Consider the following reaction for the next three questions:

$$BrO_3^-(aq) + 5\,Br^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

1. If at given moment in time, the rate of change of Br_2, $\Delta[Br_2]/\Delta t = 6.0\times10^{-4}$ M/s, what is the rate of change of Br^- at the same time? since Br^- is a reactant its conc. should be decreasing so expect a negative rate of change

(a) ~~1.0×10^{-3} M/s~~ (b) ~~3.6×10^{-4} M/s~~ [✓ (c) -1.0×10^{-3} M/s] (d) -3.6×10^{-4} M/s
(e) -3.0×10^{-3} M/s

$$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t}$$

$$\frac{\Delta[Br^-]}{\Delta t} = -\frac{5}{3}\frac{\Delta[Br_2]}{\Delta t} = -5/3\,(6.0\times10^{-4}\,M/s)$$

$$= \boxed{-1.0\times10^{-3}\,M/s}$$

2. The rate law for this reaction has been determined to be

$$\text{rate} = k\,[BrO_3^-]^{1}[Br^-]^{1}[H^+]^2$$ add up exponents $1 + 1 + 2 = 4$

What is the kinetic order of the reaction?

(a) 1st (b) 2nd [✓ (c) 4th] (d) 6th (e) 12th

3. The rate of the reaction at a particular temperature has been determined to be 8.0×10^{-4}M/s when $[BrO_3^-] = [Br^-] = [H^+] = 0.10$ M. What is the value of the rate constant at this temperature?

[✓ (a) 8.0 $M^{-3}s^{-1}$] (b) $1.25\times10^{-4}\,s^{-1}$ (c) $8.0\times10^{-3}\,s^{-1}$ (d) 0.125 $M^{-3}s^{-1}$
(e) 8.0 M^4s^{-1} (ab) 0.125 M^4s^{-1}

$$\text{rate} = k\,[BrO_3^-][Br^-][H^+]^2$$

$$k = \frac{\text{rate}}{[BrO_3^-][Br^-][H^+]^2} = \frac{8.0\times10^{-4}\,M/s}{(0.10\,M)(0.10\,M)(0.10\,M)^2}$$

$$= \frac{8.0\times10^{-4}\,M/s}{(0.10\,M)^4}$$

$$= \boxed{8.0\,\frac{1}{M^3\cdot s}}$$

4. The following data were obtained at 25 °C for the reaction shown below.

$$2\,HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2\,Cl^-(aq) + 2\,CO_2(g) + Hg_2Cl_2(s)$$

run	initial [$HgCl_2$], M	initial [$C_2O_4^{2-}$], M	inital rate, M/s
1	0.10	0.10	1.3×10^{-7}
2	0.10	0.20	5.2×10^{-7}
3	0.20	0.20	1.0×10^{-6}

What is the rate law for this reaction?

(a) rate = $k[HgCl_2]^2$
(b) rate = $k[HgCl_2]^2[C_2O_4^{2-}]^2$
(c) rate = $k[HgCl_2][C_2O_4^{2-}]$
[✓ (d) rate = $k[HgCl_2][C_2O_4^{2-}]^2$]
(e) rate = $k[HgCl_2]^2[C_2O_4^{2-}]$

$\text{rate} = k[HgCl_2]^x[C_2O_4^{2-}]^y$

to determine x, compare runs 2 & 3 ([$HgCl_2$] varies, but [$C_2O_4^{2-}$] stays same)

$$\frac{[HgCl_2]_3}{[HgCl_2]_2} = \frac{0.20M}{0.10M}^x = 2^x = \frac{1.0\times10^{-6}}{5.2\times10^{-7}} = 1.9 \sim 2$$

$$2^x = 2 \Rightarrow \boxed{x = 2}$$

to determine y, compare runs 1 & 2 ([$C_2O_4^{2-}$] varies but [$HgCl_2$] stays same)

$$\frac{[C_2O_4^{2-}]_2}{[C_2O_4^{2-}]_1} = \frac{0.20^y}{0.10^y} = 2^y = \frac{5.2\times10^{-7}}{1.3\times10^{-7}} = 4$$

$$2^y = 4 \Rightarrow \boxed{y = 2}$$

5. What would happen to the rate of the reaction in the previous question if it were run at a higher temperature?

(a) The reaction would go slower.
[✓ (b) The reaction would go faster.]
(c) The reaction would proceed at the same rate.
(d) More information is needed in order to answer this question.

rxns always go faster at a higher T

6. A particular herbicide is known to decompose in the environment by a first order process with a rate constant of 3.50×10^{-3} hr^{-1}, how many days will it take for 90.0% of the herbicide to decompose?

(a) 11.9 days
(b) 0.19 days
(c) 1.25 days
(d) 8.85×10^{-3} days
[✓ (e) 27.4 days]

10% remains

Use 1st order integrated rate law

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \Rightarrow t = \frac{-1}{k}\ln\left(\frac{[A]_t}{[A]_0}\right)$$

$$= \frac{-1}{3.5\times10^{-3}\,hr^{-1}}\ln(0.10) = 657.9\ hrs$$

$$657.9\ hrs \times \frac{1\,day}{24\,hrs} = \boxed{27.4\ days}$$

7. For the following reaction, 3 $BrO^-(aq) \rightarrow BrO_3^-(aq) + 2\,Br^-(aq)$, a plot of $1/[BrO^-]$ vs. time is linear. What is the kinetic order of the reaction?

