Examination II

Please answer all six questions. Your reasoning should be clearly and concisely indicated.

Useful Information:
\[ \Delta G = \Delta H - T\Delta S \quad \Delta G = -nFE \quad \Delta G^0 = -RT \ln K \]
\[ E = E^0 - (RT/nF) \ln Q \]
\[ pH = -\log_{10} [H^+] \]
\[ R = 8.3145 \, \text{J/mol K} \quad F = 96485 \, \text{C/mol} \]

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Emma Fink
Name

Discussion Instructor & Time

Aug 79.5
1) For each of these statements, state whether it is TRUE or FALSE.

a. $\Delta G^0$ is independent of temperature.
   
   False
   
   $\Delta G^0 = -RT \ln K$ Thus $\Delta G^0$ depends on temperature.

b. Gibbs Free energy is a state function.
   
   True
   
   $\Delta G = \Delta H - T \Delta S$
   
   Entropy and enthalpy are both state functions, thus $\Delta G$ is a state function.

c. For an isothermal process, $\Delta H$ must be zero.
   
   False
   
   Even in an isothermal process, $T$ does not have to be $0$.

   Under constant atmospheric pressure and no work conditions, this would mean that $\Delta H$ must necessarily be $0$.

d. The second law of thermodynamics requires that the entropy change associated with any chemical reaction be positive.
   
   False
   
   $\Delta S_{sys}$

The second law of thermodynamics states that $\Delta S_{univ} \geq 0$, where $\Delta S_{univ}$ only $= 0$ in a reversible process. No real process can be reversible. However, as long as:

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sys} > 0$, $\Delta S_{sys}$ may decrease.

Thus, as long as $\Delta S_{univ}$ overall $> 0$, $\Delta S_{sys}$ may be $< 0$ and this statement is false.
2) NO₂ is a reddish-brown gas that is one of the most prominent air pollutants and a poison when inhaled. N₂O₄ gas is a powerful oxidizing agent, is colorless, highly toxic, corrosive, and famous for its use as a rocket propellant. These two gases exist in equilibrium according to the reaction

\[ 2\text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_4(g) + \text{O}_2(g) \]

At 298 K, the equilibrium lies to the right (with N₂O₄ predominating), while at higher temperatures (above 330 K), NO₂ is the major species present at equilibrium. For the process described here, state whether the thermodynamic quantities listed are equal to zero, greater than zero, less than zero or cannot be decided, using the symbols =0, >0, <0 or ? respectively at 298 K. Please provide the reasoning you used to arrive at your answer.

a. \( \Delta G^0 < 0 \)

If the equilibrium lies to the right, \( k > 1 \). Since

\[ \Delta G^0 = -RT \ln(K) \]

\( \Delta G^0 < 0 \) if \( k > 1 \).

b. \( \Delta H^0 < 0 \)

Since at low temps the equilibrium lies to the right, but at high temps the equilibrium lies to the left,

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]

\( \Delta H^0 < 0 \). At low temps, the contribution of \( -T \Delta S^0 \) is minimal, so a negative \( \Delta H^0 \) can make \( \Delta G^0 < 0 \).

c. \( \Delta S^0 < 0 \)

Since at high temps, \( k < 1 \) (the equilibrium lies to the left), and \( \Delta G^0 > 0 \), \( \Delta S^0 \) must be negative. At high temps, the term \( -T \Delta S^0 \) will be positive and will overcome \( \Delta H^0 \).

d. At 350 K for this reaction, is \( \Delta G^0 = 0, >0, <0 \) or ?. Explain your answer.

\( \Delta G^0 > 0 \) At this temperature, the equilibrium lies to the left. By \( \Delta G^0 = -RT \ln(K) \), when \( k < 1 \),

\( \Delta G^0 > 0 \).
A pure sample of NO₂ at 298 K is placed into a sealed, rigid and evacuated flask. It is observed to react to form N₂O₄ predominantly. During this process, the temperature of the flask is observed to increase and then return to room temperature. For the isothermal reaction 2NO₂(g) ⇌ N₂O₄(g) at 298 K under these conditions, provide the algebraic signs for the following quantities, stating your reasons. (You may assume that both NO₂ and N₂O₄ behave as ideal gases.)

\[ PV = nRT \]

For:

\[ q \leq 0 \]

Since when the reaction is conducted under adiabatically not isochorically, the temperature is observed to increase, my would suggest that \( q \leq 0 \). While for many cases with ideal gases, \( \Delta E = 0 \) when conducted isothermally, there is a chemical law saying that the point is no longer necessarily valid.

