North Carolina State University   Physical Chemistry 331   Quiz #1

Name ___________________________ Section ______   Wednesday Oct. 30

1. A new fluorescent molecule called "fluoromol" is being studied by a startup company. The molecule is to be used as a label inside cells. The patent application states that the fluorescence quantum yield of the molecule is 0.98. A scientist measures the experimental lifetime for the fluorescence as one nanosecond. Please determine the fluorescence rate constant (k_f) and the internal conversion (or non-radiative decay) rate constant (k_{IC}).

Solution: $\tau_{obs} = 1$ ns $= 10^{-9}$ seconds

$k_{obs} = 1/\tau_{obs} = 10^9\ s^{-1}$. $\Phi_f = 0.98$.

Two equations: $k_{obs} = k_f + k_{IC}$, $\Phi_f = k_f/(k_f + k_{IC}) = k_f/k_{obs}$

Solve for unknowns: $k_f = \Phi_f k_{obs} = 0.98(10^9\ s^{-1}) = 9.8 \times 10^8\ s^{-1}$

$k_{IC} = k_{obs} - k_f = 10^9\ s^{-1} - 9.8 \times 10^8\ s^{-1} = 2.0 \times 10^7\ s^{-1}$

k_f = ________________________ k_{IC} = _______________________

2. A protein is observed to fold with an intermediate state called I. The experimental rate scheme is:

$$F \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} I \overset{k_2}{\rightarrow} U$$

Fill in the following blanks with the correct rate expressions:

d[F]/dt = ______ $-k_1[F] + k_{-1}[I]$ _______________.

d[I]/dt = ______ $k_1[F] - (k_{-1} + k_2)[I]$ _____________.

d[U]/dt = ______ $k_2[I]$ _________________________.

In this scheme the rate constant $k_2 >> k_1$ and $k_2 \sim k_{-1}$. Write an expression for the rate of unfolding (d[U]/dt) in terms of only the concentration of the folded molecule [F].

Solution: Apply the steady-state approximation

$k_1[F] - (k_{-1} + k_2)[I] = 0$

$[I] = k_1[F]/(k_{-1} + k_2)$

Substitute this into: $d[U]/dt = k_2[I]$

d[U]/dt = _____ $k_1k_2/(k_{-1} + k_2)$ [F].

3. Double helical DNA from a 20-mer is formed with an observed rate constant of $1.1 \times 10^5\ s^{-1}$ and free energy of -5.733 kJ/mol. The equilibrium is 2 ssDNA $\leftrightarrow$ dsDNA.
   a. Calculate the equilibrium constant at 300 K.

$K = \exp\{-\Delta G^o/RT\} = \exp\{-(-5733 \text{ J/mol})/(8.31 \text{J/mol-K})(300 \text{ K})\}$
$= \exp\{2.299\} = 9.964 \sim 10$

K = __10______________________.

b. Calculate the folding rate constant.

Two equations: $k_{obs} = k_h + k_d$, $K = k_h/k_d$
Solve: $k_d = k_h/K$, $k_{obs} = k_h + k_h/K$, $k_{obs} = k_h(1+ 1/K)$, $k_h= k_{obs}/(1+ 1/K)$
Substitute: $k_h= k_{obs}/(1+ 1/K) = 1.1 \times 10^5 \text{ s}^{-1}/1.1 = 10^5 \text{ s}^{-1}$

k_h = ____10^5 s^{-1}__________________.