(a) 1st
[✓ (b) 2nd]
(c) 3rd
(d) 4th
(e) none of the above

this is the test to see if it obeys the 2nd order integrated rate law:

$$\underset{y}{\frac{1}{[A]_t}} = \underset{b}{\frac{1}{[A]_0}} \underset{+\,mx}{+\,kt}$$

Since you get a straight line, it evidently does.

8. Two reactant molecules collide with an energy greater than the activation energy for a reaction that can take place between the molecules. Will the reaction occur? Choose the one best answer.

(a) Yes.
(b) No.
[✓ (c) Maybe. In general, the molecules also must collide in a specific orientation in order for a reaction to take place.]
(d) Maybe. The reaction will take place if the collision frequency is greater than the frequency factor.
(e) Probably not. A collision between three reactant molecules is generally required for a reaction to occur.

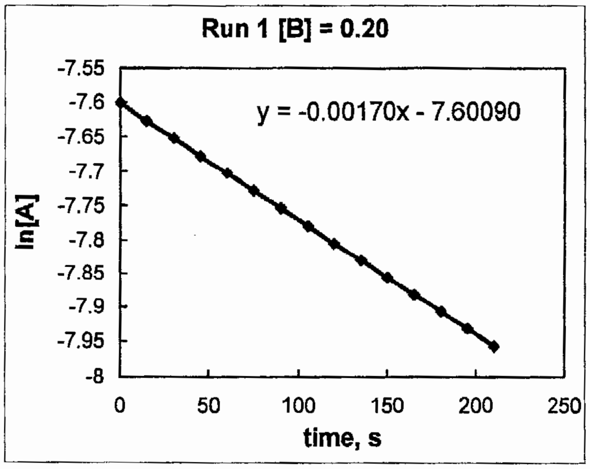
9. The kinetics of the reaction A + B → C were studied by measuring the concentration of A as a function of time starting with the following concentrations:

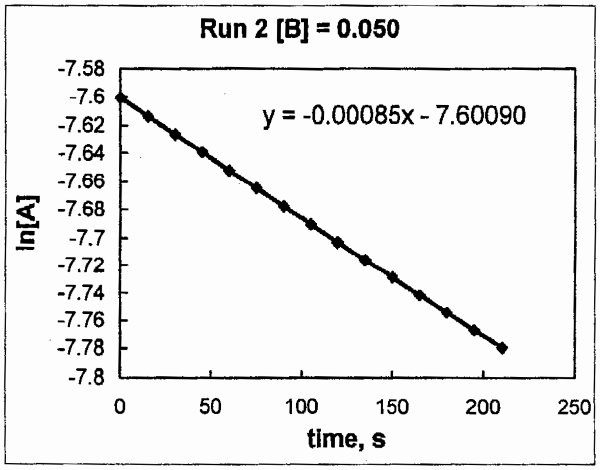
Run	[A], M	[B], M
1	5.0×10^{-4}	0.20 M
2	5.0×10^{-4}	0.050 M

← pseudo order conditions

↑ in excess

The following plots were made from the data:





Based on the above plots, what is the rate law and the value of the true rate constant for this reaction?

(a) rate = $k[A]^2[B]^{1/2}$; $k = 263\ s^{-1}$
(b) rate = $k[A]$; $k = 0.00085\ {}^{2}s^{-1}$
(c) rate = $k[A]^2[B]^2$; $k = 0.0017\ M^{-3}s^{-1}$
[✓ (d) rate = $k[A][B]^{1/2}$; $k = 0.0038\ M^{-1/2}s^{-1}$]
(e) rate = $k[A][B]^2$; $k = 0.00085\ M^{-2}s^{-1}$

$$\text{rate} = \underbrace{k[B]^y}[A]^x$$

Since [B] is in such a large excess its conc. will remain ~ constant

$$\text{rate} = k_{obs}[A]^x$$

Since ln[A] vs t gives a straight line, the behavior is first order and you know x = 1 — from slope of plot

so

$$\text{rate} = k_{obs}[A]$$

$$\frac{\text{run 1}\ k_{obs}[B]^y}{\text{run 2}\ k_{obs}[B]^y} = \frac{0.00170}{0.00085} = \frac{\cancel{k}[0.20]^y}{\cancel{k}[0.050]^y}$$

