MONDAY, MARCH 2, 2026 AP CHEMISTRY

CH. 15 READING IS DUE W 3/4

K_{eq} – EQUILIBRIUM LAB
GROUP X F 3/6
GROUP Y Tu 3/10

CH. 15 PSET Tu 3/10

CH. 15 QUIZ Th 3/12

TOPICS IN THIS CHAPTER

AS ALWAYS, REVIEW THE LEARNING TARGETS

- ★ DEF. OF EQUILIBRIUM
  - K_{eq} EXPRESSION
  - K_c VS. K_p
- ★ INTERPRETING THE SIZE OF K_{eq}
  - $K_{eq} > 1$, $K_{eq} = 1$, $K_{eq} < 1$
- ★ ALGEBRA OF K_{eq} EXPRESSIONS
- ★ HETEROGENEOUS EQUILIBRIA
- ★ APPLICATIONS OF K_{eq}
- ★ LE CHÂTELIER'S PRINCIPLE

CH. 15 EQUILIBRIUM

FOR A REVERSIBLE CHEMICAL REACTION, EQUILIBRIUM IS THE CONDITION WHEN ALL CONCENTRATIONS ARE CONSTANT DUE TO THE FACT THAT THE FORWARD RATE EQUALS THE REVERSE RATE.

MOLECULES CONTINUE TO REACT: IT IS A DYNAMIC EQUILIBRIUM.

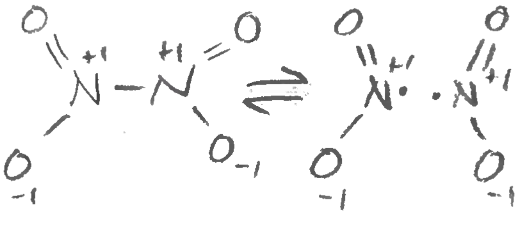
SOME EXAMPLE EQUILIBRIA:

PHYSICAL: $H_2O_{(l)} \rightleftharpoons H_2O_{(s)}$

$Br_{2(l)} \rightleftharpoons Br_{2(g)}$

"$\rightleftharpoons$" MEANS "IN EQUILIBRIUM WITH" (DO NOT USE "$\leftrightarrow$" B/C THAT'S FOR LEWIS STR. RESONANCE FORMS)

CHEMICAL: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$



$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

FORWARD RATE LAW $N_2O_4 \rightarrow 2NO_2$ RATE = $k_1[N_2O_4]^1$

REVERSE RATE LAW $2NO_2 \rightarrow N_2O_4$ RATE = $k_{-1}[NO_2]^2$

AT EQUILIBRIUM, CONCENTRATIONS HAVE BECOME CONSTANT.

WE WRITE A RATIO OF $\frac{[\text{PRODUCT}]}{[\text{REACTANT}]}$ TO CALC. AN

$$\boxed{\text{EQUILIBRIUM CONSTANT, } K_{eq}}$$

IT'S BASED ON THE EQUAL RATES IDEA:

$$\underset{\text{REACTANT}}{k_1[N_2O_4]^1} = \underset{\text{PRODUCT}}{k_{-1}[NO_2]^2}$$

$$\frac{[NO_2]^2}{[N_2O_4]^1} = \frac{k_1}{k_{-1}} = K_{eq}$$

THE EQUILIBRIUM CONSTANT FOR A GENERIC RXN IS:

$$aA + bB \rightleftharpoons cC + dD$$

COEFFICIENT

CHEMICAL FORMULA

$$\boxed{K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

THE EQUILIBRIUM CONSTANT EXPRESSION

A.K.A. THE LAW OF MASS ACTION

IT DOES NOT DEPEND ON THE REACTION MECHANISM SO THERE'S NO QUESTION ABOUT WHAT THE EXPONENTS SHOULD BE.

K_{eq} HAS NO UNITS. IT'S VALID AS LONG AS ALL CONC. UNITS USED TO CALC. IT ARE THE SAME.

STOPPED HERE M2026-03-02 GROUP Y AFTER THE CH. 14 QUIZ

M 2026-03-02 APCHEM

TWO THINGS:

① THE VALUE OF K_{eq} IS THE SAME, BY DEFINITION, EVEN IF THE STARTING AND ENDING CONCENTRATIONS ARE DIFFERENT. DIFF. SETS OF CONCENTRATIONS AT EQUILIBRIUM ARE CALLED DIFF. EQUILIBRIUM POSITIONS.

FOR EX.

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = 0.21 = \frac{(0.0310)^2}{(0.00452)}$$

$$\boxed{N_2O_4 \rightleftarrows 2NO_2}$$

$[NO_2]_{eq} = 0.0310M$

$[N_2O_4]_{eq} = 0.00452M$

$$K_{eq} = 0.21 = \frac{(0.0243)^2}{(0.00280)}$$

☆ SO, ALTHOUGH K_{eq} HAS A CONSTANT VALUE, CONC. OF REACTANTS AND PRODUCTS AT EQUILIBRIUM MAY VARY.

