

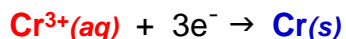
TABLE I: Reduction Potentials

reduced = ox agent = reactant reduction rxn | oxidized = red agent = product reduction rxn

Most - $\mathcal{E}^{\circ}_{\text{red}}$ = hardest to reduce

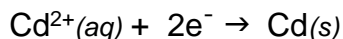
Easiest to oxidize

= worst ox agent

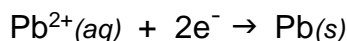


Best red agent

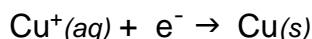
$$\mathcal{E}^{\circ}_{\text{red}} = -0.74 \text{ V}$$



$$\mathcal{E}^{\circ}_{\text{red}} = -0.40 \text{ V}$$

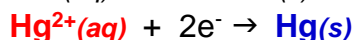


$$\mathcal{E}^{\circ}_{\text{red}} = -0.13 \text{ V}$$



$$\mathcal{E}^{\circ}_{\text{red}} = 0.52 \text{ V}$$

Most + $\mathcal{E}^{\circ}_{\text{red}}$ = easiest to reduce



Hardest to oxidize

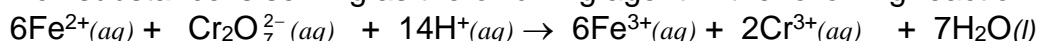
$$\mathcal{E}^{\circ}_{\text{red}} = 0.85 \text{ V}$$

= best ox agent

= worst red agent

Part One: Multiple choice. (42 points; 3 points each)

Which substance is serving as the oxidizing agent in the following reaction?

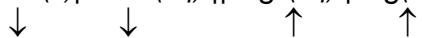


Fe +2 to +3 (more +) so Fe⁺² is oxidized = red agent

Cr +6 to +3 (more -) so Cr⁺⁶ is reduced; Cr₂O₇²⁻ is oxidizing agent

- A. Fe²⁺(aq) **B. Cr₂O₇²⁻(aq)** C. H⁺(aq) D. Fe³⁺(aq) E. Cr³⁺(aq)

Which of the following statements is **not** true for the following galvanic cell?



Cr(s) is oxidized = anode, mass Cr ↓, [Cr³⁺] ↑, anions move in, e- move away (lose e-)

Ag⁺ is reduced = cathode, mass Ag ↑, [Ag⁺] ↓, cations move in, e- move toward (gain e-)

- A. electrons move through a wire towards the silver electrode during discharge. T; e⁻'s move from anode to cathode
- B. the mass of the silver electrode increases during discharge. T (fat red cat)
- C. **anions from the salt bridge move into the compartment containing silver.** F; cations into cathode = Ag & anions into anode compartment = Cr
- D. the concentration of Cr³⁺ ions increases during discharge. T; products ↑
- E. chromium is oxidized as the reaction proceeds in this voltaic cell. T; ox occurs at anode

Which of the following will react spontaneously? (Refer to Table I above.)

- A. Cu⁺(aq) with Hg(s) -V B. Cr³⁺(aq) with Cd(s) -V C. Pb(s) with Cd(s) NR
- D. Cd(s) with Cu⁺(aq) +V** E. Cd²⁺(aq) with Pb(s) -V

Which substance is the **strongest reducing agent**? (Refer to Table I above.)

Strongest reducing agent = easiest to oxidize = most - $\mathcal{E}^{\circ}_{\text{red}}$

Also it is Cr(s) not Cr³⁺(aq) because Cr(s) loses e⁻'s, Cr³⁺ gains e⁻'s and is reduced!

- A. Cr(s)** - easiest to oxidize B. Pb(s) C. Cr³⁺(aq) D. Hg²⁺(aq) E. Hg(s)

1. Which of the following is TRUE regarding a galvanic cell?

- A. Cations in the salt bridge move into the anode compartment. F
- B. The overall cell emf is negative. F
- C. Oxidation occurs at the cathode. F

D. Electrons travel from the cathode to the anode via a connecting wire. **F**

E. The anode electrode is losing mass as the cell runs. T; anorexic ox

Which of the following is true when one mole of $\text{H}_2\text{O}(l)$ changes to $\text{H}_2\text{O}(s)$?