$$2.0 = 4^y$$

$$\log 2 = y \log 4$$

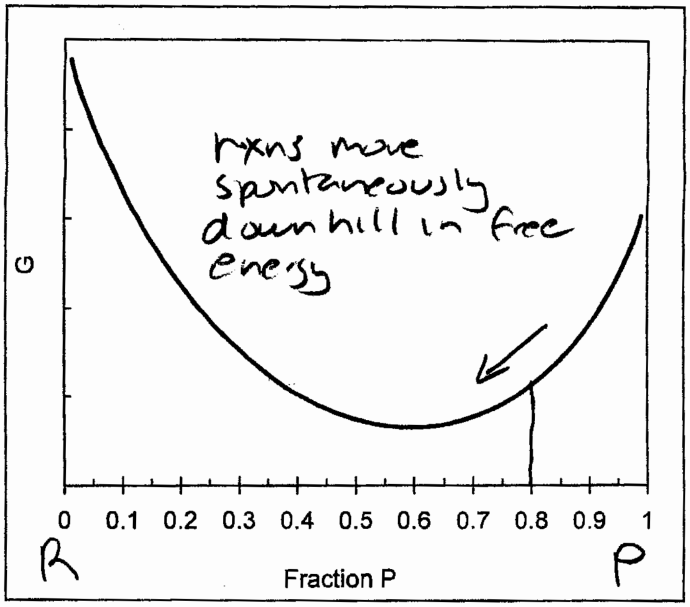
$$y = \frac{\log 2}{\log 4} = 0.5$$

so overall $\boxed{\text{rate} = k[A][B]^{1/2}}$

so $0.00170 = k[0.20]^{0.5}$

$$k = \frac{0.00170\ 1/s}{(0.20M)^{0.5}} = \boxed{3.8\times10^{-3}\frac{1}{M^{1/2}s}}$$

Consider the adjacent free energy diagram for the reaction R → P. The X axis gives the fraction of product, P, in the reaction mixture. For example, when the fraction of P = 0.20, the reaction mixture contains 20% P and 80% R. P = 0 means only R is present and P = 1 means only P is present.



10. According to the diagram, which of the following is TRUE when the fraction of P = 0.8?

(a) The reaction will spontaneously move in the direction R → P.
[✓ (b)] The reaction will spontaneously move in the direction P → R.
(c) The reaction is at equilibrium.

11. Based on the diagram, what is the value of the equilibrium constant for the reaction?

(a) 0.50 (b) 1.0 (c) 0.67 (d) 1.7 [✓ (e)] 1.5

equilibrium lies at the minimum in free energy where Fraction P = 0.6
(so fraction R = 0.4)

$R \rightleftharpoons P$

$$K = \frac{P}{R} = \frac{0.6}{0.4} = \boxed{1.5}$$

12. Which **TWO** of the following are TRUE for an oxidation reaction? (Mark two answers on your scantron.)

(a) Electrons are consumed. (They are a reactant.)
[✓ (b)] Electrons are produced. (They are a product.)
[✓ (c)] The oxidation number of at least one atom will increase in going to products.
(d) The oxidation number of at least one atom will decrease in going to products.
(e) The oxidation numbers will not change in going from reactants to products.

Consider the following reaction for the next three questions. The overall *unbalanced* reaction occurring in the lead acid (car) battery during discharge is

$$\overset{0}{Pb(s)} + \overset{+4}{PbO_2(s)} + \underset{-2}{SO_4^{2-}(aq)} \rightarrow \overset{+2}{PbSO_4(s)}$$

13. What is the oxidation number of Pb in PbO_2?

$+4-4=0$

(a) 0 (b) +2 [✓ (c) +4] (d) −2 (e) −4

14. What is being oxidized in this reaction?

[✓ (a) Pb] (b) PbO_2 (c) SO_4^{2-} (d) $PbSO_4$

$Pb^0 \rightarrow Pb^{2+}$ (in $PbSO_4$)

15. What is the balanced reduction half reaction in acid?

(a) $PbO_2(s) + SO_4^{2-}(aq) + 2\,H^+(aq) + e^- \rightarrow PbSO_4(s) + H_2O_2(l)$

(b) $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2\,e^-$

(c) $PbO_2(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + O_2(g) + 2\,e^-$

(d) $PbO_2(s) + SO_4^{2-}(aq) + 2\,H^+(aq) + 2\,e^- \rightarrow PbSO_4(s) + H_2O(l)$

[✓ (e) $PbO_2(s) + SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \rightarrow PbSO_4(s) + 2\,H_2O(l)$]

reduction half rxn involves

$SO_4^{2-} + \overset{+4}{PbO_2} \rightarrow \overset{+2}{Pb}SO_4$ Pb balanced (, SO_4^{2-})

$SO_4^{2-} + PbO_2 \rightarrow PbSO_4 + 2H_2O$ O balanced

$\underbrace{SO_4^{2-} + PbO_2 + 4H^+}_{+2} \rightarrow \underbrace{PbSO_4 + 2H_2O}_{0}$ H balanced

$$\boxed{PbO_2(s) + SO_4^{2-}(aq) + 4H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O}$$

Consider the following electrochemical cell for the next two questions:

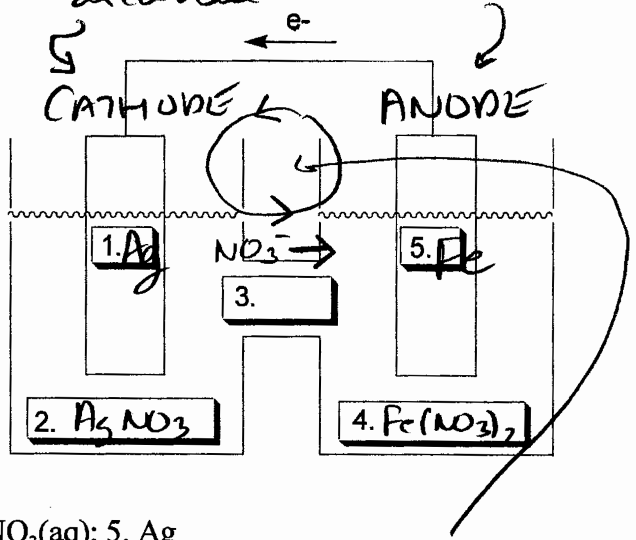
ANODE CATHODE

$Fe / Fe(NO_3)_2(aq) // AgNO_3(aq) / Ag$

e^- are consumed at cathode

e^- are produced @ anode

16. The diagram to the right shows a physical representation of the cell. Fill in the blanks to indicate where the different components are located and in what direction ions are flowing between compartments when current is flowing. **HINT: Look at the direction of e– flow to tell which electrode is the anode and which is the cathode.**