\( w = 0 \)

The flask is evacuated so it is not existing against any. But as it expands to fill the flask, once it has expanded to fill the flask, no volume change can occur in the flask is rigid, so \( PAV = 0 \)

\( \Delta H < 0 \)

Since \( \Delta H = \Delta E + \Delta PV \)

\( \Delta E + \Delta PV = \Delta H \)

\( \Delta E = RT \Delta \nabla H \)

\[ \Delta S_{\text{system}} = \frac{\Delta G}{T} \]

Two gaseous molecules change into one.

We do not know the reaction.

\[ \Delta G = \Delta H - T \Delta S \]

We do not know the reaction,

\[ \Delta S_{\text{surroundings}} = -\frac{\Delta G}{T} \]

\( \Delta S_{\text{surroundings}} > 0 \)

\( \Delta S < 0 \)

However, the fact that moles of gas is being formed from 2 moles of gas would suggest that \( \Delta S < 0 \) as does the fact that \( q \leq 0 \). However, we do not know how long it takes.
3)

a. Calculate the pH of a 0.200 M solution of HOAc (acetic acid). $K_a$ of the acid = $1.85 \times 10^{-5}$

\[ K_a = \frac{[H^+]\left[\text{OAc}^-\right]}{[\text{HOAc}]} \]

(Assume $x \ll 10^{-7}$)

\[ 1.85 \times 10^{-5} = \frac{(x)(x)}{1.2 - x} \]

\[ 3.7 \times 10^{-6} - 1.85 \times 10^{-5} x = x^2 \]

\[ x = \frac{0.019143106}{1} = H^+ \]

\[ \sqrt{0.01827} = \text{mol NaOH added} \]

b. Calculate the volume of 0.10 M NaOH solution that must be added to 500.0 ml of 0.200 M HOAc to give a solution that has pH = 3.0.

\[ \text{Add } 0.131639 \text{ mol NaOH} \]

\[ 0.131639 \text{ mol NaOH} \text{ to } 0.2 \text{ mol HOAc} \]

\[ \text{OH}^- + \text{HOAc} \rightarrow \text{OAc}^- + \text{H}_2\text{O} \]

\[ \text{pH} = 3 \text{ thus } -\log[H^+] = 3 \]

\[ \log[H^+] = -3 \left[10^{-3}\right] \]

\[ \text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \]

\[ 3 = -\log(1.85 \times 10^{-5}) + \log x \]

\[ X = \frac{0.01827}{\text{mol base} / \text{mol added}} \]

Calculate the volume of 0.10 M NaOH solution that must be added to 500.0 ml of 0.200 M HCl to give a solution that has pH = 3.0

\[ \text{pH} = 3 \text{ [H}^+] = 10^{-3} \]

\[ \text{thus } [\text{HCl}] = 10^{-3} \]

Latter addition, all discorporated

\[ \frac{0.1 \text{ mol HCl} - 0.1 \text{ mol NaOH}}{1000 \text{ ml}} = 10^{-3} \]

\[ 0.1 - 0.1 \text{ NaOH} = 5 \times 10^{-4} + 10^{-3}V \]

\[ 1 - 5 \times 10^{-4} = 10^{-3}V + 0.1 \]

\[ \frac{0.995}{101 V} = \frac{0.995}{101} \]

\[ 0.995 \times 10^{-4} = \text{mol NaOH added} \]

\[ V = 0.985 L \]
The cell potential ($E$) depends on concentrations. The Nernst equation, which expresses this dependence, is given on the cover page.

Consider a concentration cell containing 0.20 M solutions of AgNO$_3$ in both compartments. For this cell, what is the value of $\ln Q$, $E^\circ$, and $E$? (Explain your answers)

$$E^\circ = 0$$ For a concentration cell, $E^\circ$ always = 0.

When reactants and products are all at 1 M concentrations, there is no difference in concentration to lead to a voltage.

$$E = 0$$ Since the concentrations in mols.

$$E = E^\circ - \frac{RT}{nF} \ln Q$$ Concentration cell are equal, $\ln Q = 0$. Thus

$$E = -\frac{RT}{nF} \ln \frac{1}{2m}$$

$$E = 0$$

$$E = 0$$

$$\ln Q = 0$$

$$\ln Q = \ln \left( \frac{\text{products}}{\text{reactants}} \right) = \ln \frac{1}{2m} = 0$$

$$Q = \frac{[\text{products}]}{[\text{reactants}]}$$ in this cell, the products and reactants are the same species at the same concentration (any $\chi n$)

Thus $Q = 1$

$$\ln Q \; \ln Q = 0$$
5) An electrochemical cell is built around the overall reaction

$$\text{Cr}_2\text{O}_7^{2-} (\text{aq}) + 14 \text{H}^+ (\text{aq}) + 6 \text{I}^- \rightarrow 2 \text{Cr}^{3+} (\text{aq}) + 3 \text{I}_2 (\text{sol}) + 7 \text{H}_2\text{O} (\text{liq})$$