② THE VALUE OF K_{eq} DEPENDS ON TEMP. (°C or K).

EXOTHERMIC RXNS	ENDOTHERMIC RXNS
K_{eq} DECREASES AS TEMP RISES	K_{eq} INCR AS TEMP RISES
K_{eq} INCREASES AS TEMP FALLS	K_{eq} DECR. AS TEMP FALLS

COMPARING EQUILIBRIUM POSITIONS MATHEMATICALLY:

CONDITION A

$$N_2O_4 \rightleftarrows 2NO_2$$

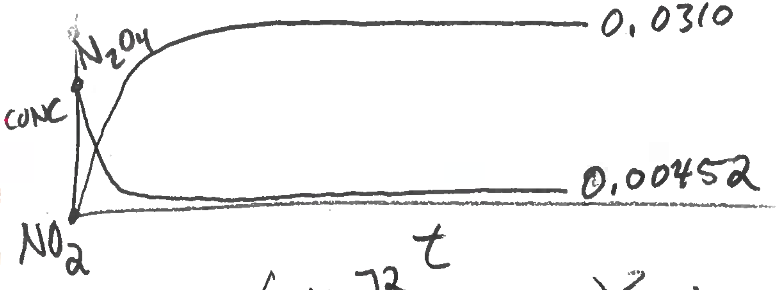
	N_2O_4	$2NO_2$
INITIAL	0.0200M	0
CHANGE	$-x$	$+2x$
EQUIL.	$(0.0200-x)$	$2x$

ICE TABLE

MEAS. SHOWS:

$[N_2O_4]_{eq} = 0.00452M$

$[NO_2]_{eq} = 0.0310M$



$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]^1} = \frac{(0.031)^2}{0.00452} = \boxed{0.21}$$

CONDITION B

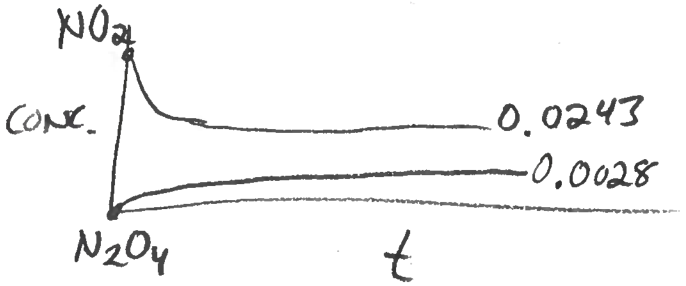
$$N_2O_4 \rightleftarrows 2NO_2$$

	N_2O_4	$2NO_2$
i.	0	0.0300M
c.	$+x$	$-2x$
e.	x	$(0.0300-2x)$

MEAS. SHOWS:

$[N_2O_4]_{eq} = 0.00280M$

$[NO_2]_{eq} = 0.0243M$



$$K_{eq} = \frac{(0.0243)^2}{(0.0028)} = \boxed{0.21}$$

SO THE VALUE OF K_{eq} IS THE SAME EVEN WITH DIFF. STARTING AND FINAL CONCENTRATIONS.

HOW CAN K_{eq} BE USEFUL?

YOU CAN CALC. $\underset{\text{FINAL}}{[A]_{eq}}$ USING $\underset{\text{INITIAL}}{[A]_0}$ AND THE VALUE OF K_{eq}

FOR EX: $N_2O_4 \rightleftarrows 2NO_2$

	N_2O_4	$2NO_2$
i	0M	0.0400M
c	$+x$	$-2x$
e	x	$(0.04-2x)$

CALC. x, $[N_2O_4]_{eq}$, AND $[NO_2]_{eq}$

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = 0.21$$

$$\frac{(0.04-2x)^2}{(x)} = 0.21$$

$4x^2 - 0.37x + 0.0016 = 0$

QUADRATIC MAGIC!

$$x = \begin{cases} \cancel{0.0880} \\ 0.00455 \end{cases}$$

$[N_2O_4]_{eq} = x = 0.00455M$

$[NO_2]_{eq} = 0.04 - 2x = 0.0309M$

YOU CAN CHECK YOUR WORK! M 2026-03-02 AP CHEM

$$K_{eq} = 0.21 \overset{?}{=} \frac{(0.0309)^2}{0.00455} = 0.21$$ (IT DOES! YAY!)

EQUIL. FOR GAS-PHASE RXNS CAN BE STUDIED USING PARTIAL PRESSURES B/C $P = \frac{n}{V} RT$ (P IS PROP. TO $\frac{n}{V}$, OR CONC.).

FOR A GIVEN RXN, WE COULD WRITE K_{eq} IN TERMS OF CONC.

