EXAM 3 – Form A

Consider the following *unbalanced* oxidation reduction reaction for the next three questions.

$$2\,CrO_3 + 12\,HCl \rightarrow 3\,Cl_2 + 6\,H_2O + 2\,CrCl_3$$

1. The oxidation state of Cr in CrO_3 is ____.

[✓ (a) +6] (b) +4 (c) -2 (d) +2 (e) +3

2. The oxidation state of Cr in $CrCl_3$ is ____.

(a) +6 (b) +4 (c) -2 (d) +2 [✓ (e) +3]

3. The complete balanced equation in for the reaction has the following stoichiometry coefficients:

_____ CrO_3 + _____ HCl → ______ Cl_2 + ______ H_2O + _____ $CrCl_3$

The stoichiometry coefficients, in order are

(a) 1, 3 → 3, 3, 1 (b) 3, 12 → 3, 9, 3 (c) 1, 3 → 3, 3, 1
[✓ (d) 2, 12 → 3, 6, 2] (e) 1, 4 → 2, 2, 1 (ab) 2, 10 → 3, 5, 2

$$\begin{array}{l|c||c|c} Cr^{6+} \xrightarrow{+3e^-} Cr^{3+} & 3 & 1 & 2 \\ Cl^- \xrightarrow{+1e^-} Cl^0 & 1 & 3 & 6 \end{array}$$

Cl_2 => we have to multiply by 2

Consider the following reaction for the next 3 questions. About four percent of hydrogen gas produced worldwide is created by electrolysis. The majority of this hydrogen produced through electrolysis is a side product in the production of chlorine. The overall reaction occurring in the electrochemical cell can be formulated as shown below:

$$2\,NaCl\,(aq) + 2\,H_2O\,(l) \rightarrow 2\,NaOH\,(aq) + H_2(g) + Cl_2(g)$$

4. In which one of the following electrochemical cells the reaction would take place? Note that all the ions below are assumed to be in aqueous media (aq sign omitted)

(a) $Na(s)\,|\,Cl_2(g), Cl^-\,||\,H_2O(l), H^+, H_2(g)\,|\,Pt(s)$ (b) $Na(s)\,|\,Na^+, Cl^-\,||\,H_2O(l), OH^-\,|\,C(s)$

(c) $Pt(s)\,|\,Cl_2(g), Cl^-\,||\,H_2O(l), H^+, H_2(g)\,|\,Pt(s)$ [✓ (d)] $C(s)\,|\,Cl_2(g), Cl^-\,||\,H_2O(l), OH^-, H_2(g)\,|\,C(s)$ $\leftarrow$

cathode $2H_2O + 2\bar{e} \rightarrow H_2 + 2OH^- \leftarrow$ this reduction occurs

anode $Cl_2 + 2\bar{e} \rightarrow 2Cl^-$ $\Rightarrow$

$n = 2$

5. What would be E°_{cell} in the above cell at 25°C?

(a) -0.83 V (b) 2.71 V (c) 2.19 V (d) 1.36 V [✓ (e)] -2.19 V (ab) -3.54 V

$E^\circ_{cathode} = -0.83\,V$

$E^\circ_{anode} = +1.358\,V$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.83 - 1.358 = -2.188 \approx$

$\boxed{\approx -2.19\,V}$

6. Based on E°_{cell} what would be ΔG° for this reaction (per mole of reactions)?

(a) 160kJ (b) -523kJ (c) -423kJ (d) -262kJ [✓ (e)] 423kJ (ab) 683 kJ

$\Delta G^\circ = -nFE^\circ$; $n = 2$ (see above)

$= -2 \cdot 96485 \frac{C}{mol} \cdot (-2.19\,V) \approx 422604 \frac{J}{mol} \approx +423 \frac{kJ}{mol}$

7. Which of the following solids is commonly used as an inactive electrode in electrochemical cells?

(a) zinc [✓ (b)] graphite (c) iron (d) sodium

Consider the following electrochemical cell for the next 4 questions:

$$Co \mid \underset{\uparrow}{CoCl_2(aq)} \parallel Hg_2Cl_2(s), NaCl(aq) \mid Hg(l)$$

8. What is the name of the **aqueous ionic** compound in the compartment on the left?

(a) copper (II) chloride
[✓ (b) cobalt (II) chloride]
(c) copper perchlorate
(d) cobalt (III) chloride
(e) copper(I) chloride

