

## Chemical Equilibrium

Some more complicated applications

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The ICE chart is a powerful tool for many different equilibrium problems

But you can't always make a simplifying assumption, and that means that you may need to do a little algebra

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## A Quadratic Equation

A quadratic equation is a 2<sup>nd</sup> order polynomial of the general form:

$$a x^2 + b x + c = 0$$

Where a, b, and c represent number coefficients and x is the variable

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### The Quadratic Formula

$$a x^2 + b x + c = 0$$

All quadratic equations have a solution for  $x$  that is given by:

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

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### Equilibrium & the Quadratic Formula

If you cannot make a simplifying assumption, many times you will end up with a quadratic equation for an equilibrium constant expression.

You can end up with a 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup>, etc. order polynomial, but I will not hold you responsible for being able to solve those as there is no simple formula for the solution.

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### A sample problem.

A mixture of 0.00250 mol  $\text{H}_2(g)$  and 0.00500 mol of  $\text{I}_2(g)$  was placed in a 1.00 L stainless steel flask at 430 °C. The equilibrium constant, based on concentration, for the creation of HI from hydrogen and iodine is 54.3 at this temperature.

What are the equilibrium concentrations of all 3 species?

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### Determining the concentrations

ICE - ICE - BABY - ICE - ICE

The easiest way to solve this problem is by using an ICE chart.

We just need a BALANCED EQUATION

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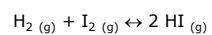
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### An ICE Chart



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### An ICE Chart

	$\text{H}_2 (\text{g})$	$\text{I}_2 (\text{g})$	$\leftrightarrow 2 \text{HI} (\text{g})$
I	0.00250 M	0.00500 M	0 M
C	-x	-x	+2x
E	0.00250 - x	0.00500 - x	2x

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Plug these numbers into the equilibrium constant expression.

$$K_c = 54.3 = \frac{[HI]^2}{[H_2][I_2]}$$

$$54.3 = \frac{(2x)^2}{(0.00250-x)(0.00500-x)}$$

I could start by assuming  $x \ll 0.00250$ , it is always worth taking a look at the "easy" solution.

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Assuming  $x$  is small...

$$54.3 = \frac{(2x)^2}{(0.00250-x)(0.00500-x)}$$

IF  $x \ll 0.00250$

$$54.3 = \frac{(2x)^2}{(0.00250)(0.00500)}$$

$$6.788 \times 10^{-4} = 4x^2$$

$$1.697 \times 10^{-4} = x^2$$

$$0.0130 = x$$

THE ASSUMPTION DOES NOT WORK!

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We're going to have to use the quadratic formula

$$54.3 = \frac{(2x)^2}{(0.00250-x)(0.00500-x)}$$

$$54.3 = \frac{(2x)^2}{(x^2 - 0.00750x + 1.25 \times 10^{-5})}$$

$$54.3(x^2 - 0.00750x + 1.25 \times 10^{-5}) = 4x^2$$

$$54.3x^2 - 0.407x + 6.788 \times 10^{-4} = 4x^2$$

$$50.3x^2 - 0.407x + 6.788 \times 10^{-4} = 0$$

On to the Quadratic Formula

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### Using the quadratic formula

$$50.3x^2 - 0.407x + 6.788 \times 10^{-4} = 0$$

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

$$x = \frac{-(-0.407) \pm \sqrt{(-0.407)^2 - 4(50.3)(6.78 \times 10^{-4})}}{2(50.3)}$$

$$x = \frac{0.407 \pm \sqrt{0.1656 - 0.1366}}{100.6}$$

$$x = \frac{0.407 \pm \sqrt{0.170}}{100.6}$$

$$x = 0.005736 \text{ OR } 0.002356$$

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### There are 2 roots...

All 2<sup>nd</sup> order polynomials have 2 roots, BUT only one will make sense in the equilibrium problem

$$x = 0.005736 \text{ OR } 0.002356$$

Which is correct?

Look at the ICE chart and it will be clear.

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$$x = 0.005736 \text{ OR } 0.002356$$

	$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2 \text{HI}(\text{g})$		
I	0.00250 M	0.00500 M	0 M
C	-x	-x	+2x
E	0.00250 - x	0.00500 - x	2x

If  $x = 0.005736$ , then the equilibrium concentrations of the reactants would be NEGATIVE! This is a physical impossibility.

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$$SO \quad x = 0.002356$$

	$H_2 (g)$	$I_2 (g)$	$\leftrightarrow$	$2 HI (g)$
I	0.00250 M	0.00500 M		0 M
C	-0.002356	-0.002356		+2(0.002356)
E	0.000144 M	0.002644 M		0.00471 M

And you are done!

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### Another Itty Bitty Problem

$CaCO_3 (s)$  will decompose to give  $CaO (s)$  and  $CO_2 (g)$  at  $350^\circ C$ . A sample of calcium carbonate is sealed in an evacuated 1 L flask and heated to  $350^\circ C$ . When equilibrium is established, the total pressure in the flask is 0.105 atm. What is  $K_c$  and  $K_p$ ?