★ $$K_{eq} = K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

K_c → K_{eq} IN TERMS OF CONC

$$K_{eq} = K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

K_p → K_{eq} IN TERMS OF PARTIAL PRESSURES

NOT ON YOUR QUIZ OR ON THE AP EXAM:

K_p AND K_c ARE RELATED: $$K_p = K_c (RT)^{\Delta n}$$

$\Delta n = (c+d) - (a+b)$

$R = 0.08206$ L atm/K mol

T IS IN KELVIN (K)

OTHER K SYMBOLS:

K_a IS FOR A WEAK ACID } CH. 16, 17

K_b IS FOR A WEAK BASE } CH. 16, 17

K_{sp} IS FOR SOLUBILITY PRODUCT CH. 17

INTERPRETING THE SIZE OF K_{eq} $$K_{eq} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$

RANGE OF POSSIBLE VALUES: 10^{-60} TO 10^{100}

$K_{eq} << 1$ (SO 10^{-n})

"REACTANTS ARE FAVORED"

$$\boxed{R} \rightleftarrows \boxed{P}$$

$K_{eq} >> 1$ (SO 10^{+n})

"PRODUCTS ARE FAVORED"

$$\boxed{R} \rightleftarrows \boxed{P}$$

F 2026-03-06 GROUP X START
GROUP Y CONT FROM pg2 OF NEW

Tu 2025-03-18 AP CHEM

THE ALGEBRA OF EQUILIBRIUM CONSTANT EXPRESSIONS

CHEM EQNS CAN BE MODIFIED AND COMBINED IN ORDER TO MAKE CALC. REGARDING EQUILIBRIUM FOR RXNS WE DON'T HAVE EXPERIMENTAL DATA ON. (REM: STATE FUNCTIONS).

HERE'S HOW K_{eq} CHANGES FOR MODIFICATIONS OF CHEM EQNS:

① REVERSE A CHEM. EQN. $K_{NEW} = (K_{OLD})^{-1}$ OR $\frac{1}{K_{OLD}}$

FOR EX $N_2O_4 \rightleftharpoons 2NO_2$

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$$

$2NO_2 \rightleftharpoons N_2O_4$

$$K_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$$

WHICH IS $1/K$ FOR THE ORIG. EQN.

② MULTIPLY A CHEM. EQN. BY A CONSTANT

$K_{NEW} = (K_{OLD})^n$ WHERE n IS OUR MULTIPLIER

$(N_2O_4 \rightleftharpoons 2NO_2) \times 2$ SO $2N_2O_4 \rightleftharpoons 4NO_2$

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_{eq} = \frac{[NO_2]^4}{[N_2O_4]^2} = \left(\frac{[NO_2]^2}{[N_2O_4]}\right)^2$$

③ COMBINE CHEM. EQNS.

$$K_{NEW} = K_1 \times K_2$$

COMBINE

$\boxed{1}$ $2NOBr \rightleftharpoons 2NO + \cancel{Br_2}$ $K_1 = \frac{[NO]^2[\cancel{Br_2}]}{[NOBr]^2} \times$

$\boxed{2}$ $\cancel{Br_2} + Cl_2 \rightleftharpoons 2BrCl$ $K_2 = \frac{[BrCl]^2}{[\cancel{Br_2}][Cl_2]}$

$2NOBr + Cl_2 \rightleftharpoons 2NO + 2BrCl$

$$K_{NEW} = \frac{[NO]^2[BrCl]^2}{[NOBr]^2[Cl_2]}$$

IN THESE MANIPULATIONS WE ARE INTERESTED IN THE RESULTING NUMERICAL VALUES.

SAMP. EX. 15.4 pg 640

$$\boxed{\begin{array}{lll} \boxed{1} & HF \rightleftharpoons H^+ + F^- & K_1 = 6.8\times10^{-4} \\ \boxed{2} & H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-} & K_2 = 3.8\times10^{-6} \end{array}}$$

GIVEN.

TASK: CALC K_{eq} VALUE FOR $2HF + C_2O_4^{2-} \rightleftharpoons 2F^- + H_2C_2O_4$

TAKE RXN $\boxed{1}$ × 2 $\quad 2HF \rightleftharpoons 2H^+ + 2F^- \quad K = (6.8\times10^{-4})^2$

TAKE RXN $\boxed{2}$ IN REVERSE $\quad 2H^+ + C_2O_4^{2-} \rightleftharpoons H_2C_2O_4 \quad K = (3.8\times10^{-6})^{-1}$

K_{eq} FOR THE COMBINED, MODIFIED EQNS IS

$$K_{NEW} = (K_1)^2 \cdot (K_2)^{-1}$$

$$(6.8\times10^{-4})^2 \cdot (3.8\times10^{-6})^{-1} = \boxed{0.12}$$

15.4 HETEROGENEOUS EQUILIBRIA

HETEROG. MEANS THAT A PURE SOLID OR LIQUID IS PART OF THE EQUILIBRIUM SYSTEM.

