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?

$K_c = 4.9 \times 10^{-10}$ at 22°C

R	$HCN(aq)$	$\rightleftharpoons$ $H^+(aq)$	+ $CN^-(aq)$
I	0.15	ϕ	ϕ
C	$-x$	$+x$	$+x$
E	$0.15-x$	x	x

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

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

$$x^2 = 7.3\underline{5}\text{E-}11 - 4.9\text{E-}10x$$

$$\Rightarrow x^2 + 4.9\text{E-}10x - 7.3\underline{5}\text{E-}11 = \phi$$

] Need the quadratic eqt'n to solve!

$a = 1$

$b = 4.9\text{E-}10$

$c = -7.3\underline{5}\text{E-}11$

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

$$x = \frac{-4.9\text{E-}10 \pm \sqrt{(4.9\text{E-}10)^2 + 4(1)(+7.3\underline{5}\text{E-}11)}}{2(1)} \Rightarrow x = \pm 8.\underline{5}7\text{E-}6$$

but... x can't be negative! (b/c its a concentration)

$$\Rightarrow x = 8.\underline{5}7\text{E-}6M$$

$$\Rightarrow [HCN]_{eq} = 0.15 - 8.\underline{5}7\text{E-}6 = \boxed{0.15M} \text{ (w/ s.f.)}$$

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

Check:

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

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)

$[HCN]_{eq} = 0.15 - \underbrace{0.0000086}_{\text{negligible!}}$

$\approx 0.15\,M$

The "X is Negligible" Approximation

↳ aka too tiny to affect addition or subtraction

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

a. Very **Small** K values (where $K < 10^{-5}$ or Initial Molarity ≥ 1000 x K) when starting from reactants: in this case, barely any products will be made. want $K \ll [\text{reactants}]_{\text{initial}}$

b. Very **large** K values (where $K > 10^{5}$) when starting from products: in this case, barely any reactants will be made. want $K \gg [\text{products}]_{\text{initial}}$

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.

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

$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$ $\qquad K_c = 4.9 \times 10^{-10}$ at 22°C

HCN	H^+	CN^-
0.15	∅	∅
−x	+x	+x
0.15−x	x	x

check assumption:

$\frac{\overset{x}{8.6E\text{-}6}}{0.15} \times 100 = 0.0057\%$ ($\ll 5\%$)

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

$K_c \ll 0.15$
⇒ x negligible!

Yes, you MUST justify for FRQ credit!

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

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

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

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

2. 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, $\boxed{[N_2O_4] = 1.0\text{ M}}$ and $K_c = 4.0 \times 10^{-7}$.

   starting w/ reactants and $K_c \ll 1.0$

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

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

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

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

3. Consider the equilibrium reaction: $I_2(g) \rightleftharpoons 2\,I(g)$, where $K_c = 5.6 \times 10^{-12}$. If $\boxed{1.58 \text{ moles of of } I_2(g)}$ are placed into a $\boxed{3.5\ L}$ reaction vessel, what are the equilibrium concentrations of the reactant and the product?

$$I_2(g) \rightleftharpoons 2\,I(g)$$

	I_2	I
	0.45	∅
	$-x$	$+2x$
	$0.45 - x$	$2x$

$$K_c = \frac{[I]^2}{[I_2]} = \frac{(2x)^2}{\underbrace{0.45 - x}} \approx \frac{4x^2}{0.45} = 5.6E{-12}$$

$K_c << 0.45$
$\Rightarrow x$ negligible

$$x = \sqrt{\frac{(0.45)(5.6E{-12})}{4}} = 7.94E{-7}\ M$$

$$[I_2]_{eq} = 0.45 - x \approx \boxed{0.45\ M}$$

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

Check K:

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

Check approximation: $x < 5\%$?

$$\frac{7.94E{-7}}{0.45} \times 100 = 0.0002\%\ ✓$$

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

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

H_2	I_2	HI
0.20	0.20	∅
$-x$	$-x$	$+2x$
$0.20 - x$	$0.20 - x$	$2x$

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \frac{(2x)^2}{\underbrace{(0.20 - x)^2}} = 64 \Rightarrow \frac{2x}{0.20 - x} = 8 \Rightarrow 1.6 - 8x = 2x$$

$$1.6 = 10x$$

$$x = 0.16\ atm$$

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

at equil:

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

$$P_{H_2} = P_{I_2} = 0.20 - x = 0.20 - 0.16 = \boxed{0.04\ atm}$$

Check:

$$\frac{(0.32)^2}{(0.04)^2} = 64\ ✓$$