CHEM 130 **Name** ______________________________

Quiz 5 – July 21, 2016

Complete the following problems. You must show your work to receive full credit. Show your answers to the correct number of significant figures with the correct units.

1. The initial rate for the reaction A + B → C + D is determined for different initial conditions, with the results below. Determine the rate law and the value of the rate constant for the reaction. (9 points)

Expt.	**[A], M**	**[B], M**	**Initial Rate, Ms^{-1}**
1	0.185	0.133	3.35×10^{-4}
2	0.185	0.266	1.35×10^{-3}
3	0.370	0.133	6.75×10^{-4}
4	0.370	0.266	2.70×10^{-3}

From Expt. 1 to Expt. 3, [A] is doubled, while [B] remains fixed. This causes the rate to increases by a factor of $\frac{6.75\times10^{-4}\ \text{M s}^{-1}}{3.35\times10^{-4}\ \text{M s}^{-1}} = 2.01 \approx 2$.

Thus, the reaction is first-order with respect to A.

From Expt. 1 to Expt. 2, [B] doubles, while [A] remains fixed. This causes the rate to increases by a factor of $\frac{1.35\times10^{-3}\ \text{M s}^{-1}}{3.35\times10^{-4}\ \text{M s}^{-1}} = 4.03 \approx 4$.

Thus, the reaction is second-order with respect to B.

Overall reaction order = order with respect to A + order with respect to B = 1 + 2 = 3. The reaction is third-order overall.

$$\text{Rate} = 3.35\times10^{-4}\ \text{M s}^{-1} = k(0.185\ \text{M})(0.133\ \text{M})^2$$

$$k = \frac{3.35\times10^{-4}\ \text{M s}^{-1}}{(0.185\ \text{M})(0.133\ \text{M})^2} = 0.102\ \text{M}^{-2}\ \text{s}^{-1}$$

2. The *half-life* (denoted $t_{1/2}$) is the time it takes for the concentration of a reactant to be decreased to half of its original value. Mathematically, after one half-life $[R] = ½ [R]_0$. Consider the integrated rate law for a first order reaction. If the half-life of the reaction is 949 seconds, what is the rate constant for the reaction (with appropriate units)? (8 points)

The integrated rate law for a first order reaction is $\ln[R]_t = -kt + \ln[R]_0$. From the problem, we are told that at t=949 seconds, the $[R]_t = ½ [R]_0$. Inserting these values into the rate law:

$$\ln(0.5[R]_0) = -k(949\ \text{s}) + \ln[R]_0$$

We do not know $[R]_0$ explicitly, but we can use the rules of logarithms to simplify the expression:

$$\ln(0.5) + \ln[R]_0 = -k(949\ \text{s}) + \ln[R]_0$$

Subtracting $\ln[R]_0$ from both sides:

$$\ln(0.5) = -k(949\ \text{s})$$

Rearranging:

$$k = -(\ln(0.5))/(949\ \text{s}) = \mathbf{7.30 \times 10^{-4}\ s^{-1}}$$

3. If even a tiny spark is introduced into a mixture of H_2(g) and O_2(g), a highly explosive exothermic reaction occurs. Without the spark, the mixture remains unreacted indefinitely. Explain this observation in terms of the reaction thermodynamics and kinetics. A reaction coordinate diagram may be useful.(8 points)

The activation energy for the reaction of hydrogen with oxygen is quite high, too high, in fact, to be supplied by the energy ordinarily available in a mixture of the two gases at ambient temperatures. However, the spark supplies a suitably concentrated form of energy to overcome the activation barrier and initiate the reaction of at least a few molecules. Since the reaction is highly exothermic, the reaction of these first few molecules supplies sufficient energy for yet other molecules to react and the reaction proceeds to completion or to the elimination of the limiting reactant.

Possibly Useful Information

R = 0.08206 L atm mol^{-1} K^{-1} R = 8.314 J mol^{-1} K^{-1}	$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$	$k = Ae^{-E_a/RT}$
rate = $k[A]^0$	rate = $k[A]^1$	rate = $k[A]^2$
$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.00794																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 †Ac 227.028	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)							

*Lanthanide series	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)