Liquid to solid = more order = $-\Delta S$, liquid loses heat to form solid = exo = $-\Delta H$

A. ΔS is + and ΔH is +

B. ΔS is + and ΔH is -

C. ΔS is - and ΔH is +

D. ΔS is - and ΔH is -

Which of the following has the largest absolute entropy at 25 °C?

largest S° = gas with most atoms

A. $\text{H}_2\text{O}(l)$

B. $\text{Pt}(s)$

C. $\text{C}_4\text{H}_{10}(g)$

D. $\text{Ar}(g)$

E. $\text{FePO}_4(s)$

In which of the following reactions is ΔS° negative?

1. $\text{C}_4\text{H}_{10}(s) \rightarrow \text{C}_4\text{H}_{10}(g)$ **s to g = + ΔS (more disorder)**

2. $\text{CS}_2(g) + 4\text{H}_2(g) \rightarrow \text{CH}_4(g) + 2\text{H}_2\text{S}(g)$ **# gas particles \downarrow = - ΔS (more order)**

3. $\text{NH}_3(g) + \text{H}_2\text{S}(g) \rightarrow \text{NH}_4\text{HS}(s)$ **g to s = - ΔS (more order)**

A. 1 only

B. 2 only

C. 3 only

D. 1 and 2 only

E. 2 and 3 only

Which of the following does not have a standard free energy of formation of zero?

A. $\text{Ne}(g)$

B. $\text{I}_2(l)$ I_2 is solid

C. $\text{N}_2(g)$

D. $\text{Au}(s)$

E. $\Delta G_f^\circ = 0$ for all of these

Some standard entropies (S°) are given at 25 °C:

$\text{N}_2\text{O}_5(g)$ 355.2 $\frac{J}{K \cdot mol}$	$\text{NO}_2(g)$ 239.9 $\frac{J}{K \cdot mol}$	$\text{O}_2(g)$ 204.8 $\frac{J}{K \cdot mol}$
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Calculate ΔS° in $\frac{J}{K}$ for the reaction: $2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$

$$\Delta S^\circ = (4 \text{ mol})(239.9 \frac{J}{K \cdot mol}) + (1 \text{ mol})(204.8 \frac{J}{K \cdot mol}) - (2 \text{ mol})(355.2 \frac{J}{K \cdot mol}) = +454 \frac{J}{K}$$

A. 89.5 $\frac{J}{K}$

B. -89.5 $\frac{J}{K}$

C. -454.0 $\frac{J}{K}$

D. +454.0 $\frac{J}{K}$

E. 227.0 $\frac{J}{K}$

$\Delta H^\circ = -90.84 \text{ kJ}$ for the following reaction: $2 \text{Hg}(l) + \text{O}_2(g) \rightarrow 2\text{HgO}(s)$. This reaction is most likely to be **- ΔH° = exo; more order = - ΔS° ; ΔG° = - at low T but + at high T**

A. spontaneous at all temperatures

B. spontaneous at high temperatures but nonspontaneous at low temperatures

C. spontaneous at low temperatures but nonspontaneous at high temperatures

D. nonspontaneous at all temperatures

Calculate ΔG° for the following reaction at 25 °C:

$\text{I}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{ICl}(g)$; $\Delta H^\circ = -26.9 \text{ kJ}$; $\Delta S^\circ = 11.3 \text{ J/K}$

$$\Delta G^\circ = -26.9 \text{ kJ} - (298 \text{ K})(0.0113 \text{ J/K}) = -30.3 \text{ kJ}$$

A. -30.3 kJ

B. -23.5 kJ

C. -27.2 kJ

D. 18.4 kJ

E. -3394 kJ

$\Delta G^\circ = -36.2 \text{ kJ}$ for a given reaction at 25 °C. Calculate the equilibrium constant, K , at 25 °C.

