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rate equation and constant rate. Experience 1 – 3 would be sufficient to answer the questions posed. 10. In the reaction A → product, we find that when [A] has fallen to half of its initial value, the reaction continues at the same rate as its initial rate. Do order zero reaction, first order, or Order? Explain. Since the percentage has not changed as a two-time function, the reaction must be order zero. 11. In the reaction, a → product, and the initial concentration [A]0 = 1.512M, [A] were found to be 1.496M at t = 30 s. With the initial concentration [A]0 = 2.584M, [A] was found to be 2.552 M at t = 1 min. What is the order of this reaction? First, get the rate of reaction in each experience, being sure to be consistent in their units. Then use the Initial Rate Method to get the order of reaction. Experience [A]0(M)[A](M) of t(s)Percent(s-1) 1.512 1.496 of 30 s 2.584<2.552 in 60 since rates are the same for both experiments, the reaction must be order zero. Mathematically: , which can only be true for i = 0. 12. A reaction first order, A product →, has a percentage of reactions 0.00250 M s-1 when [A]=0.484 M.(A) What is the constant constant, k, for this reaction? (B) Does t3/4 depend on the initial concentration? Is t4 / 5? Explain. (A) For an initial order reaction, Percentage = which [A]. Since the rate and concentration are known, resolve the equation to give the requested response. Ki = Percentage/[A] = 0.00250M s-1/0.0484M = 5.17×10-3 s-1. (b) Neither t3/4 or t4/5 depends on initial concentration because this is a first order reaction, which means that the associated time reaction is simply related to the percentage constant. 13. In the first-order decomposition of dinitrogen pentoxid of 335 K, N2O5(g) → 2 NO2(g)+1/2 O2(g) if we start with a 2.50-g sample of N2O5 at 335 K and have 1.50 g remaining after 109 s, (a) What is the value of the constant constant? (B) What is the half-life reaction? (C) Which mass N2O5 will remain after 5.0 min? Since the concentration unit is canceled out, we can work directly in grams for this issue.(A)[N2O5]0=2.50g/[N2O5]t=1.50g, t = 109 s, so that = 4.69×10-3 s-1 (b)t1/2=0.693/ki=0.693/4.69×10-3=148 s.(c)=5.0 min=300. so is 14. Smog constituent peoxycetyl nitate (PAN) dissociates of radical peroxyacetyl and NO2(g) in a first order reaction with a half-life in 32 min. If the initial concentration of panes in a sample when the 2.7×1015 molecule/L, what will be the 2.24h concentration later? For a first order reaction, the integrated rate law is and the constant rate can be found in half the lifetime: . So that =0.693/t1/2=0.693/32=0.022 min-1. For an initial concentration [PAN]0=2.7×1015 molecule/L and at t = 2.24h = 134 min: [PAN]= [PAN]oe -kt = (2.7×1015)e-(0.022)(134) = 1.4×1014 molecules / L. 15. The following data were found in two separate experiences of the reaction: a → product. Determine the rate law for this reaction, including the value of k. Experience 1 Experience 2 [A] Time(M) Time(s)[A] Time(s) 0.800 0.400 0.775 40 0.390 64 0.0750 0.380 132 0.725 129 0.370 203 0.700 179 0.360 278 Act of General Rate is Percentage = The method of initial rates can be used to establish the order of reaction and provide an estimate of the percentage constant. The initial percentage is found in the first two points of each experience: Use the initial concentrations and the initial rates: So this is a second order reaction. The rate constant can be estimated from which = - Missed/[A]2 per experience: which (OS 1) = -(6.25×10-4) / [0.800] 2 = 9.8×10-4 M-1-1 and (display. 2) =-(1.56×10-4)/[0.400]2=9.8×10-4 M-1 s-1. Which = 9.8×10-4 M-1 s-1 Confirm this and get a better value for the percentage constant, a tablet of [A]-1 vs. t should be linear with a slope equal to the constant rate: the slopes in these polls show that a better value for the constant is that = 1.0×10-3 M-1 s-1. 