9. What is E°_{cell} ?

(a) -0.55 V
[✓ (b) 0.55 V]
(c) 0.012 V
(d) -0.012 V
(e) 0.28 V
(ab) -0.28 V

+0.268 cathode $Hg_2Cl_2 + 2\bar{e} \rightarrow 2Hg + 2Cl^-$

-0.28 anode $Co^{2+} + 2e \rightarrow Co$

$$E^\circ_{cell} = 0.268 - (-0.28) = +0.548 \approx \boxed{0.55\ V}$$

10. What is E_{cell} when [NaCl] = 1.0 M and $[CoCl_2]$ = 0.010 M?

(a) -0.55V
(b) 0.49 V
(c) -0.61 V
(d) 0.93 V
[✓ (e) 0.61 V]

$$E_{cathode} = E^\circ_{cathode} = 0.268 \left(E = E^\circ - \frac{RT}{2F}\overbrace{\ln[Cl]^2}^{0}\right)$$

$$E_{anode} = -0.28 - \frac{RT}{2F}\ln\frac{1}{[Co^{2+}]} = -0.28 + \frac{0.0591}{2}\cdot(-2) =$$

$$= -0.28 - 0.0591 = -0.3391\ V$$

$$E_{cell} = 0.268 - (-0.3391) = 0.607\ V \approx \boxed{0.61\ V}$$

11. What is the overall reaction occurring in the cell when current flows?

(a) $CoCl_2(aq) + Hg_2SO_4(s) \rightarrow 2\,Hg(l) + Co(s) + 2\,Cl^-(aq)$
(b) $2\,Hg(l) + CoCl_2(aq) \rightarrow Hg_2Cl_2(s) + Co(s)$
(c) $2\,Hg(l) + Co(s) + 4\,Cl^-(aq) \rightarrow CoCl_2(aq) + Hg_2Cl_2(s)$
[✓ (d) $Hg_2Cl_2(s) + Co(s) \rightarrow 2\,Hg(l) + CoCl_2(aq)$]
(e) $Hg_2Cl_2(s) \rightarrow Hg_2^{2+}(aq) + 2\,Cl^-(aq)$

(rxn) = (cathode) − (anode)

Consider the following unbalanced reaction for the next two questions:

$$6\,\overset{+4}{NO_2(g)} + 8\,\overset{-3}{NH_3(g)} \rightarrow 7\,\overset{0}{N_2(g)} + 12\,H_2O(g)$$

12. If at a given moment the rate of change of $NO_2(g)$ = -0.100 M/s, what is the rate of change of $N_2(g)$ at the same time (you will need to balance the reaction to answer this question)?

(a) +0.100 M/s (b) +0.150 M/s (c) +0.133 M/s [✓ (d) 0.117 M/s]
(e) -0.050 M/s (ab) +0.075 M/s

$$\overset{+4}{N} \xrightarrow{+4e} N^0 \;/\; 4 \;//\; \overset{12\bar{e}}{3} \;/\; 6$$

$$\overset{-3}{N} \xrightarrow{-3\bar{e}} N^0 \;/\; 3 \;//\; 4 \;/\; 8$$

$$-\frac{d[NO_2]}{6\,dt} = \frac{d[N_2]}{7\,dt}$$

N_2 => # of N should be even
=> × 2

$$\frac{d[N_2]}{dt} = -\frac{7}{6}\frac{d[NO_2]}{dt} = -\frac{7}{6}\cdot(-0.1) \approx 0.1167 \approx \boxed{0.117\ \frac{M}{s}}$$

13. The rate of the above reaction has been determined by experiment to be 2nd order in NO_2, 1st order in NH_3, and third order overall. What is the rate law for this reaction? (Read carefully, some of the answer choices are very similar.)

✓ k is missing

(a) rate = $[NO_2]^2[NH_3]$ (b) rate = k $([NO_2][NH_3])^3$ (c) rate = $k([N_2][H_2O])^3$
(d) rate = $K[N_2][H_2O]^2$ [✓ (e) rate = k $[NO_2]^2[NH_3]$]

14. The rate law for the following reaction is rate = $k[SO_2Cl_2]$:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

If the rate constant for this reaction is 2.20×10^{-5} s^{-1} at 593 K, what percent of SO_2Cl_2 will remain after 2.00 hr at this temperature?