PURE SOLIDS AND LIQUIDS HAVE CONSTANT CONCENTRATIONS AND SO THEY CAN'T CHANGE AS WE GO FROM INITIAL CONDITIONS TO EQUILIBRIUM. NO MATTER WHAT VOL. YOU HAVE IT IS ALWAYS THE SAME $\frac{mol}{L}$

$\frac{n}{V}$ = CONC $\quad n = \frac{m}{M}$ MASS / MOLAR MASS

$$\frac{n}{V} = \frac{m/M}{V} = \frac{m}{V\cdot M} = D\cdot\frac{1}{M} = \frac{D}{M}$$

$$\frac{m}{V} = D$$

CONC. IS EQUAL TO THE RATIO OF TWO CONSTANTS!

FOR THIS REASON PURE SOLIDS AND PURE LIQUIDS ARE <u>LEFT OUT</u> OF EQUIL. CONSTANT EXPRESSIONS.

Tu 2025-03-18 AP CHEM

FOR EX. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ $K_{eq} = [CO_2]$

$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$ $K_{eq} = [Ca^{2+}][CO_3^{2-}]$

SOLUBILITY PRODUCT OR K_{sp}

AN IMPORTANT POINT: THE VALUE FOR K_{eq} IS ONLY VALID AS LONG AS THERE IS A NON-ZERO AMOUNT OF THE PURE SOLID OR LIQUID.

STOPPED HERE GROUP X Tu 2025-03-18

15.5 CALCULATING THE VALUE OF K_{eq}

TO CALC. A VALUE FOR K_{eq} FOR A RXN YOU NEED TO HAVE MEASUREMENTS OF CONC. AT EQUILIBRIUM. PLUG THOSE VALUES INTO THE K_{eq} EXPRESSION.

FOR EX. SAMP. EX. 15.7 PG 644 $N_2 + 3H_2 \rightleftharpoons 2NH_3$

e 2.43atm 7.38atm 0.166atm

↑ @ EQUIL.

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}^3}$$

$K_p = 2.8\times10^{-5}$

SOMETIMES YOU NEED TO USE STOICH. TO CALC. EQUIL. CONC.

SAMP. EX. 15.8 PG 645

		H_2	$+ \; I_2$	$\rightleftharpoons 2HI$
i	INITIAL	1.00×10^{-3} M	2.00×10^{-3} M	0
c	CHANGE	$-x$	$-x$	$+2x$
e	EQUIL	$1\times10^{-3}-x$	$2\times10^{-3}-x$	$2x$

INFO GIVEN IN THE PROB:

$[HI]_{eq} = 1.87\times10^{-3}$ M

so $2x = 1.87\times10^{-3}$ M AND $x = 9.35\times10^{-4}$ M

$[H_2]_{eq} = 1\times10^{-3} - x = 6.5\times10^{-5}$ M

$[I_2]_{eq} = 2\times10^{-3} - x = 1.065\times10^{-3}$ M

(STOPPED HERE GROUP X F 2026-03-06)

Th 2025-03-20 AP CHEM

TAKE THE eq CONC. WE CALC. AND PLUG IN TO...

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \boxed{51}$$

(WE WILL DO THIS EXACT THING FOR YOUR LAB NEXT WEEK!)

(STOPPED HERE GROUP F 2025-03-06)

15.6 APPLICATIONS OF EQUIL. CONSTANTS

PROBLEMS YOU'LL NEED TO BE ABLE TO SOLVE WILL GIVE YOU A VALUE FOR K_{eq} AND YOUR TASK WILL BE TO CALC. CONC. OF ALL SPECIES AT EQUILIBRIUM.

YOU NEED TO BE ABLE TO TELL WHICH WAY CONCENTRATIONS WILL SHIFT AS THEY CHANGE TO EQUILIBRIUM VALUES

SHIFT RIGHT: [PRODUCT] INCR AND [REACTANT] DECR

SHIFT LEFT: [PRODUCT] DECR AND [REACTANT] INCR.

$$A + B \rightleftharpoons C$$

CASE 1

	A	+ B	$\rightleftharpoons$ C
i	1M	1M	0
c	$-x$	$-x$	$+x$
e	$1-x$	$1-x$	x

SHIFT RIGHT B/C $[PRODUCT]_0 = 0M$

CASE 2

	A	+ B	$\rightleftharpoons$ C
i	0	0	1M
c	$+x$	$+x$	$-x$
e	x	x	$1-x$

SHIFT LEFT B/C $[REACTANT]_0 = 0M$

CASE 3

	A	+ B	$\rightleftharpoons$ C
i	0.955M	0.110M	1.0M
c			
e			

THIS IS IMPOSSIBLE TO SAY B/C WE HAVENT YET BEEN GIVEN A VALUE OF K_{eq}

IN ORDER TO DECIDE IF A RXN SHIFTS RIGHT OR LEFT WE COMPARE A REACTION QUOTIENT (Q) CALC. USING INITIAL CONC. TO THE VALUE OF K_{eq}.