charge has to flow in a continous loop

(a) 1. Fe; 2. $Fe(NO_3)_2(aq)$; 3. $\leftarrow NO_3^-$; 4. $AgNO_3(aq)$; 5. Ag

(b) 1. Fe; 2. $Fe(NO_3)_2(aq)$; 3. $NO_3^- \rightarrow$; 4. $AgNO_3(aq)$; 5. Ag

(c) 1. Ag; 2. $AgNO_3(aq)$; 3. $\leftarrow NO_3^-$; 4. $Fe(NO_3)_2(aq)$; 5. Fe

[✓ (d)] 1. Ag; 2. $AgNO_3(aq)$; 3. $NO_3^- \rightarrow$; 4. $Fe(NO_3)_2(aq)$; 5. Fe

(e) 1. Ag; 2. $Fe(NO_3)_2(aq)$; 3. $NO_3^- \rightarrow$; 4. $AgNO_3(aq)$; 5. Fe

17. What is E°cell?

[✓ (a)] 1.25 V (b) 0.35 V (c) –1.25 V (d) 0.03 V (e) –0.03 V

Cathode half rxn E°

$Ag^+ + e^- \rightarrow Ag(s)$ 0.80V

Anode half rxn

$Fe^{+2} + 2e \rightarrow Fe(s)$ −0.45V

$$E^\circ_{CELL} = E^\circ_{CAT} - E^\circ_{AN} = 0.80 - (-0.45)$$
$$= \boxed{1.25V}$$

18. K for the following reaction is 22.5 at 25 °C. If this reaction was the overall reaction occurring in an electrochemical cell, what would be E°cell at 25 °C?

$$\mathrm{Fe(s)} \overset{2e^-}{\curvearrowright} + \mathrm{Cd^{2+}(aq)} \rightleftharpoons \mathrm{Fe^{2+}(aq)} + \mathrm{Cd(s)}$$

(a) 0.22 V (b) −0.04 V [✓ (c) 0.04 V] (d) −1.52 V
(e) 1.52 V (ab) −0.22 V

$$\Delta G° = -RT\ln K = -\left(8.314\times10^{-3}\tfrac{\mathrm{kJ}}{\mathrm{mol\cdot K}}\right)(298.15\,\mathrm{K})\ln(22.5)$$

$$= -7.718\ \mathrm{kJ/mol} = -7.718\times10^{3}\ \tfrac{\mathrm{J}}{\mathrm{mol}}$$

$$\Delta G° = -nFE° \Rightarrow E° = -\frac{\Delta G°}{nF} = -\frac{-7.718\times10^{3}\ \mathrm{J}/\cancel{\mathrm{mol}}}{\left(2\,\frac{\cancel{\mathrm{mol}\,e^-}}{\cancel{\mathrm{mol}}}\right)\left(96485\,\frac{\mathrm{coul}}{\cancel{\mathrm{mol}\,e^-}}\right)}$$

$$= 0.04\,\frac{\mathrm{J}}{\mathrm{coul}} = \boxed{0.04\,\mathrm{V}}$$

19. Which of the following would be the best reducing agent?

$$\frac{1\,\mathrm{J}}{\mathrm{coul}} = 1\,\mathrm{V}$$

$\underbrace{\text{(a) } \mathrm{Zn^{2+}(aq)} \quad \text{[✓ (b) } \mathrm{Zn(s)}\text{]}}_{E° = -0.76\mathrm{V}}$ $\underbrace{\text{(c) } \mathrm{Br_2(l)} \quad \text{(d) } \mathrm{Br^-(aq)}}_{1.09\mathrm{V}}$ $\underbrace{\text{(e) } \mathrm{Fe^{2+}(aq)} \quad \text{(ab) } \mathrm{Fe(s)}}_{-0.45}$

best reducing agent will be reduced form in half rxn w/ most negative E°

20. The following concentration cell could be used to measure pH:

$\mathrm{Ni / Ni(OH)_2(s), NaOH\ (aq,\ 1\ M)\ //\ OH^-\ (aq,\ ?)\ ,\ Ni(OH)_2\ (s) / Ni}$
↑ standard conditions

If E_{cell} = 0.245 V, what is the pH of the solution on the right?