(a) 50% (b) 92% (c) 15% [✓ (d) 85%] (e) 8%

$$\frac{[SO_2Cl_2]_t}{[SO_2Cl_2]_0} = e^{-kt} = e^{-2.2\cdot10^{-5}s^{-1}\cdot 7200s} \approx 0.853$$

$$0.853 \cdot 100\% \approx 85\%$$

$2\,hr = 7200\,s$

15. The following data was obtained for the reaction:

$$2\,ClO_2(aq) + 2\,OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O$$

initial $[ClO_2]$, M	initial $[OH^-]$, M	initial rate, M/s
0.060	0.030	0.0248
0.020	0.030	0.00276
0.020	0.090	0.00828

What is the rate law for this reaction?

[✓ (a)] rate = $k[ClO_2]^2[OH^-]$ (b) rate = $k[ClO_2]^2[OH^-]^2$ (c) rate = $k[ClO_2]^2$
(d) rate = $k[ClO_2][OH^-]^2$ (e) rate = $k[ClO_2][OH^-]$

$\frac{\text{run 1}}{\text{run 2}}$: $\left(\frac{0.06}{0.02}\right)^x = \frac{0.0248}{0.00276} \approx 9$

$3^x \approx 9 \Rightarrow x \approx 2$

$\frac{\text{run 3}}{\text{run 1}}$: $\left(\frac{0.09}{0.03}\right)^y = \frac{0.00828}{0.00276} \approx 3 \quad 3^y = 3 \Rightarrow y = 1$

16. For the reaction shown below, calculate the equilibrium constant (from standard free energy change) at 298 K. Is this equilibrium established in nature?

$$C(graphite) \rightleftharpoons C(diamond)$$

Data: ΔH_f°(diamond) = 1.895 kJ/mol; S°(diamond) = 2.337 J mol^{-1} K^{-1};
S°(graphite) = 5.740 J mol^{-1} K^{-1}.

[✓ (a)] K=0.31; no (b) K=3.2; no (c) K=0.46; no
(d) K=0.31; yes (e) K=0; yes, in coal mines

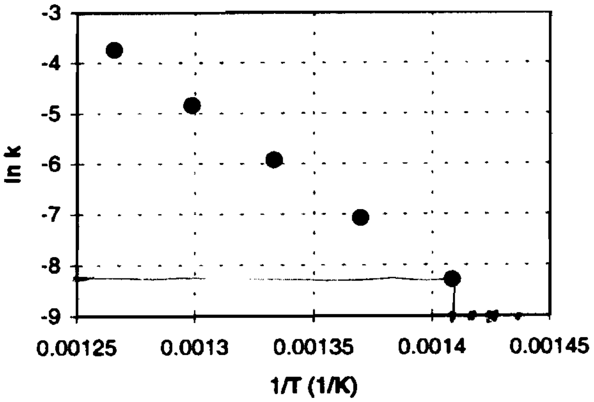
$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ = (1.895 - 0) - 298\cdot\left(\frac{2.337 - 5.740}{1000}\right) =$$

≈ 2.909 kJ/mol

$$K = e^{-\frac{\Delta G^\circ r}{RT}} = e^{-\frac{2909}{8.314\cdot 298.15}} \approx 0.31$$ pretty large

but we don't find diamonds in coal (~25%!), so it is not established

17. Cyclobutane decomposes to ethene in a first-order reaction. From five measurements of the rate constant k (measured in s^{-1}) at various absolute temperatures T, the accompanying Arrhenius plot was obtained ($\ln k$ versus $1/T$, shown on the right). What is the approximate value of the rate constant obtained at the lowest temperature measurement?



(a) 2.5×10^{-2} s^{-1} (b) 8.3 s^{-1} (c) 8.2×10^{-3} s^{-1} (d) -3.7 s^{-1} [✓ (e)] 2.5×10^{-4} s^{-1}

lowest $T \Rightarrow$ highest $\frac{1}{T}$

highest measured $\frac{1}{T} \approx 0.00141$

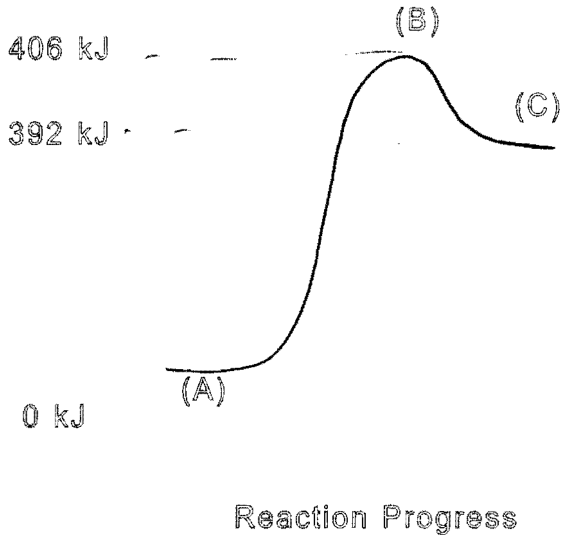
$\ln k \approx -8.3$

$k = e^{-8.3} \approx 2.49 \cdot 10^{-4} s^{-1}$

18. Which one of the following changes would cause the value of the rate constant, k, for a reaction to INCREASE?

(a) Decreasing the temperature of the reaction.
[✓ (b)] Decreasing the activation energy required for the reaction.
(c) Increasing the concentration of a reactant.
(d) Decreasing the concentration of a reactant.