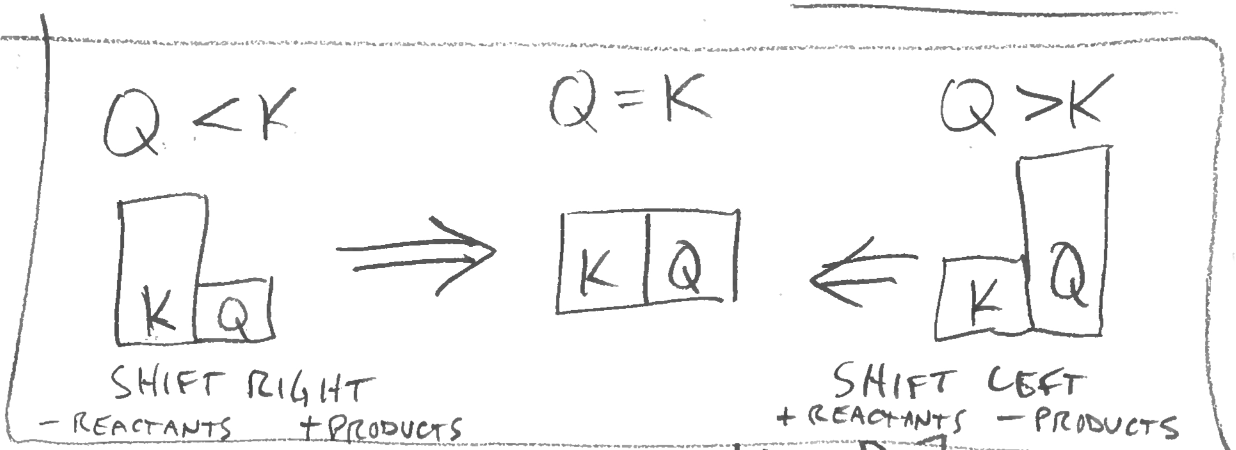
A REACTION QUOTIENT IS THE NUMBER YOU GET BY INSERTING INITIAL CONC. INTO THE EQUIL. CONSTANT EXPRESSION.

$$K_{eq} = \frac{[C]_{eq}}{[A]_{eq}[B]_{eq}} \qquad Q = \frac{[C]_0}{[A]_0[B]_0}$$

IF $Q = K$ THEN THE INITIAL CONC. ARE EQUIL. CONC.
IT'S ALREADY AT EQUILIBRIUM

IF $Q < K$ IT MEANS $[\text{PRODUCT}]_0$ IS LOWER THAN IT NEEDS TO BE AND $[\text{REACTANT}]_0$ IS HIGHER
AND SO THE RXN SHIFTS RIGHT.

IF $Q > K$ IT MEANS $[\text{PRODUCT}]_0$ IS TOO LARGE AND $[\text{REACTANT}]_0$ IS TOO SMALL
AND SO THE RXN SHIFTS LEFT.



CASE 3 $\quad A + B \rightleftharpoons C \qquad K = \frac{[C]}{[A][B]} = 100$

$0.955 \quad 0.110 \quad 1.0$

$$Q = \frac{1.0}{0.955 \cdot 0.110} = 9.5$$

SINCE $9.5 < 100$ THE RXN SHIFTS RIGHT : C (CHANGE) $-x \quad -x \quad | \quad +x$

SAMP. EX. 15.9 pg 647

$H_2 + I_2 \rightleftharpoons 2HI$ AT 448°C $K = 50.5$

	H_2	I_2	$2HI$
i	$\frac{1.00\times10^{-2}\text{ mol}}{2L}$	$\frac{3.00\times10^{-2}\text{ mol}}{2L}$	$\frac{2.00\times10^{-2}\text{ mol}}{2L}$
i	$0.500\times10^{-2}M$	$1.5\times10^{-2}M$	$1.0\times10^{-2}M$
c	$-x$	$-x$	$+2x$
e	$0.5\times10^{-2}-x$	$1.5\times10^{-2}-x$	$1\times10^{-2}+2x$

CALC $[\ ]_0$

HOW DOES THE RXN SHIFT TO REACH EQUIL?