16. The list below are first rates, expressed in terms of the rate of decreased partial pressure of a reaction reaction to this reaction to 826°C. Determine the rate law for that reaction, including the value for k.NO(g)+H2(g) → 1/2N2(g)+H2O(g) With first PH2 = 400 mmHg and first PNO = 400 mmHg In Initial PNO(mmHg) Percentage(mmHg/s) First PH2(mmHg) Percentage (mmHg) Percent (mmHg) Percent (mmHg/s) Percentage(mmHg) Percentage(mmHg/s) Percentage(mmHg)First PH2(mmHg) Rate(mmHg/s) Percent (mmHg/s) Percent (mmHg)Percent (mmHg) Percentage(mmHg) Percentage(mmHg)Rate(mmHg)Rate(mm) Percent (mmHg) Rate(mm) Percent (mmHg) Percent (mm) Percentage(mmHg)Percent (mmHg) Percent (mmHg) Percentage(mmHg)Percent (mmHg) Percent (mmHg) Percentage(mmHg/s) Prime PH2 (mmHg) Percentage (mmHg) Percentage (mmHg/s) Initial PH2(mmHg/s) 359 0.750 289 0.800 300 0.515 205 0.550 152 0.125 147 0.395 The Unknown Law provided by Percentage=K[NO][M][H2]n. Use the Method of Initial Rate shall be awarded the percentage law and the value of the percentage constant. Since units are canceled in Initial Rate Methods, we do not need to convert to molarities. To get the order of NO, use the first set of data where the pressure of H2 is maintaining constants. Experience 2 and 3 are on a factor of 2 differences at first pressure in NO, so will provide easier numbers to work with: In experimental errors, i=2, or second order in NO. To get the order of H2, use handlers 1 and 3 for the easiest numbers: In experimental error, n=1, or first order of H2. The rate constant can now be found from the rate law: ki = Rate/[NO]2[H2] for each experiment: Initial PH2 (mmHg) Initial PNO (mmHg) Initial Rate (mmHg/s) ki (mmHg-2 s-1) 400 359 0.750 (0.750)/(400)(359)2 = 1.45×10-8 400 300 0.515 (0.515)/(400)(300)2 = 1.43×10-8 400 152 0.125 (0.125)/(400)(152)2 = 1.35×10-8 289 400 0.800 (0.800)/(289)(400)2 = 1.73×10-8 205 400 0.550 (0.550)/(205)(400)2 = 1.68×10-8 147 400 0.395 (0.395)/(147)(400)2 = 1.68×10-8 Averaging all of the ki values gives ki = 1.55×10-8 mmHg-2 s-1 17. Constant rate for the first-order decomposition of acetonedicarboxylic acid CO (CH2COOH) 2 (aq) → CO(CH3)2(aq) +2 CO2(g)acetonedicarboxy Asdacetone s are = 4.75 ×10-4 s-1 of 293 K and 1.63 ×10-3 in 303 K. Which activation energy, Ea, for that reaction Use the two-point form of the Arrhenius equation to answer this question: where k2=1.63×10-3 in T2=303 K and k1=4.75×0-4 of T1=293 K.18. The following is proposed as a plausible reaction mechanism: Abe B<8> my → (slow) i + B → C + D (fast) What is the permanent reaction described by this mechanism and (b) a plausible rate law for the reaction? (A) To get the net reaction, sum up all the reactions of the mechanism and eliminate common species on each side of the equation: A + B + I + B + B →I + C + D net: A + 2B → C + D (B) Is the rate law determined by the slow step of the reaction mechanism. Since it is a composite reaction mechanism of elementary reactions, the rate law for steps slowly can be written by inspection, and the orders of reactions have been the stoichiometric coefficient: percentage = which [A][B]19. This reaction exposes the rate law: Percentage = which [NO]2[Cl2]. 2 NO (g) + Cl2(g) → NOCL(g) Explain why this mechanism is not plausible for this reaction. NAME(g) + Cl2 → → NOCL(g) + Cl(g) Fast NO(g) + CL(g) → NOCL(g)Slow The Slow Act determined by the slow step: Percentage = Kslow[NAME][Cl] However, This law includes and intermediates who cannot be part of the rate law for overall reactions – only NO or Cl2 may be part of the rate law. The term [Cl] can be eliminated using the fast, reversible step where the percentage of the front reaction is the same as the percentage of the reverse reaction: Rateforward =Rateverse Rateforward=kforward[NO][Cl]2 Ratereverse=Premierevers Premiereverse [NOCl] [Cl] so kforward [NO][Cl]2=kreverse[NOCl] replacement for [Cl] at the slow stage rate provided: This rate doesn't match the experimental law so this may not be a plausible mechanism. 