Consider the following transition state diagram for the reaction $O_2(g) + O_2(g) \rightarrow O_3(g) + O(g)$ for the next two questions.



19. What is the activation energy for the *reverse* reaction, $O_3(g) + O(g) \rightarrow O_2(g) + O_2(g)$?

[✓ (a) 14 kJ] (b) -406 kJ (c) 392 kJ (d) -392 kJ (e) 406 kJ

406 - 392 = 14

20. What is located at point (B) in the diagram?

(a) $O_2(g) + O_2(g)$ (b) $O_3(g) + O(g)$ [✓ (c) the transition state for the reaction]
(d) the equilibrium state for the reaction (e) a reaction intermediate

EQUATIONS and ADDITIONAL INFO

$$\Delta G^0_{rxn} = -nFE_{rxn} \qquad E_{cell} = E_{cathode} - E_{anode} \qquad E_{rxn} = E^0_{rxn} - \frac{RT}{nF}\ln Q = E^0_{rxn} - \frac{0.0591}{n}\log Q \text{ at 298K}$$

F = 96485 coul/mol e- R = 8.314×10^{-3}kJ/(mol·K) Q – reaction quotient n – number of electrons

$$\Delta G^\circ = -RT\ln K \qquad K = e^{-\frac{\Delta G^0}{RT}} \qquad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = \sum \Delta G^\circ_{f\ products} - \sum \Delta G^\circ_{f\ reactants} \qquad \Delta H^\circ = \sum \Delta H^\circ_{f\ products} - \sum \Delta H^\circ_{f\ reactants}$$

$$\Delta S^\circ = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$

Arrhenius equation: $k = k_0 e^{-\frac{E_a}{RT}}$

Order: elementary process	**First order:** A → B	**Second order:** A + A → B
Rate law	rate = $k[A]$	rate = $k[A]^2$
Integrated rate law	$[A]_t = [A]_0 \exp(-kt)$	$[A]_t = [A]_0/([A]_0\, kt + 1)$
Integrated rate law in straight line form	$\ln[A]_t = -kt + \ln[A]_0$	$1/[A]_t = kt + 1/[A]_0$
Half life	$(\ln 2)/k$	$1/(k[A]_0)$

Half Reaction	E° (V)
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.799V
$Au^{3+}(aq) + 3e- \rightarrow Au(s)$	+1.50 V
$Cl_2(g) + 2e- \rightarrow 2\,Cl^-(aq)$	+1.358 V
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82 V
$Co^{2+}(aq) + 2e^- \rightarrow Co\,(s)$	-0.28 V
$Cu^+(aq) + e- \rightarrow Cu(s)$	+0.520 V
$Cu^{2+}(aq) + 2e- \rightarrow Cu(s)$	+0.340V
$Fe^{2+}(aq) + 2\,e- \rightarrow Fe(s)$	-0.44 V
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.771 V
$Fe(CN)_6^{3-}(aq) + e- \rightarrow Fe(CN)_6^{4-}(aq)$	+0.361V
$2\,H^+(aq) + 2\,e- \rightarrow H_2(g)$	0.000V
$2H_2O\,(l) + 2\,e- \rightarrow H_2(g) + 2\,OH^-$	-0.83V
$Hg_2^{2+}(aq) + 2e- \rightarrow 2\,Hg(l)$	+0.796 V
$Hg_2Cl_2(s) + 2e- \rightarrow 2\,Hg(l) + 2\,Cl^-(aq)$	+0.268 V
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71 V
$Ni^{2+}(aq) + 2\,e^- \rightarrow Ni(s)$	-0.257 V
$Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s)$	-0.138 V
$Sn^{4+}(aq) + 2\,e^- \rightarrow Sn^{2+}(aq)$	+0.13 V
$Zn^{2+}(aq) + 2\,e- \rightarrow Zn(s)$	-0.763 V