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = 50.5$$

$$Q = \frac{(1\times10^{-2})^2}{0.5\times10^{-2}\cdot1.5\times10^{-2}} = 1.3$$

SO $Q < K$ AND RXN SHIFTS RIGHT

TO CALC $[\ ]_{eq}$ WE PLUG THESE EXPRESSIONS INTO THE K_{eq} EXPRESSION:

$$K_{eq} = \frac{(1\times10^{-2}+2x)^2}{(0.5\times10^{-2}-x)(1.5\times10^{-2}-x)} = 50.5$$

SOLVE FOR X

YOU'LL HAVE TO USE THE QUADRATIC FORMULA TO GET X

★ THEN: $[H_2]_{eq} = [H_2]_0 - x$

SAMP. EX. 15.10 pg 648

CALC. AN EQUIL. CONC. VALUE USING $[\ ]_{eq}$ AND K_{eq} VALUE.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$K_p = \frac{P_{NH_3}^2}{P_{N_2}\cdot P_{H_2}^3} = 1.45\times10^{-5} \text{ AT } 500°C$$

	N_2	$3H_2$	$2NH_3$
i			
c			
e	0.432 atm	0.928 atm	x

GIVEN

CALC THE VALUE OF X

NOT 2X B/C WE ARE NOT CALC. BASED ON A CHANGE — JUST... WHAT IS IT?

$$1.45\times10^{-5} = \frac{x^2}{0.432\cdot0.928^3}$$

$x^2 = 5.0\times10^{-6}$ so $x = 2.24\times10^{-3}$ atm $= P_{NH_3}$

CHECKING: $\frac{(2.24\times10^{-3})^2}{0.432\cdot(0.928)^3} = 1.45\times10^{-5}$ (YAY!)

SAMPLE EX. 15.11 pg 648 Th 2025-03-20 AP CHEM

$H_2 + I_2 \rightleftharpoons 2HI$ $K_c = \frac{[HI]^2}{[H_2][I_2]} = 50.5$ AT 448°C

i	1.0M	2.0M	0 ← GIVEN VALUES
c	$-x$	$-x$	$+2x$
e	$1-x$	$2-x$	$2x$

CALC. [ ]eq FOR ALL 3

$(2x)^2 = 4x^2$ NOT $2x^2$!

$$50.5 = \frac{(2x)^2}{(1.0-x)(2.0-x)}$$

$$4x^2 = 50.5(1-x)(2-x)$$

SO...

$$\boxed{46.5x^2 - 151.5x + 101 = 0}$$

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

PUT IT IN YOUR CALCULATOR PROGRAM

STOPPED HERE GROUP X Th 2025-03-20 (MID-EXAMPLE, TRYING TO INPUT THE PROGRAM)

ROOTS: $X = \cancel{2.323}$ NOT THE ROOT WE NEED B/C 1 − 2.3 IS NEGATIVE

$\boxed{0.935}$

$[H_2]_{eq} = 1 - x = 1 - 0.935 = 0.065M$

$[I_2]_{eq} = 2 - x = 2 - 0.935 = 1.065M$

$[HI]_{eq} = 2x = 2(0.935) = 1.87M$

CHECK! → $\frac{(1.87)^2}{0.065 \cdot 1.065} = 50.5$ ✓

STOPPED HERE Th 2025-03-20 GROUP Y WITH 40 min LEFT — DO SOME OF THE ADDITIONAL PROBLEMS IN THE REF. PACKET I HANDED OUT

GIVEN THE CHEM. EQN. BELOW, AND THE TABULATED INITIAL CONCENTRATIONS, CALC. ALL EQUIL. CONC. AT 700K

$K_c = 5.10$ AT 700K

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

	$CO_{(g)}$	$H_2O_{(g)}$	$CO_{2(g)}$	$H_{2(g)}$
i	1.0M	1.0M	1.0M	1.0M
c	$-x$	$-x$	$+x$	$+x$
e	$1-x$	$1-x$	$1+x$	$1+x$

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

① CALC Q, THE RXN QUOTIENT = $Q = \frac{1 \cdot 1}{1 \cdot 1} = 1$

② FILL IN ROWS "c" AND "e"

$1 < 5.10$

$Q < K$ SO RXN SHIFTS RIGHT

③ SET UP AN EQUATION TO SOLVE FOR x.

$$K_c = 5.10 = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$

$$5.10 = \frac{(1+x)^2}{(1-x)^2} = \left(\frac{1+x}{1-x}\right)^2$$

$$\sqrt{5.10} = \frac{1+x}{1-x} \Rightarrow x = \frac{\sqrt{5.1}-1}{\sqrt{5.1}+1} = 0.386$$

SO EQUIL. CONC. ARE:

$[CO]_{eq} = [H_2O]_{eq} = 1.000 - 0.386 = 0.614M$

$[CO_2]_{eq} = [H_2]_{eq} = 1.000 + 0.386 = 1.386M$

CHECK = $\frac{(1.386)^2}{(0.614)^2} = 5.095$ CLOSE ENOUGH TO 5.10

M 2025-03-24 AP CHEM

SYSTEMS WITH SMALL EQUILIBRIUM CONSTANTS

WHEN THE VALUE OF K_{eq} IS VERY SMALL (10^{-4} OR SMALLER) AND WE HAVE TO CALC. EQUIL. CONC. STARTING WITH [PRODUCTS] = 0 WE CAN SOMETIMES TAKE A MATHEMATICAL SHORTCUT.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)} \qquad K_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