The standard reduction potential for dichromate ion to chromium (III) ion is 1.33 V and the standard reduction potential of solid iodine to iodide ion is 0.54 V.

a) Calculate the standard voltage of this cell.

$$E^o = 1.33 \text{ V}$$

$$E^o = -0.54 \text{ V}$$

$$E^o = 0.79 \text{ V}$$

b) Calculate the equilibrium constant of the overall reaction.

$$N_0^o = -nE^o$$

$$\Delta G^o = -RT \ln K$$

$$\frac{nF \times E^o}{nF} = \frac{RT \ln K}{nF}$$

$$E^o = \frac{RT \ln K}{nF}$$

$$-0.79 \text{ V} = \frac{(8.3145 \text{ g} \text{mol}^{-1} \text{K}^{-1})(298 \text{ K}) \ln K}{(6)(96485 \text{ g} \text{mol}^{-1})}$$

$$e^{+184.580.4673} = \ln K$$

$$1.453042818 \times 10^{80} \not{= 1.45 \times 10^{80}} = K$$
c) At pH=0, with \([\text{Cr}_2\text{O}_7^{2-}] = 1.5 \text{ M}\) and \([\text{I}^-] = 0.40 \text{ M}\), the measured voltage is 0.87 V. Find the concentration of \([\text{Cr}^{3+}]\) in the cell.

\[
\varepsilon = E^0 - \frac{RT}{nF} \ln Q
\]

\[
0.87 = 0.79 - \frac{(0.3145 \text{ mol/L})(298K)}{(6)(96485 \text{ cmol/L})} \ln \frac{[\text{Cr}^{3+}]^2}{(1.5 \text{ M})^6(0.4 \text{ M})^6(1)^4}
\]

\[
0.08 = -0.004279975 \ln Q
\]

\[
Q = \frac{[\text{Cr}^{3+}]^2}{[\text{I}^-]^6[\text{H}^+]^4[\text{Cr}_2\text{O}_7^{2-}]}
\]

\[
e = 7.62 \times 10^{-9} \times 10^{-9} = \frac{[\text{Cr}^{3+}]^2}{(1.5 \text{ M})(0.4 \text{ M})^6}
\]

\[
4.685 \times 10^{-11} = [\text{Cr}^{3+}]^2
\]

\[
6.85 \times 10^{-10} \text{ M} = [\text{Cr}^{3+}] \times 6.85 \times 10^{-8} \text{ M}
\]
6) 40.0 mL of 0.0800 M Sr(NO₃)₂ and 80.0 mL of 0.0500 KF are mixed, producing a precipitate of strontium fluoride, whose Kₚ is 2.8E-9. Find the concentrations of strontium ion and fluoride ion remaining in solution.

Kₛ₀ₚ = [Sr²⁺][F⁻]²

2.8 x 10⁻⁹ = [Sr²⁺][F⁻]²

But Kₛ₀ₚ refers to

2.8 x 10⁻⁹ = \( \frac{(0.0032-x)(0.004-2x)(0.004-2x)}{0.12} \)

12 from \( \frac{120 \text{ mL}}{1000 \text{ mL}} \)

Start with 0.0032 mol Sr(NO₃)₂

1004 mol KF

\( 2.8 \times 10^{-9} = \frac{(0.0032-x)(0.004-2x)(0.004-2x)}{0.001728} \)

\( 4.18384 \times 10^{-12} = (0.0032-x)(0.004-2x)(0.004-2x) \)

\( 4.18384 \times 10^{-12} = (0.0032-x)(1.6 \times 10^{-5} - 0.016 x + 4x^2) \)

\( 0 = 5.12 \times 10^{-5} - 5.12 \times 10^{-5} x + 0.0128 x^2 - 1.6 \times 10^{-5} x^3 - 0.016 x^2 + 4x^2 \)

\( 0 = 5.12 \times 10^{-5} - 5.12 \times 10^{-5} x + 0.0128 x^2 - 1.6 \times 10^{-5} x^3 - 0.016 x^2 + 4x^2 \)

We get \( x = 0.0019686577 \)

\( y = 0.0020322135 \)

\( y = 0.0031991588 \)

Since \( 2x \) must be less than 0.004 if we can't have

\[ \text{[Sr}^{2+}] = \frac{0.0032 - 0.0019686577}{0.12} \approx 0.010 M \]

\[ \text{[F}^-] = \frac{0.004 - 2(0.0019686577)}{0.12} \approx 5.2 \times 10^{-4} M \]

F⁻ that wasn't added in the first place these two ions are rejected.