(a) 12.32 (b) 10.55 (c) 5.67 [✓ (d) 9.86] (e) 3.84

half rxn $\mathrm{Ni(OH)_2\,(s) + 2e \rightleftharpoons Ni\,(s) + 2OH^-(aq)}$

$$E_{cell} = E_{right} - E_{left}$$

$$= \quad 0.245\mathrm{V} = \cancel{E°} - \frac{0.0592\mathrm{V}}{2}\log[\mathrm{OH^-}]^2 - \cancel{E°}$$

$$0.245\,\mathrm{V} = -\frac{\cancel{(2)}\,(0.0592\mathrm{V})}{\cancel{2}}\log[\mathrm{OH^-}]$$

$$\frac{0.245\mathrm{V}}{-0.0592\mathrm{V}} = \log[\mathrm{OH^-}] = -4.1385 = -\mathrm{pOH}$$

$$\mathrm{pH} = 13.9965 - \mathrm{pOH}$$

$$= 13.965 - 4.1385 = \boxed{9.86}$$

EQUATIONS and ADDITIONAL INFO

$$E_{cell} = E_{cat} - E_{an} \qquad \text{oO} + \text{ne}^- \rightleftharpoons \text{rR}$$

$$\Delta G = -nFE_{cell} \qquad E = E^\circ - \frac{0.0592V}{n}\log\frac{[R]^r}{[O]^o} \quad at\ 25^\circ C$$

$$\Delta G^\circ = -RT\ln K \quad or \quad \Delta G^\circ = -2.303RT\log K$$

$$K = e^{-\frac{\Delta G^\circ}{RT}} \quad or \quad K = 10^{-\frac{\Delta G^\circ}{2.303RT}}$$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \quad or \quad \log\left(\frac{[A]_t}{[A]_0}\right) = -\frac{kt}{2.303}$$

$$\ln[A]_t = -kt + \ln[A]_0 \quad or \quad \log[A]_t = -kt/2.303 + \log[A]_0$$

$$1/[A]t = kt + 1/[A]_0$$

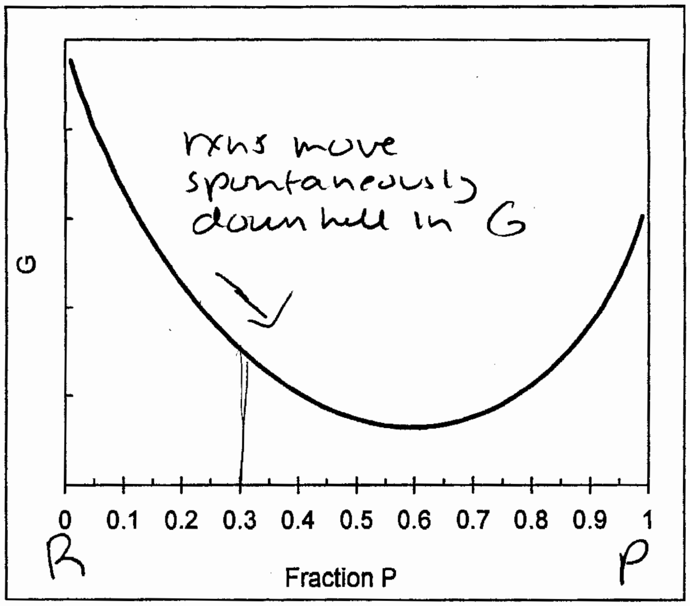
$$k = Ae^{-E_A/(RT)}$$

F = 96485 coul/mol R = 8.314×10^{-3} kJ/(mol·K) Volt = Joule/coul 0° C = 273.15 K

Standard Electrode Potentials at 25°C

Half Reaction	E° (V)
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80 V
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	+0.2223 V
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$	+0.07 V
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09 V
$Cl_2(g) + 2e- \rightleftharpoons 2Cl^-(aq)$	+1.36 V
$Co^{3+}(aq) + e- \rightleftharpoons Co^{2+}(aq)$	+1.82 V
$Cu^+(aq) + e- \rightleftharpoons Cu(s)$	+0.52 V
$Cu^{2+}(aq) + 2e- \rightleftharpoons Cu(s)$	+0.34 V
$Cu^{2+}(aq) + e- \rightleftharpoons Cu^+(aq)$	+0.159 V
$Fe^{2+}(aq) + 2e- \rightleftharpoons Fe(s)$	−0.45 V
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77 V
$2H^+(aq) + 2e- \rightleftharpoons H_2(g)$	0.000V
$2H_2O(aq) + 2e- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.828 V
$2Hg^{2+}(aq) + 2e- \rightleftharpoons 2Hg_2^{2+}(aq)$	+0.905 V
$Hg_2^{2+}(aq) + 2e- \rightleftharpoons 2Hg(l)$	0.7961 V
$Hg_2SO_4(s) + 2e- \rightleftharpoons 2Hg(l) + SO_4^{2-}(aq)$	0.6158 V
$I_2(s) + 2e- \rightleftharpoons 2I^-(aq)$	+0.54 V
$Mg^{2+}(aq) + 2e- \rightleftharpoons Mg(s)$	−2.37 V
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.257 V
$Ni(OH)_2(s) + 2e- \rightleftharpoons Ni(s) + 2OH^-(aq)$	−0.72 V
$Pb^{2+}(aq) + 2e- \rightleftharpoons Pb(s)$	−0.126 V
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	+2.01 V
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15 V
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.138 V
$Zn^{2+}(aq) + 2e- \rightleftharpoons Zn(s)$	−0.76 V

Consider the adjacent free energy diagram for the reaction R → P. The X axis gives the fraction of product, P, in the reaction mixture. For example, when the fraction of P = 0.20, the reaction mixture contains 20% P and 80% R. P = 0 means only R is present and P = 1 means only P is present.