	$2NOCl_{(g)}$	$2NO_{(g)}$	$Cl_{2(g)}$
i	0.50M	0	0
c	$-2x$	$+2x$	$+x$
e	$0.50-2x$	$2x$	x

$K_c = 1.6\times10^{-5}$

FIRST TRY

$$1.6\times10^{-5} = \frac{\overset{4x^2}{(2x)^2}(x)}{(0.50-2x)^2}$$

$$K_c\cdot(0.50-2x)^2 = 4x^3$$

$$K_c\cdot(4x^2-2x+0.25) = 4x^3$$

$$4x^3-(4K_c)x^2-(2K_c)x+0.25K_c = 0$$

NO SIMPLE SOLUTION LIKE A QUADRATIC

SHORTCUT METHOD

SINCE $K_c \ll 1$ WE CAN ASSUME THAT x WILL BE VERY SMALL

IF SO THEN $0.5-2x \cong 0.5$

A SIMPLIFIED EQN

$$K_c = \frac{(2x)^2(x)}{(0.50)^2} = \frac{4x^3}{0.5^2}$$

$$K_c\cdot0.5^2 = 4x^3$$

$$x = \sqrt[3]{\frac{K_c\cdot0.5^2}{4}} = 1.0\times10^{-2}M$$

* CHECK VALIDITY OF ASSUMPTION

IS $0.5-2x$ IN FACT $\cong 0.50$ TO WITHIN 5%?

$$\frac{0.5-(0.5-1\times10^{-2}\cdot2)}{0.5}\times100\% = 4\%$$

(<5% IS OKAY)

SO THIS WAS OKAY!

* $[NOCl]_{eq} = 0.5-(2)(1.0\times10^{-2}) = 0.48$

$[NO]_{eq} = 2(1.0\times10^{-2}) = 2\times10^{-2}M$

$[Cl_2]_{eq} = 1.0\times10^{-2}M$

15.7 LE CHÂTELIER'S PRINCIPLE

WHEN A SYSTEM AT EQUILIBRIUM IS DISTURBED THE REACTION WILL PROCEED TO A NEW EQUIL. POSITION BY CHANGING CONCENTRATIONS IN SUCH A WAY AS TO COUNTERACT THE DISTURBANCE.

POSSIBLE DISTURBANCES

① ADD OR REMOVE PRODUCTS OR REACTANTS.
② CHANGE IN VOLUME OF THE RXN VESSEL FOR GAS PHASE REACTIONS
③ CHANGE THE TEMPERATURE

DISTURBANCES ① AND ② RESULT IN CHANGES IN CONC. OF REACTANTS AND PRODUCTS WITHOUT CHANGING THE VALUE OF K_{eq}.

DISTURBANCE ③, A CHANGE IN TEMP. ALTERS THE VALUE OF K_{eq} AND NEW CONC. ARE A RESULT OF THAT CHANGE.

ADD OR REMOVE SPECIES

$$\underset{\text{(LEFT)}}{\text{REACTANTS}} \rightleftharpoons \underset{\text{(RIGHT)}}{\text{PRODUCTS}} \qquad K = \frac{\text{PRODUCTS}}{\text{REACTANTS}}$$

A RXN SHIFTS RIGHT (TOWARDS PRODUCTS) WHEN:

a. REACTANT CONC OR PARTIAL PRESSURE IS INCREASED
b. PRODUCT CONC. OR PART. P IS DECREASED

A RXN SHIFTS LEFT (TOWARDS REACTANTS) WHEN:

a. REACTANT CONC. OR PART. P IS DECREASED
b. PRODUCT CONC. OR PART P. IS INCREASED

IN SUMMARY, A RXN SHIFTS TO CONSUME ADDED MATERIALS OR TO MAKE UP FOR A DEFICIT.

NOTE FOR GASES: ONLY CHANGING PARTIAL PRESSURES OF GASES INVOLVED IN THE EQUILIBRIUM AFFECTS THE EQUILIBRIUM POSITION.

CHANGING <u>TOTAL</u> PRESSURE BY ADDING OR REMOVING AN INERT GAS (He, Ne, Ar, Kr, Xe OR SOMETIMES N_2) <u>DOES NOT</u> AFFECT REACTANT OR PRODUCT PARTIAL PRESSURES.

