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|--------|-----|
| Quiz 7 |     |

1. For the equilibrium below,  $K_c = 2.0 \times 10^{-6}$ . What is the equilibrium concentration of oxygen (in moles/L) if 0.20 mol CO<sub>2</sub> and 0.10 mol CO were initially placed into an evacuated 0.50 L vessel and the system is allowed to come to equilibrium? (9 points)

 $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ 

Since we have zero  $O_2$  initially, we know we cannot be at equilibrium so we must use an ICE table or some other approach to find equilibrium concentrations.

|   | 2CO <sub>2</sub> | $\rightleftharpoons$ | 2CO     | + | <b>O</b> <sub>2</sub> | Kc | = | $[CO]^{2}[O_{2}]$ | = | $(0.20+2x)^2x$ |
|---|------------------|----------------------|---------|---|-----------------------|----|---|-------------------|---|----------------|
| L | 0.40 M           |                      | 0.20 M  |   | 0                     |    |   | $[CO_2]^2$        |   | $(0.40-2x)^2$  |
| С | -2x              |                      | +2x     |   | +x                    |    |   |                   |   |                |
| Е | 0.40-2x          |                      | 0.20+2x |   | Х                     |    |   |                   |   |                |

Without some simplification, we will need to solve a third order polynomial. Can we simplify? Since K is small, we would not expect the reaction to proceed very far to the right. Also, the presence of CO intitially will further impede the reaction. So, we expect x to be small. Lets assume x < 0.20. If this is so, the K<sub>c</sub> expression changes.

$$K_{c} = (0.20+2x)^{2}x = (0.20)^{2}x (0.40-2x)^{2} (0.40)^{2}$$

After rearranging we find that  $x = K_c(0.40)^2/(0.20)^2 = 8.0 \times 10^{-6}$ . So,  $[O_2] = 8.0 \times 10^{-6}$ M. Was our assumption OK? 0.20 - 0.0000080 = 0.1999920, which to the correct number of sig figs is indistinguishable from 0.20, so our assumption is fine. We could have used a calculator or computer to solve the third order polynomial. Doing so on my calculator gave a value for x of 7.998x10^{-6}.

Solid ammonium nitrate can decompose to dintrogen oxide gas and liquid water by the reaction below. What is the ∆G° at 298K? At what temperature, if any, does spontaneity of the reaction change? (9 points)

|   | Species              | ∆H° <sub>f</sub> (kJ/mol) | S <sup>°</sup> f (J/mol) |  |  |
|---|----------------------|---------------------------|--------------------------|--|--|
|   | $NH_4NO_3(s)$        | -365.6                    | 151.1                    |  |  |
| $NH_4INO_3(S) \to ZIN_2O(G) + H_2O(\ell)$ | N <sub>2</sub> O (g) | +82.05                    | 219.9                    |  |  |
|   | H <sub>2</sub> O (ℓ) | -285.8                    | 69.91                    |  |  |

For my incorrectly balanced reaction above:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

 $\Delta H^{\circ} = 2\Delta H^{\circ}_{f}(N_{2}O) + \Delta H^{\circ}_{f}(H_{2}O)] - [\Delta H^{\circ}_{f}(NH_{4}NO_{3})]$  $\Delta H^{\circ} = [2(+82.05) + (-285.8)] - [(-365.6)]kJ$  $\Delta H^{\circ} = +243.9 kJ$ 

$$\begin{split} \Delta S^{\circ} &= 2\Delta S^{\circ}{}_{f}(N_{2}O) + \Delta S^{\circ}{}_{f}(H_{2}O)] - [\Delta S^{\circ}{}_{f}(NH_{4}NO_{3})] \\ \Delta S^{\circ} &= [2(219.9) + (69.91)] - [(151.1)]J/K \\ \Delta S^{\circ} &= +358.6 \text{ J/K} \end{split}$$

 $\Delta G^{\circ} = 243.9 \text{ kJ/mol} - 298 \text{ K}(0.3586 \text{ kJ/mol} \text{ K}) = +137.0 \text{ kJ}$ 

To find the temperature where spontaneity changes, set  $\Delta G^{\circ} = 0$  and solve for T: T =  $\Delta H^{\circ}/\Delta S^{\circ} = 243.9/0.3586 =$  **680 K**. For the correctly balanced reaction:

 $NH_4NO_3$  (s)  $\rightarrow N_2O$  (g) + 2  $H_2O$  ( $\ell$ )