20. Show that the proposed mechanism is consistent with the rate law for this reaction to aqueous solutions, Hg22+ (aq) + Ti3 + (aq) → 2 Hg2+ (aq) + Ti+ (aq) for which rate laws observe the proposed Mechanism: Hg2+ (aq) → → Hg2 + (aq) + Hg(s) Fast Hg(s) + Ti3 + (aq) → Hg2 + (aq) + Ti + (aq) Slow First, check to see that the proposed mechanism matches the experimental stoichiometry. Add two reactions together provided: Hg22+(aq) + Hg(s) + Ti3 + (aq) → Hg2 + (aq) + Hg(s) + Hg2 + (aq) + Ti + (aq) Hg(s) common to both sides of the equation are canceled out and the two moles of Hg2+ (aq) can be collected to provide the observed reaction, so matches the stoichiometry. The proposed mechanism can be recruited as Hg22+(aq) → K1 Hg2+ (aq) + Hg(s) Percentage = k1 [Hg22+](Fast) Hg2+(aq) + Hg(s) → k-1 Hg22+(aq) Rates = k-1 [Hg2+ [Hg2+ [Hg] (fa)g](fa)Hg(s)+Ti3+(aq) → k2 Hg2+(aq)+Ti+(aq) Percentage=k2[Hg2+][Hg](slow) Percentage in general determined by the slow stage, but this has an intermediary ([Hg]) that must be eliminated in order to evaluate the mechanism. This can be done using the following two fast steps, which must have roughly the same rate, or k1[Hg22+]=k-1 [Hg2+][Hg] so [Hg]=k1[Hg22+]/k-1[Hg2+] using the following expression in law the rate slows =k2[Hg2+][k1[Hg22+]/k-1[Hg2+] or Percentage =(k2k1/k-1) [Hg22+ [Hg22+]/[Hg22+] which matches the observed law when wa == 21. Benzenediazonium chlorium decomposed in water bay N2(g). C6H5N2Cl(aq) → C6H5Cl(aq) + N2(g) The data set below is found for the decomposition of a solution 0.071M to 50°C (t = ∞ match the completed reaction). To get [C6H5N2Cl] as a two-time function, remember that during the first 3 min, the volume of N2(g) generated was 10.8 mL at a total of 58.3 mL, corresponding to this fraction of the total reaction: 10.8 mL/58.3 mL = 0.185. An equal fraction of the available C6H5N2Cl was consumed during the same time.time(min)N2(g)(mL) 00 310.8 619.3 926.3 1232.4 1537.3 1841.3 3 2144.3 2446 5.2748.4 3050.4 ≈58.3 (a) Plot Graphs showing extinction of C6H5N2Cl and the training of N2(g) as a function of time. (b) What is the initial rate of formation N2(g)? (C) What is the rate of extinction of C6H5N2Cl in t = 20 min? (D) What is the half-life, t1/2, of the reaction? (e) Write the rate law for this reaction, including a value for k. (a) First, find the concentrations of C6H5N2Cl remaining at each time: time (min)N2(g) (mL) fraction N2 = mL/58.3 mL C6H5N2Cl (M) = 0.071×(1 – fraction) 00 0/58.3 = 0.00 0.071(1 – 0) = 0.071 310.8 10.8/58.3 = 0.185 0.071(1 – 0.185) = 0.058 619.3 19.3/58.3 = 0.331 0.071(1 – 0.331) = 0.047 926.3 26.3/58.3 = 0.451 0.071(1 – 0.451) = 0.039 1232.4 32.4/58.3 = 0.556 0.071(1 – 0.556) = 0.032 1537.3 37.3/58.3 = 0.640 0.071(1 – 0.640) = 0.026 1841.3 41.3/58.3 = 0.708 0.071(1 – 0.708) = 0.021 2144.3 44.3/58.3 = 0.760 0.071(1 – 0.760) = 0.017 2446.5 46.5/58.3 = 0.798 0.071(1 – 0.798) = 0.014 2748.4 48.4/58.3 = 0.830 0.071(3 – 0.830) = 0.012 3050.4 50.4/58.3 = 0.864 0.071(1 – 0.864) = 0.0097 ≈58.3 58.3/58.3 = 1.00 0.071(1 – 1.00) = 0.00 The plots are : (B) From the definition of percentage, (c) Again, using percentage definition and approximation t = 20 min using the t = 18 min and t = 21 min points. (D) The initial concentration of benzenediazonium chloride is 0.071 M, so the first half-life occurs when the concentration occurred at 0.0355 M. Use the graph from part(a) to give t1/2–10 min. (e) The order of the reaction can be determined by looking at the time of the second half-life, when the concentration of benzenzenediaum chloride was reduced to 1/2 of its initial value, 0.018 M. This happens at ~21 min, just twice the time for the first half of life. Since t1/2 is the same for the two different time intervals, it means that the reaction is first ordered. Percentage = K[C6H5N2Cl] Plotting ln [C6H5N2Cl] vs. t confirms this with the slope of the trace given the percentage constant, k. The slope of the vote = - 0.0664, so that = 0.0664 min -1. (This allows a better estimate of half the life to be t1/2=0.693/ki=0.693/0.064=10.4 min). 