1. According to the diagram, which of the following is TRUE when the fraction of P = 0.3?

[✓ (a)] The reaction will spontaneously move in the direction R → P.
(b) The reaction will spontaneously move in the direction P → R.
(c) The reaction is at equilibrium.

2. Based on the diagram, what is the value of the equilibrium constant for the reaction?

(a) 0.67 (b) 1.0 (c) 1.7 [✓ (d)] 1.5 (e) 0.50

See Form B, #11

3. Which **TWO** of the following are TRUE for an reduction reaction? (Mark two answers on your scantron.)

[✓ (a)] Electrons are consumed. (They are a reactant.)
(b) Electrons are produced. (They are a product.)
(c) The oxidation number of at least one atom will increase in going to products.
[✓ (d)] The oxidation number of at least one atom will decrease in going to products.
(e) The oxidation numbers will not change in going from reactants to products.

Consider the following reaction for the next three questions. The overall *unbalanced* reaction occurring in the lead acid (car) battery during discharge is

$$\overset{0}{\text{Pb}}(s) + \overset{+4}{\text{PbO}_2}(s) + \text{SO}_4^{2-}(aq) \rightarrow \overset{+2}{\text{PbSO}_4}(s)$$

4. What is the oxidation number of Pb in $\overset{+2}{\text{Pb}}(\text{SO}_4)^{-2}$?

(a) 0 [✓ (b) +2] (c) +4 (d) −2 (e) −4

5. What is being oxidized in this reaction?

[✓ (a) Pb] (b) PbO_2 (c) SO_4^{2-} (d) PbSO_4

$\text{Pb}^0 \rightarrow \text{Pb}^{2+}$ ox # ↑

6. What is the balanced reduction half reaction in acid?

(a) $\text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 2\,\text{H}^+(aq) + e^- \rightarrow \text{PbSO}_4(s) + \text{H}_2\text{O}_2(l)$

(b) $\text{Pb}(s) + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(s) + 2\,e^-$

[✓ (c) $\text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 4\,\text{H}^+(aq) + 2\,e^- \rightarrow \text{PbSO}_4(s) + 2\,\text{H}_2\text{O}(l)$]

(d) $\text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 2\,\text{H}^+(aq) + 2\,e^- \rightarrow \text{PbSO}_4(s) + \text{H}_2\text{O}(l)$

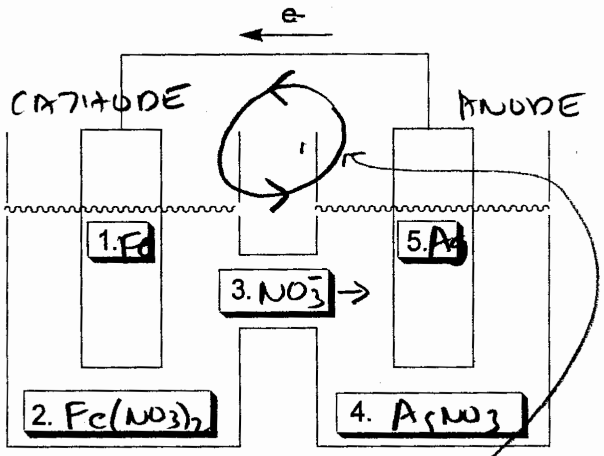
(e) $\text{PbO}_2(s) + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(s) + \text{O}_2(g) + 2\,e^-$

See Form B, #15

Consider the following electrochemical cell for the next two questions:

ANODE CATHODE
Ag / $AgNO_3$(aq) // $Fe(NO_3)_2$ (aq) / Fe

7. The diagram to the right shows a physical representation of the cell. Fill in the blanks to indicate where the different components are located and in what direction ions are flowing between compartments when current is flowing. **HINT: Look at the direction of e– flow to tell which electrode is the anode and which is the cathode.**



always has to be complete loop of current

(a) 1. Ag; 2. $AgNO_3$(aq); 3. ←NO_3^- ; 4. $Fe(NO_3)_2$(aq); 5. Fe

(b) 1. Ag; 2. $Fe(NO_3)_2$(aq); 3. NO_3^-→; 4. $AgNO_3$(aq); 5. Fe

(c) 1. Ag; 2. $AgNO_3$(aq); 3. NO_3^-→; 4. $Fe(NO_3)_2$(aq); 5. Fe

(d) 1. Fe; 2. $Fe(NO_3)_2$(aq); 3. ←NO_3^-; 4. $AgNO_3$(aq); 5. Ag

[✓ (e)] 1. Fe; 2. $Fe(NO_3)_2$(aq); 3. NO_3^-→; 4. $AgNO_3$(aq); 5. Ag

8. What is E°cell?

(a) 0.03 V [✓ (b)] –1.25 V (c) –0.03 V (d) 0.35 V (e) 1.25 V

Anode $Ag^+ + e \rightarrow Ag$ $E^\circ = 0.80v$

Cathode $Fe^{+2} + 2e \rightarrow Fe$ $E^\circ = -0.45v$

$$E^\circ_{CELL} = E^\circ_{CAT} - E^\circ_{AN}$$
$$= -0.45 - (0.80) = \boxed{-1.25V}$$