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

$$\Delta H^{\circ} = \Delta H^{\circ}_{f}(N_{2}O) + 2\Delta H^{\circ}_{f}(H_{2}O)] - [\Delta H^{\circ}_{f}(NH_{4}NO_{3})]$$
  
$$\Delta H^{\circ} = [(+82.05) + 2(-285.8)] - [(-365.6)]kJ$$
  
$$\Delta H^{\circ} = -123.95 \text{ kJ}$$

$$\begin{split} \Delta S^{\circ} &= \Delta S^{\circ}_{f}(N_{2}O) + 2\Delta S^{\circ}_{f}(H_{2}O)] - [\Delta S^{\circ}_{f}(NH_{4}NO_{3})] \\ \Delta S^{\circ} &= [(219.9) + 2(69.91)] - [(151.1)]J/K \\ \Delta S^{\circ} &= +208.6 \ J/K \end{split}$$

 $\Delta G^{\circ} = -123.95 \text{ kJ/mol} - 298 \text{ K}(0.2086 \text{ kJ/mol} \text{ K}) = -186.1 \text{ kJ}$ 

Since  $\Delta H^{\circ}$  is negative and  $\Delta S^{\circ}$  is positive and since  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ , there is no temperature where the reaction is nonspontaneous. Since T is always positive,  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$  will be negative at all temperatures when  $\Delta H^{\circ}$  is negative and  $\Delta S^{\circ}$  is positive.

 25.4 mL of 0.116 M H<sub>2</sub>SO<sub>4</sub> is mixed with 22.4 mL of 0.282 M NaOH. What is the pH of the resulting solution? (7 points) This is a strong acid/strong base reaction. The pH will be determined by what's left after the acid and base react.

 $\begin{array}{c} H_2SO_4 + 2NaOH \rightarrow 2NaCI + 2 \ H_2O \\ 25.4 \ mL \ x \ \underline{0.116 \ mol \ H_2SO_4} \ x \ \underline{2 \ mol \ NaOH} \ = \ \underline{5.89_3 \ mmol \ NaOH \ needed} \\ L \ 1 \ mol \ H_2SO_4 \ to \ consume \ all \ H_2SO_4 \end{array}$ 

 $22.4 \text{ mL x } \underline{0.282 \text{ mol } H_2SO_4} = 6.31_7 \text{ mmol NaOH present}$  LSo,H<sub>2</sub>SO<sub>4</sub> is the limiting reagent, some NaOH will be left over, how much? (6.31<sub>9</sub>-5.89<sub>3</sub>) = 0.424 mmol This will dissociate completely to give 0.426 mmol of OH<sup>-</sup> or an [OH] of:

 $\frac{0.424 \text{ mmol OH}^{-}}{(25.4+22.4)\text{mL}} = 8.87_0 \text{ x } 10^{-3}\text{M}$ 

pOH = -log(8.87<sub>0</sub> x 10<sup>-3</sup>) = 2.05<sub>2</sub> pH = 14-pOH = 11.95

