})^2}{0.45} = 5.6 \times 10^{-12} \checkmark$$

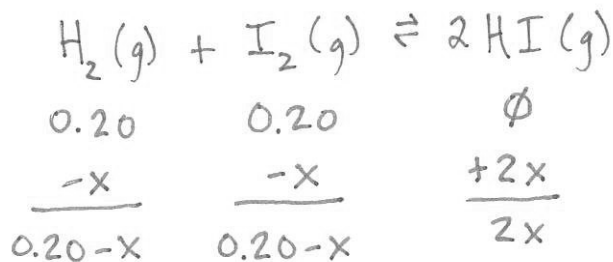
check approximation: $x < 5\%$?

$$\frac{7.94 \times 10^{-7}}{0.45} \times 100 = 0.0002\% \checkmark$$

What if x isn't negligible??

The Perfect Square: if keeping "-x" is necessary, see if the problem is a perfect square and thus easy to solve using delicious algebra.

Example: Consider the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$, $K_p = 64$ (at 25°C). A reaction mixture at 25°C initially contains $P_{\text{H}_2} = P_{\text{I}_2} = 0.20 \text{ atm}$. Find the equilibrium partial pressures of H_2 , I_2 , and HI .



$$K_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = \frac{(2x)^2}{(0.20-x)^2} = 64 \Rightarrow \frac{2x}{0.20-x} = 8 \Rightarrow 1.6 - 8x = 2x \\ 1.6 = 10x \\ x = 0.16 \text{ atm}$$

at equil:

$$P_{\text{HI}} = 2x = 2(0.16) = 0.32 \text{ atm}$$

$$P_{\text{H}_2} = P_{\text{I}_2} = 0.20 - x = 0.20 - 0.16 = 0.04 \text{ atm}$$

Check:

$$\frac{(0.32)^2}{(0.04)^2} = 64 \checkmark$$

note: K_p is NOT greater than 1000 (0.2) $\Rightarrow x$ is NOT negligible