9. K for the following reaction is 0.0444 at 25°C. If this reaction was the overall reaction occurring in an electrochemical cell, what would be E°cell at 25°C?

$$\mathrm{Fe^{2+}(aq)} \overset{2e^-}{\longleftarrow} + \mathrm{Cd(s)} \rightleftarrows \mathrm{Fe(s)} + \mathrm{Cd^{2+}(aq)}$$

(a) 0.04 V (b) −1.52 V (c) 0.22 V (d) 1.52 V
[✓ (e)] −0.04 V (ab) −0.22 V

$\Delta G° = -RT \ln K = -\left(8.314\times10^{-3}\frac{kJ}{mol \cdot K}\right)(298.15\,K)\ln(0.0444)$

$= 7.720\,\frac{kJ}{mol} \times \frac{1000\,J}{1\,kJ} = 7.720\times10^{3}\,J/mol$

$\Delta G° = -nFE° \Rightarrow E° = \frac{\Delta G°}{-nF} = \frac{7.720\times10^{3}\,J/mol}{-\left(2\,\frac{mol\,e^-}{mol}\right)\left(96485\,\frac{coul}{mol\,e^-}\right)} = -0.04\,\frac{J}{coul} = \boxed{-0.04\,V}$

10. Which of the following would be the best oxidizing agent?

(a) Zn^{2+}(aq) (b) Zn(s) [✓ (c)] Br_2(l) (d) Br^-(aq) (e) Fe^{2+}(aq) (ab) Fe(s)

$\underbrace{\text{(a), (b)}}_{E° = -0.76V}$ $\underbrace{\text{(c), (d)}}_{E° = 1.09V}$ $\underbrace{\text{(e), (ab)}}_{E° = -0.45V}$

best oxidizing agent will be oxidized form in half rxn w/ most positive E°

11. The following concentration cell could be used to measure pH:

Ni / $Ni(OH)_2$(s), NaOH (aq, 1 M) // OH^- (aq, ?) , $Ni(OH)_2$ (s) / Ni

If E_{cell} = 0.0992 V, what is the pH of the solution on the right?

[✓ (a)] 12.32 (b) 5.67 (c) 10.55 (d) 9.86 (e) 3.84

See #20 form B for set up

$0.0992V = -0.0592V \log[OH^-]$

$\frac{0.0992V}{-0.0592V} = \log[OH^-] = -1.676 = -pOH$

$pH = 13.9965 - pOH = 13.9965 - 1.676$

$= \boxed{12.32}$

Consider the following reaction for the next three questions:

$$BrO_3^-(aq) + 5\,Br^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

12. If at given moment in time, the rate of change of Br^-, $\Delta[Br^-]/\Delta t$, = -6.0×10^{-4} M/s, what is the rate of change of Br_2 at the same time? Since Br_2 is product, will be increasing so rate of change is positive

(a) ~~-1.0×10^{-3}~~ M/s (b) ~~-3.6×10^{-4}~~ M/s (c) 1.0×10^{-3} M/s [✓ (d) 3.6×10^{-4} M/s]
(e) 1.8×10^{-3} M/s

$$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t}$$

$$-3/5\,\frac{\Delta[Br^-]}{\Delta t} = \frac{\Delta[Br_2]}{\Delta t} = -3/5\,(-6.0\times10^{-4}\ M/s)$$

$$= \boxed{3.6\times10^{-4}\ M/s}$$

13. The rate law for this reaction has been determined to be

$$\text{rate} = k\,[BrO_3^-\overset{1}{]}[Br^-\overset{1}{]}[H^+]^2$$

What is the kinetic order of the reaction?

(a) 1st (b) 6th (c) 12th (d) 2nd [✓ (e) 4th]

14. The rate of the reaction at a particular temperature has been determined to be 1.25×10^{-5}M/s when $[BrO_3^-] = [Br^-] = [H^+] =$ 0.10 M. What is the value of the rate constant at this temperature?

(a) $8.0\times10^{-3}\ s^{-1}$ (b) $0.125\ M^4s^{-1}$ [✓ (c) $0.125\ M^{-3}s^{-1}$]
(d) $1.25\times10^{-4}\ s^{-1}$ (e) $8.0\ M^4s^{-1}$ (ab) $8.0\ M^{-3}s^{-1}$

$$\text{rate} = k[BrO_3^-][Br^-][H^+]^2$$

$$k = \frac{\text{rate}}{[BrO_3^-][Br^-][H^+]^2} = \frac{1.25\times10^{-5}\ M/s}{(0.10\ M)^4} = \boxed{0.125\ M^{-3}s^{-1}}$$

15. The following data were obtained at 25 °C for the reaction shown below.

$$2\,HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2\,Cl^-(aq) + 2\,CO_2(g) + Hg_2Cl_2(s)$$

run	initial [$HgCl_2$], M	initial [$C_2O_4^{2-}$], M	inital rate, M/s
1	0.10	0.20	5.2×10^{-7}
2	0.10	0.10	1.3×10^{-7}
3	0.20	0.20	1.0×10^{-6}

What is the rate law for this reaction?

