ASIDE

1

```
do
{
  fx = ~~~
  fprimex= ~~~
  error =
  value= value-error
}
while (abs(error) > tolerance);
```

2 VARIABLE NAMES

tempF A

tempK B

$$\boxed{X_A = X_{AEQ}\left(1 - e^{-qt}\right)}$$ WHERE $q = \dfrac{k_1(\gamma+1)}{(\gamma + X_{AEQ})}$

ALSO RELATIONSHIPS, $X_{AEQ} = \dfrac{K_{EQ} - \gamma}{K_{EQ}+1}$ & $K_{EQ} = \dfrac{\gamma + X_{AEQ}}{1 - X_{AEQ}}$

COMMENTS ① IF K_{EQ} IS LARGE (ALMOST IRREVERSIBLE)

$$A \rightleftharpoons B$$

THEN $X_{AEQ} = \dfrac{K_{EQ} - \gamma}{K_{EQ}+1} \longrightarrow 1$

AND IF $X_{AEQ} \approx 1$ THEN $q = \dfrac{k_1(\gamma+1)}{\gamma + X_{AEQ}} \longrightarrow k_1$

INSERTING THESE TWO SIMPLIFICATIONS IN EQUATION ABOVE YIELDS $X_A = 1 - e^{-qt}$ SAME RESULT AS FIRST ORDER IRREVERSIBLE

AND $x_A \approx 1 - e^{-k_1 t}$ ... EXACTLY SAME RESULT THAT WE OBTAINED IN IRREVERSIBLE CASE!

(2) WE CAN USE THESE EQUATIONS IN 2 WAYS:

1A) GIVEN x_{AEQ} FIND K_{EQ}

1B) GIVEN K_{EQ} FIND x_{AEQ}

2A) GIVEN K_{EQ} & x_{AEQ} $\nearrow$ FIND x_A AT A SPECIFIC TIME

2B) $\searrow$ FIND TIME TO REACH A SPECIFIC x_A

EXAMPLE 4

THE POLLUTANT DESCRIBED IN EXAMPLE 3 ACTUALLY UNDERGOES A SLOW REVERSIBLE REACTION WITH A RATE CONSTANT (k_{-1}) OF 8.80×10^{-5} $DAYS^{-1}$.

$$A \rightleftharpoons B$$

A) HOW LONG WILL IT TAKE POLLUTANT ("A") TO FALL BELOW A CONCENTRATION OF 5.0 ppb IF $C_{B0} = 0$?

B) HOW LONG WILL IT TAKE POLLUTANT TO FALL BELOW A CONCENTRATION OF 5.0 ppb IF $C_{B0} = 1.0 \times 10^{-7}$ mol/L?

C) IF $C_{B0} = 0$, WHAT IS THE LOWEST CONC. THAT THE POLLUTANT CAN ACHIEVE?

DATA FROM EXAMPLE 3:

$k_1 = 5.20 \times 10^{-3}$ DAYS^{-1}

$C_{A0} = 8.453 \times 10^{-7}$ mol/L

$C_A(5.0_{ppb}) = 0.274 \times 10^{-7}$ mol/L

ALSO $K_{EQ} = \dfrac{k_1}{k_{-1}} = \dfrac{5.20\times10^{-3}\ day^{-1}}{8.80\times10^{-5}\ day^{-1}} = 59.1$

A) $C_{B0} = 0 \quad \gamma = \dfrac{C_{B0}}{C_{A0}} = 0$

GIVEN K_{EQ} CALCULATE $\chi_{AEQ} = \dfrac{K_{EQ} - \gamma}{K_{EQ}+1} = \dfrac{59.1}{60.1} = 0.9834$

$\chi_A = \chi_{AEQ}\left(1 - e^{-q t}\right)$ WILL SOLVE FOR t

$q = \dfrac{k_1(\gamma+1)}{\gamma + \chi_{AEQ}} = \dfrac{(5.20\times10^{-3})(0+1)}{0+0.9834} = 5.288\times10^{-3}$ DAYS^{-1}

AT "5.0 ppb"

$$\chi_A = \frac{C_{A0} - C_A}{C_{A0}} = \frac{8.453 - 0.274}{8.453} = 0.9676$$

ASIDE

THE PROBLEM COULD BE RESTATED AS

"HOW LONG WILL IT TAKE FOR χ_A TO REACH 0.9676 GIVEN THAT THE EQUILIBRIUM χ_{AEQ} IS 0.9834"

$$0.9676 = 0.9834\left(1 - e^{-5.288\times10^{-3}t}\right)$$

$$\underline{t = 781 \text{ DAYS}}$$

(COMPARE WITH ANSWER IN EXAMPLE 3)

B) $C_{B0} = 10.0 \times 10^{-7}$ mol/L $\qquad A \rightleftharpoons B$

WE HAVE TO ASK WHAT IS THE INITIAL CONC. OF "A" BEFORE THE SPILL?

ASSUME THAT "A" IS IN EQUILIBRIUM WITH "B" PRIOR TO SPILL. THE SPILL JUST ADDS TO THAT "A".

BEFORE SPILL

$$K_{EQ} = 59.1 = \frac{C_{Beq}}{C_{Aeq}} = \frac{10.0 \times 10^{-7}}{C_{AEQ}} \Rightarrow C_{AEQ} = 0.169 \times 10^{-7} \text{ mol/L}$$

AFTER SPILL

$$C_{A0} = 8.453 + 0.169 = 8.622 \times 10^{-7} \text{ mol/L}$$

SAME PROCEDURE AS IN PART A)

$$\gamma = \frac{C_{B0}}{C_{A0}} = \frac{10}{8.622} = 1.16$$

$$X_{AEQ} = \frac{K_{EQ} - \gamma}{K_{EQ} + 1} = \frac{59.1 - 1.16}{59.1 + 1} = 0.9641$$

$$q = \frac{k_1(\gamma + 1)}{(\gamma + X_{AEQ})} = \frac{(5.20 \times 10^{-3})(2.16)}{(1.16 + 0.9641)} = 5.288 \times 10^{-3}\ \text{days}^{-1}$$

$$X_A = \frac{8.622 - 0.274}{8.622} = 0.9682$$

ASIDE HOW LONG WILL IT TAKE X_A TO REACH 0.9682 GIVEN THAT THE EQUILIBRIUM X_{AEQ} IS 0.9641?