AN EXAMPLE CALC. FOR A DISTURBANCE

$$A \rightleftharpoons 2B \qquad K_{eq} = \frac{[B]^2}{[A]} = \frac{(0.5)^2}{(0.1)} = 2.5$$

	A	$2B$
e	0.1	0.5

DISTURB THIS EQUIL. POSITION BY INCR. $[A]$ TO 0.2

$[A]_0 = 0.2$ AND $[B]_0 = 0.5$

	$A \rightleftharpoons$	$2B$
i	0.2	0.5
C	$-x$	$+2x$
e	$0.2-x$	$0.5+2x$

$Q = \frac{0.5^2}{0.2} = 1.25$ 1.25 < 2.5 SO SHIFT RIGHT

$$2.5 = \frac{(0.5+2x)^2}{(0.2-x)}$$

$$0 = 4x^2 + 4.5x - 0.25$$

(QUADRATIC MAGIC)

$$x = \begin{cases} 0.05305 \\ -1.178 \end{cases}$$ UNPHYSICAL/IMPOSSIBLE

NEW EQUIL POSITION

$[A]_{eq} = 0.2 - 0.053$
$= 0.147\,M$ (DECR. REL. TO 0.2)

$[B]_{eq} = 0.5 + 2(0.053)$
$= 0.606\,M$ (INCR. REL. TO 0.5)

$\frac{0.606^2}{0.147} = 2.498 \cong 2.5$ ✓

FOR GAS PHASE REACTIONS CHANGES IN VOL. MAY RESULT IN A CHANGE IN EQUIL. POSITION. THE DIRECTION OF THE CHANGE AND WHETHER THERE IS ONE AT ALL DEPENDS ON RXN. STOICH.

DECREASE IN TOTAL VOL.

ALL PARTIAL PRESSURES INCREASE. AS A RESULT THE RXN SHIFTS TOWARD THE SIDE WITH FEWER MOLES OF GAS.

FOR EX. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

FOR $-\Delta V$ ALL GASES HAVE $+\Delta P$

LET'S SAY CUT VOL. IN HALF SO ALL P. DOUBLE.

$$Q = \frac{(2P_{NH_3})^2}{(2P_{N_2})\cdot(2P_{H_2})^3} = \frac{4}{16} K_{eq}$$

$Q = \frac{1}{4}K$ SO $Q < K$

SO THE RXN SHIFTS RIGHT TOWARD FEWER MOLES OF GAS.

INCREASE IN TOTAL VOL

ALL PARTIAL PRESSURES DECREASE. AS A RESULT THE RXN SHIFTS TOWARD THE SIDE WITH MORE MOLES OF GAS.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

FOR $+\Delta V$ ALL GASES HAVE $-\Delta P$

DOUBLE VOL. THIS TIME SO ALL $P \rightarrow \frac{1}{2}P$

$$Q = \frac{(\frac{1}{2}P_{NH_3})^2}{(\frac{1}{2}P_{N_2})(\frac{1}{2}P_{H_2})^3} = \frac{1/4}{1/16} = 4K_c$$

$Q > K$

SO THE RXN SHIFTS LEFT TOWARD THE LARGER NO. OF MOLES OF GAS

NOTE: IF THERE ARE THE SAME NO. OF MOLES OF GAS AS REACTANTS AND AS PRODUCTS THEN CHANGES IN VOL DO NOT AFFECT THE EQUIL. POSITION.

FOR EX $\underbrace{CO_{(g)} + H_2O_{(g)}}_{2\,mol} \rightleftharpoons \underbrace{CO_{2(g)} + H_{2(g)}}_{2\,mol}$

M 2025-03-24 AP CHEM

CHANGING TEMPERATURE

$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$ $\Delta H = +6$ kJ/mol (ENDOTHERMIC)

$K = \frac{[H_2O\ell]}{[H_2Os]}$

FOR TEMP	Keq WILL BE	
BELOW 0°C	$K < 1$	SHIFT TOWARD SOLID
AT 0°C	$K = 1$	
ABOVE 0°C	$K > 1$	SHIFT TOWARD LIQUID

THE DIRECTION OF THE CHANGE IN THE VALUE OF K DEPENDS ON TEMP **AND** WHETHER THE REACTION IS ENDO- OR EXO-THERMIC.

ENDOTHERMIC REACTIONS $A + B + \text{HEAT} \rightleftharpoons C + D$

HEAT IS AN HONORARY REACTANT.

AS TEMP **RISES** WE SHIFT RIGHT SO Keq **INCREASES**

AS TEMP **FALLS** WE SHIFT LEFT SO Keq **DECREASES**

EXOTHERMIC REACTIONS $A + B \rightleftharpoons C + D + \text{HEAT}$

HEAT IS AN HONORARY PRODUCT

AS TEMP. **RISES** WE SHIFT LEFT SO Keq **DECREASES**

AS TEMP. **FALLS** WE SHIFT RIGHT SO Keq **INCREASES**

REGARDING CATALYSTS

CATALYSTS INCR. REACTION **RATE** BY PROVIDING AN ALT. MECHANISM BUT THEY DO **NOT** AFFECT OVERALL ΔE, WHICH IS WHAT DETERMINES THE VALUE OF Keq. REACH EQUIL. SOONER