22. Hydroxide ion involves the mechanism, but not consumed in this reaction to aqueous solutions. OCl-(aq) + I-(aq) → OH-(aq) + HOCl(aq) (A) From the data in the table, determine the order of reaction with respect to OCl-, I-, and OH-, and the overall order. [OCl-] (M) [I-] (M) [OH-] (M) Rate of formation of OI- (mol L-1 s-1) 0.00400.0020 1.00 4.8×10-4 0.00200.0040 1.00 5.0×10-4 0.00200.0020 1.00 2.4×10-4 0.00200.0020 0.50 4.6×10-4 0.00200.0020 0.25 9.4×10-4 (b) Write the rate law, and determine the value of the rate constant, k. (c) Show that the following mechanism is consistent with the net equation and with the rate law. Which is the rate-determining stage? OCl-(aq) + H2O(l) → → HOCL(aq) + OH -(aq) -(aq) -(aq) + HOCL(aq) → HOI(aq) + Cl -(aq) -(aq) HOI(aq) + OH -(aq) → H2O(l) + OI -(aq) (d) Is it appropriate to refer to the OH - as a catalyst to this reaction? Explain. (A) Use the initial percentage method for a general law rate = which [OCl-m][I] [n][OH-jp. Experience 1 and 3 order the order of hypochrites ion (iodoxide and hydroxide are constant): doubling the concentration of hypochrites doubles the initial rate, meaning that the reaction is 1st order in hypochrites ion, i = 1. Experience 2 and 3 can be used to find the order of iodide ion (hypochlority and hydroxide are changed): doubling half the concentration, so the order of hydroxide must be -1, p = -1. Mathematically: The overall order is the sum of each individual order = 1 + 1 + -1 = 1 (b) Based on order found above, The percentage law is: The constant rate case using the Rate Act and the data: [OCl-](M)(M)[OH-(M) Percentage of OI- (mol L-1 s-1) 0.04 billion20.020 1.48× 0.00-00-0. 4 60.0 s =10.0020.00 1.00 5.0×10-4 62.5 s =10.0020.0020 1.00 2.4×10-460.0-1 0.02020.020 0.50 4.6×10-4 57.5 s =10.0020.020 25.4×10-4 58.75s = 1 Constant average (at the correct number of important figures) = 60. s-1 (c) first, add all the equations of the mechanism together to see if the stoichiometry of the mechanism is correct: OCl-(aq →-) + H2O(l) + I-(aq) + HOCL (aq) + HOI(aq) + OH (aq) + HOC LL(aq)K+OH(aq)+HOI(aq)+Cl-(aq)+H2O(l)+OI-(aq) After eliminating common species: OCl-(aq)+I-(aq) → OI-(aq) + Cl-(aq) which is the correct stoichiometry. To obtain the rate-determining step, consider the percentage law for each elementary reaction: Step 1, Forward reaction: Percentage = kforward [OCl-][H2O] Step 1, reverse reaction: Percentage = kreverse [HOCI][OH-] Step 2: Percentage = k2[I][HOCL] Step 3: Percentage = k3[I][HOI][OH]Step 1, ahead there are not enough terms of the rate act. Step 1, reverse and Step 3 both have hydroxide in the numerator but the experimental law in the denominator. This left Step 2 as the step is likely to slow down, but this has an intermediary that must be eliminated using Step 1, suppose it to be a fast step: For step 1, Rateforward = Raterverse is so kforward [OCl-][H2O]=kreverse[HOCI][OH-] Resolve for the intermediary, [HOCI] provided: This replacement of the law for step 2 , the proposed slow step, provided: Since the water is solvent, its concentration has not changed and should be grouped with the constants: This currently matched the experimental rate law. (D) Since hydroxide is found in the denominator of the rate law, an increase in concentrations slows the reaction down so OH – is an inhibitor, not a catalyst. Compare handlers 3, 4, and 5 to see how to reduce the hydroxide to increase the reaction rate.rate.

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