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As always, we 1<sup>st</sup> need a balanced equation:

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$\text{CaCO}_3(s) \leftrightarrow \text{CaO}(s) + \text{CO}_2(g)$

Then we can immediately write the equilibrium constant expressions:

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Then we can immediately write the equilibrium constant expressions:

$K_c = [\text{CO}_2]$

$K_p = P_{\text{CO}_2}$

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### Another Itty Bitty Problem

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$$K_c = [\text{CO}_2]$$

$$[\text{CO}_2] = \text{moles CO}_2/\text{L}$$

How do we determine the # of moles?

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All of the pressure must be due to the carbon dioxide.

As a gas, carbon dioxide should obey the ideal gas law.

$$P V = n R T$$

And we know P, V, R, and T!!

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$$P V = n R T$$

And we know P, V, R, and T!!

In fact, we could calculate moles/L directly:

$$P V = n R T$$

$$P/RT = n/V$$

Either way will work.

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$$\frac{P}{RT} = \frac{n}{V}$$

$$\frac{0.105 \text{ atm}}{0.0821 \frac{\text{L atm}}{\text{mol K}} * (350\text{C} + 273.15\text{K})} = \frac{n}{V}$$

$$2.05 \times 10^{-3} \text{ M} = \frac{n}{V}$$

We can use this to directly calculate  $K_c$

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$$K_c = [\text{CO}_2]$$

$$K_c = 2.05 \times 10^{-3}$$

And we're done!!! (Boring when there's no exponents, isn't it? ☺)

What about  $K_p$ ?

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$$K_p = P_{\text{CO}_2}$$
$$K_p = 0.105$$

And we're essentially done!

Now, that may have seemed simple, but it does point out something interesting about the relationship between  $K_c$  and  $K_p$

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$$K_c \text{ vs } K_p$$

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$K_c$  depends on concentration (moles/L)

$K_p$  depends on pressure (atm)

For gases, pressure and concentration are directly related.

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$$K_c \text{ vs } K_p$$

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$$P V = nRT$$
$$\frac{P}{RT} = \frac{n}{V} = M$$

The only difference between P and M is (RT)

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### $K_c$ vs $K_p$

$$K_c = [\text{CO}_2] = \frac{n}{V} = \frac{P_{\text{CO}_2}}{RT} = K_p$$

Or, alternatively

$$K_p = K_c (RT)$$

This can be generalized.

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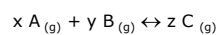
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### $K_c$ vs $K_p$ - in general

Consider a general reaction:



And I can quickly write  $K_c$  and  $K_p$ :

$$K_c = \frac{[\text{C}]^z}{[\text{B}]^y[\text{A}]^x}$$

$$K_p = P_C^z / P_B^y P_A^x$$

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### Using the Ideal Gas Law...

$$K_c = \frac{[\text{C}]^z}{[\text{B}]^y[\text{A}]^x}$$

$$K_c = \frac{\left(\frac{n_C}{V}\right)^z}{\left(\frac{n_B}{V}\right)^y \left(\frac{n_A}{V}\right)^x}$$

$$K_c = \frac{\left(\frac{P_C}{RT}\right)^z}{\left(\frac{P_B}{RT}\right)^y \left(\frac{P_A}{RT}\right)^x}$$

If I collect all the  $(1/RT)$  terms separately

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If I collect all the  $(1/RT)$  terms separately

$$K_C = \frac{\left(\frac{P_C}{RT}\right)^z}{\left(\frac{P_B}{RT}\right)^y \left(\frac{P_A}{RT}\right)^x}$$

$$K_C = \left\{ \frac{P_C^z}{P_B^y P_A^x} \right\} \left( \frac{\left(\frac{1}{RT}\right)^z}{\left(\frac{1}{RT}\right)^y \left(\frac{1}{RT}\right)^x} \right)$$

$$K_C = K_P \left(\frac{1}{RT}\right)^{z-y-x}$$

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Simplifying...

$$K_C = K_P \left(\frac{1}{RT}\right)^{z-y-x}$$

Z-Y-X is just the change in the stoichiometry of the reaction:

Z moles of products - Total moles of reactants (Y+X)

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Simplifying...

$$K_C = K_P \left(\frac{1}{RT}\right)^{\Delta n}$$

$\Delta n$  = total moles of product gas - total moles of reactant gas

This is the general relationship between  $K_p$  and  $K_c$  for all gas phase reactions.

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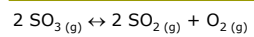
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### Another $K_p$ vs $K_c$ problem



The above reaction has a  $K_p$  value of  $1.8 \times 10^{-5}$  at  $360^\circ\text{C}$ . What is  $K_c$  for the reaction?

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If we recall that:

$$K_c = K_p \left( \frac{1}{RT} \right)^{\Delta n}$$

The solution is simple.

$$\Delta n = 3 \text{ moles product gas} - 2 \text{ moles reactant gas}$$

So:

$$K_c = 1.8 \times 10^{-5} \left( \frac{1}{(0.0821 \frac{\text{L atm}}{\text{mol K}})(360\text{C} + 273.15 \text{ K})} \right)^1$$

$$K_c = 3.46 \times 10^{-7}$$

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