(a) rate = $k[HgCl_2][C_2O_4^{2-}]$
[✓ (b) rate = $k[HgCl_2][C_2O_4^{2-}]^2$]
(c) rate = $k[HgCl_2]^2[C_2O_4^{2-}]^2$
(d) rate = $k[HgCl_2]^2$
(e) rate = $k[HgCl_2]^2[C_2O_4^{2-}]$

See Form B, #4

For this version of the problem compare runs 1 & 3 to determine x and runs 1 & 2 to determine y

rate = $k[HgCl_2]^x[C_2O_4^{2-}]^y$

16. What would happen to the rate of the reaction in the previous question if it were run at a higher temperature?

(a) The reaction would proceed at the same rate.
(b) The reaction would go slower.
[✓ (c) The reaction would go faster.]
(d) More information is needed in order to answer this question.

rxns are always faster @ higher T

17. A particular herbicide is known to decompose in the environment by a first order process with a rate constant of 3.50×10^{-3} hr^{-1}, how many days will it take for 10.0% of the herbicide to decompose?

↑ 90% remain

(a) 8.85×10^{-3} days (b) 11.9 days (c) 27.4 days
[✓ (d) 1.25 days] (e) 0.19 days

Use first order integrated rate eqn

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \quad \text{or} \quad t = -\frac{1}{k}\ln\left(\frac{[A]_t}{[A]_0}\right)$$

$$= -\frac{1}{3.50\times10^{-3}\ hr^{-1}} \times \ln(0.90)$$

$$= 30.1 \text{ hrs}$$

$$30.1 \text{ hrs} \times \frac{1 \text{ day}}{24 \text{ hrs}} = \boxed{1.25 \text{ days}}$$

18. For the following reaction, $3\ BrO^-(aq) \rightarrow BrO_3^-(aq) + 2\ Br^-(aq)$, a plot of $1/[BrO^-]$ vs. time is linear. What is the kinetic order of the reaction?

[✓ (a) 2nd] (b) 4th (c) 3rd (d) 1st (e) none of the above

test for 2nd order kinetics

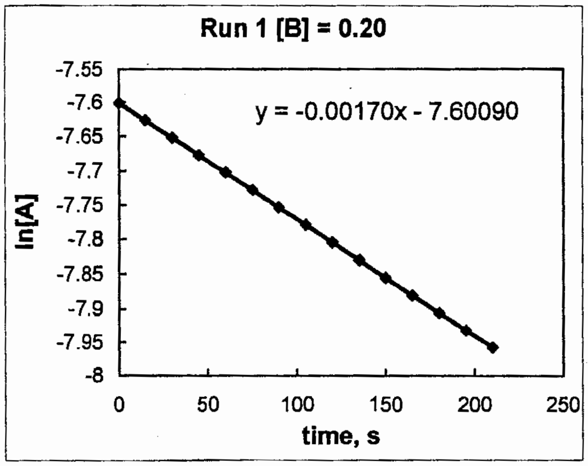
19. Two reactant molecules collide with an energy greater than the activation energy for a reaction that can take place between the molecules. Will the reaction occur? Choose the one best answer.

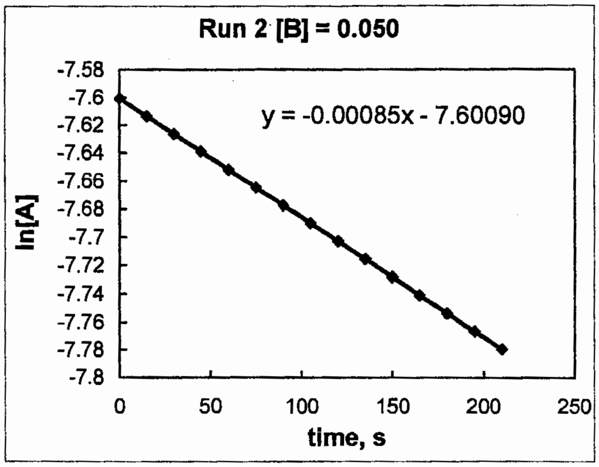
(a) No.
(b) Yes.
(c) Probably not. A collision between three reactant molecules is generally required for a reaction to occur.
(d) Maybe. The reaction will take place if the collision frequency is greater than the frequency factor.
[✓ (e) Maybe. In general, the molecules also must collide in a specific orientation in order for a reaction to take place.]

20. The kinetics of the reaction A + B → C were studied by measuring the concentration of A as a function of time starting with the following concentrations:

Run	[A], M	[B], M
1	5.0×10^{-4}	0.20 M
2	5.0×10^{-4}	0.050 M

The following plots were made from the data:





Based on the above plots, what is the rate law and the value of the true rate constant for this reaction?

[✓ (a)] rate = $k[A][B]^{1/2}$; $k = 0.0038\ M^{-1/2}s^{-1}$
(b) rate = $k[A][B]^2$; $k = 0.00085\ M^{-2}s^{-1}$
(c) rate = $k[A]^2[B]^2$; $k = 0.0017\ M^{-3}s^{-1}$
(d) rate = $k[A]^2[B]^{1/2}$; $k = 263\ s^{-1}$
(e) rate = $k[A]$; $k = 0.00085\ ^2s^{-1}$

See Form B, #9