$$K = e^{\left(\frac{-36.2 \frac{kJ}{mol}}{8.314 \times 10^{-3} \frac{kJ}{K \cdot mol} \times 298 \text{ K}} \right)}$$

A. 0.985

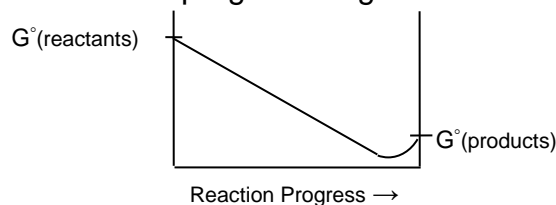
B. 1.01

C. 4.51×10^{-7}

D. 2.22×10^6

E. 4.08×10^{14}

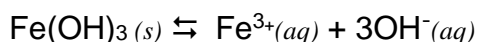
The free energy vs. reaction progress diagram below is characteristic of a reaction with:



- A. $\Delta G^\circ > 0$, $\xi^\circ < 0$, $K < 1$ B. $\Delta G^\circ > 0$, $\xi^\circ < 0$, $K > 1$ C. $\Delta G^\circ = 0$, $\xi^\circ = 0$, $K = 1$
 D. $\Delta G^\circ < 0$, $\xi^\circ > 0$, $K < 1$ **E. $\Delta G^\circ < 0$, $\xi^\circ > 0$, $K > 1$**

Part Two. Short Answer and Numerical Problems. For calculation questions, you must SHOW YOUR WORK, including UNITS, to receive full credit. (58 points)

1. Calculate the molar solubility of $\text{Fe}(\text{OH})_3$ in pure water. For $\text{Fe}(\text{OH})_3$, $K_{\text{sp}} = 1.1 \times 10^{-36}$. (8 pts)



	$\text{Fe}(\text{OH})_3(s)$	$\text{Fe}^{3+}(aq)$	$3\text{OH}^-(aq)$
I		0	0
C		+x	+3x
E		x	3x

$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3$$

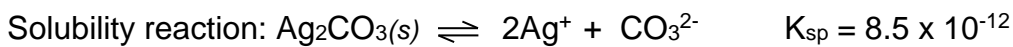
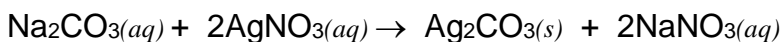
$$1.1 \times 10^{-36} = x(3x)^3$$

$$1.1 \times 10^{-36} = 27x^4$$

$$x = \left(\frac{1.1 \times 10^{-36}}{27} \right)^{1/4} = (4.07 \times 10^{-38})^{1/4} = 4.5 \times 10^{-10} \text{ M}$$

solubility = $4.5 \times 10^{-10} \text{ M}$

2. If you mix 200.0 mL of $2.40 \times 10^{-3} \text{ M Na}_2\text{CO}_3(aq)$ with 400.0 mL of $1.50 \times 10^{-3} \text{ M AgNO}_3(aq)$, does Ag_2CO_3 precipitate? Show your work mathematically by calculating the Q value. For Ag_2CO_3 , $K_{\text{sp}} = 8.5 \times 10^{-12}$. (10 pts)



$$Q = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$$

$$[\text{Na}_2\text{CO}_3] = [\text{CO}_3^{2-}] = 2.40 \times 10^{-3} \text{ M} \text{CO}_3^{2-} \left(\frac{200.0 \text{ ml}}{600.0 \text{ ml}} \right) = 8.00 \times 10^{-4} \text{ M} \text{CO}_3^{2-}$$

$$[\text{AgNO}_3] = [\text{Ag}^+] = 1.50 \times 10^{-3} \text{ M} \text{Ag}^+ \left(\frac{400.0 \text{ ml}}{600.0 \text{ ml}} \right) = 1.00 \times 10^{-3} \text{ M} \text{Ag}^+$$

$$Q = (1.00 \times 10^{-3})^2(8.00 \times 10^{-4})$$

$Q = 8.00 \times 10^{-10}$

$Q > K_{\text{sp}}$, so Ag_2CO_3 precipitates

3. Answer the following questions about this galvanic cell: $\text{Cr(s)} \mid \text{Cr}^{3+}(\text{aq}) \parallel \text{Cd}^{2+}(\text{aq}) \mid \text{Cd(s)}$. Refer to Table I on page 1 for the standard reduction potentials. (20 pts)