| $\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$               |                     |                      |                    |                     |                     | °C = K – 273.15     |                    |                     |                    |                             | $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ |                     |                     |                     |                    |                     |                     |
|--|---------------------|----------------------|--------------------|---------------------|---------------------|---------------------|--------------------|---------------------|--------------------|-----------------------------|--|---------------------|---------------------|---------------------|--------------------|---------------------|---------------------|
| pH + pOH = 14  |                     |                      |                    |                     | $K_a K_b = K_w$     |                     |                    |                     |                    | $K_p = K_c (RT)^{\Delta n}$ |  |                     |                     |                     |                    |                     |                     |
| 1<br>1A  |                     |                      |                    |                     |                     |                     |                    |                     |                    |                             |  |                     |                     |                     |                    |                     | 18<br>8A            |
| 1<br>H<br>1.00794  | 2<br>2A             |                      |                    |                     |                     |                     |                    |                     |                    |                             |  | 13<br>3A            | 14<br>4A            | 15<br>5A            | 16<br>6A           | 17<br>7A            | 2<br>He<br>4.00260  |
| 3<br>Li<br>6.941   | 4<br>Be<br>9.01218  |                      |                    |                     |                     |                     |                    |                     |                    |                             |  | 5<br>B<br>10.811    | 6<br>C<br>12.011    | 7<br>N<br>14.0067   | 8<br>O<br>15.9994  | 9<br>F<br>18.9984   | 10<br>Ne<br>20.1797 |
| 11<br>Na<br>22.9898  | 12<br>Mg<br>24.3050 | 3<br>3B              | 4<br>4B            | 5<br>5B             | 6<br>6B             | 7<br>7B             | 8                  | 9<br>               | 10                 | 11<br>1B                    | 12<br>2B                                 | 13<br>Al<br>26.9815 | 14<br>Si<br>28.0855 | 15<br>P<br>30.9738  | 16<br>S<br>32.066  | 17<br>Cl<br>35.4527 | 18<br>Ar<br>39.948  |
| 19<br>K<br>39.0983   | 20<br>Ca<br>40.078  | 21<br>Sc<br>44.9559  | 22<br>Ti<br>47.88  | 23<br>V<br>50.9415  | 24<br>Cr<br>51.9961 | 25<br>Mn<br>54.9381 | 26<br>Fe<br>55.847 | 27<br>Co<br>58.9332 | 28<br>Ni<br>58.693 | 29<br>Cu<br>63.546          | 30<br>Zn<br>65.39                        | 31<br>Ga<br>69.723  | 32<br>Ge<br>72.61   | 33<br>As<br>74.9216 | 34<br>Se<br>78.96  | 35<br>Br<br>79.904  | 36<br>Kr<br>83.80   |
| 37<br>Rb<br>85.4678  | 38<br>Sr<br>87.62   | 39<br>Y<br>88.9059   | 40<br>Zr<br>91.224 | 41<br>Nb<br>92.9064 | 42<br>Mo<br>95.94   | 43<br>Tc<br>(98)    | 44<br>Ru<br>101.07 | 45<br>Rh<br>102.906 | 46<br>Pd<br>106.42 | 47<br>Ag<br>107.868         | 48<br>Cd<br>112.411                      | 49<br>In<br>114.818 | 50<br>Sn<br>118.710 | 51<br>Sb<br>121.757 | 52<br>Te<br>127.60 | 53<br>I<br>126.904  | 54<br>Xe<br>131.29  |
| 55<br>Cs<br>132.905  | 56<br>Ba<br>137.327 | 57<br>*La<br>138.906 | 72<br>Hf<br>178.49 | 73<br>Ta<br>180.948 | 74<br>W<br>183.84   | 75<br>Re<br>186.207 | 76<br>Os<br>190.23 | 77<br>Ir<br>192.22  | 78<br>Pt<br>195.08 | 79<br>Au<br>196.967         | 80<br>Hg<br>200.59                       | 81<br>Tl<br>204.383 | 82<br>Pb<br>207.2   | 83<br>Bi<br>208.980 | 84<br>Po<br>(209)  | 85<br>At<br>(210)   | 86<br>Rn<br>(222)   |
| 87<br>Fr<br>(223)  | 88<br>Ra<br>226.025 | 89<br>†Ac<br>227.028 | 104<br>Rf<br>(261) | 105<br>Db<br>(262)  | 106<br>Sg<br>(266)  | 107<br>Bh<br>(264)  | 108<br>Hs<br>(277) | 109<br>Mt<br>(268)  | 110<br>Ds<br>(271) | 111<br>Rg<br>(272)          |  |                     |                     |                     |                    |                     |                     |
| *Lanthanide series 58 59<br>Ce Pr<br>140.115 140.998                                 |                     |                      | 60<br>Nd<br>144.24 | 61<br>Pm<br>(145)   | 62<br>Sm<br>150.36  | 63<br>Eu<br>151.965 | 64<br>Gd<br>157.25 | 65<br>Tb<br>158.925 | 66<br>Dy<br>162.50 | 67<br>Ho<br>164.930         | 68<br>Er<br>167.26                       | 69<br>Tm<br>168.934 | 70<br>Yb<br>173.04  | 71<br>Lu<br>174.967 |                    |                     |                     |
| <sup>†</sup> Actinide series<br><sup>90</sup> 91<br>Pa<br><sup>232,038</sup> 231.036 |                     |                      |                    | 92<br>U<br>238.029  | 93<br>Np<br>237.048 | 94<br>Pu<br>(244)   | 95<br>Am<br>(243)  | 96<br>Cm<br>(247)   | 97<br>Bk<br>(247)  | 98<br>Cf<br>(251)           | 99<br>Es<br>(252)                        | 100<br>Fm<br>(257)  | 101<br>Md<br>(258)  | 102<br>No<br>(259)  | 103<br>Lr<br>(262) |                     |                     |

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