A. What is the overall balanced cell reaction? (3 pts)



B. What is the standard cell potential, $\mathcal{E}_{\text{cell}}^{\circ}$? (2 pts) $\mathcal{E}_{\text{cell}}^{\circ} = 0.74 \text{ V} + (-0.40 \text{ V}) = +0.34 \text{ V}$

C. What is the oxidation $\frac{1}{2}$ reaction? (2 pts) $\text{Cr(s)} \rightarrow \text{Cr}^{3+}(\text{aq}) + 3\text{e}^{-}$

D. Which electrode is gaining mass? (2 pts) **Cd(s) (the cathode)**

E. Calculate ΔG° for this cell. (5 pts)

$$\Delta G^{\circ} = (-6 \text{ mol e}^{-})(96500 \text{ J/Vmol e}^{-})(0.34 \text{ V}) = -2.0 \times 10^5 \text{ J or } -2.0 \times 10^2 \text{ kJ}$$

F. Calculate the equilibrium constant, K, for this cell. (6 pts)

$$\mathcal{E}^{\circ} = \frac{0.0592}{n} \log K, \quad n = 6, \quad \log K = \frac{6(0.34)}{0.0592} = 34.46 \quad K = 10^{34.46} = 2.9 \times 10^{34}$$

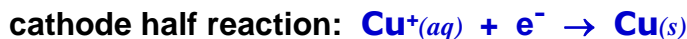
$$\Delta G^{\circ} = -RT \ln K \quad \ln K = \left(\frac{-2.0 \times 10^2 \frac{\text{kJ}}{\text{mol}}}{8.314 \times 10^{-3} \frac{\text{kJ}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} \right) \quad \ln K = +80.42 \quad K = e^{80.42} = 1.14 \times 10^{35}$$

If you use the free energy, it comes out a bit different due to rounding -200 kJ (0.0592 is also rounded off in the standard emf formula).

4. A certain galvanic cell is constructed based on the following half reactions: (20 pts)



A. Assign the anode and cathode half reactions for the cell. (Make sure to write the reactions in the appropriate direction!) (4 pts)



B. Write an overall balanced reaction for the cell and determine the standard cell potential, $\mathcal{E}_{\text{cell}}^{\circ}$. (6 pts)



$$\mathcal{E}_{\text{cell}}^{\circ} = 0.52 \text{ V} + (-0.15 \text{ V}) = +0.37 \text{ V}$$

C. (1 pt) atom oxidized: **Sn^{2+}** (1 pt) atom reduced: **Cu^{+}**

D. Calculate the cell potential, $\mathcal{E}_{\text{cell}}$, when $[\text{Cu}^{+}] = 1.75 \text{ M}$, $[\text{Sn}^{4+}] = 0.45 \text{ M}$ and $[\text{Sn}^{2+}] = 1.15 \text{ M}$ at 25°C . (8 pts)

$$E = \mathcal{E}^{\circ} - \frac{0.0592}{n} \log Q \quad n = 2 \quad Q = \frac{[\text{Sn}^{4+}]}{[\text{Cu}^{+}]^2 [\text{Sn}^{2+}]} = \frac{[0.45]}{[1.75]^2 [1.15]} \quad \text{Thus, } Q = 0.128$$

$$E = 0.37 \text{ V} - \frac{0.0592 \text{ V}}{2} (\log 0.128) = 0.37 \text{ V} - [(0.0296 \text{ V})(-0.893)]$$

$$E = 0.37 \text{ V} - (-0.0264 \text{ V})$$

$$E = 0.40 \text{ V}$$