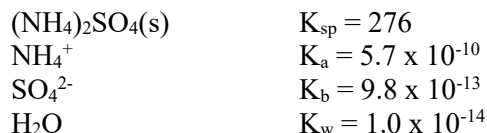


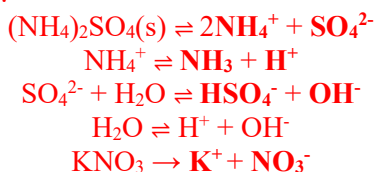
Complete problem 1 and four of problems 2-6. CLEARLY mark the problems you do not want graded. You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures.

You MUST complete problem 1. (16 pts.)

1. When ammonium sulfate dissolves, both the anion and the cation can participate in acid-base equilibria. Considering all the equilibria reflected by the equilibrium constants below, write enough equations so that you could solve for the concentration of each species in **a solution that is saturated with ammonium sulfate and also contains 0.20 M potassium nitrate.** You must write the charge balance expression and at least one mass balance. *Identify all unknowns and write enough explicit, independent equations so that only algebra remains to solve for the unknowns. A numerical answer is not necessary. Ignore activities.*



Reactions (Unknowns are in **Bold**):



So, we need a total of eight equations for our eight unknowns.

Charge Balance (4)

$$[\text{NH}_4^+] + [\text{H}^+] + [\text{K}^+] = 2[\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{OH}^-] + [\text{NO}_3^-]$$

Mass Balance: (8)

total concentration of nitrogen from ammonium = 2(total concentration of sulfur from sulfate)

$$\begin{aligned}[\text{N}]_{\text{total}} &= 2[\text{S}]_{\text{total}} \\ [\text{NH}_3] + [\text{NH}_4^+] &= 2[\text{SO}_4^{2-}] + 2[\text{HSO}_4^-]\end{aligned}$$

Concentrations of Na^+ and NO_3^- are constant

$$\begin{aligned}[\text{K}^+] &= 0.20 \text{ M} \\ [\text{NO}_3^-] &= 0.20 \text{ M}\end{aligned}$$

Equilibrium constant expressions: (4)

$$K_{\text{a}} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \quad K_{\text{sp}} = [\text{NH}_4^+]^2 [\text{SO}_4^{2-}] \quad K_{\text{w}} = [\text{H}^+][\text{OH}^-]$$

$$K_{\text{b}} = \frac{[\text{HSO}_4^-][\text{OH}^-]}{[\text{SO}_4^{2-}]}$$

We now have enough equations to solve for all of the unknowns

Do four of problems 2-6. Clearly mark the problems you do not want graded. (16 pts. ea.)

2. Consider the table of activity coefficients below. As you move from left to right across any row on the table, the values for activity coefficient decrease. As you move down in a given column, the activity coefficient also decreases. Clearly describe the phenomena that cause these trends. **Do not simply point out the trends; *you must explain why the trends are observed.*** No calculations are necessary.

| Species | Ionic Strength | | |
|---------------|----------------|--------|-------|
| | 0.001 M | 0.01 M | 0.1 M |
| hydronium ion | 0.967 | 0.914 | 0.830 |
| nitrate ion | 0.964 | 0.899 | 0.755 |
| calcium ion | 0.870 | 0.675 | 0.405 |
| sulfate ion | 0.867 | 0.660 | 0.355 |
| phosphate ion | 0.725 | 0.395 | 0.095 |

The cause for both trends is rooted in electrostatic interactions between the ion of interest and other materials in solution. Moving left to right across a row in the table, the ionic strength of the solution increases. As μ increases, there is a greater probability that the ion of interest will undergo an interaction with a third-party ion in solution, thus decreasing its activity in the reaction of interest. Moving down in the table, the charge on the ion is increasing. This increase in charge provides for stronger electrostatic interactions with all other ions in solution, also reducing activity. For ions of the same charge, the ion with smaller hydrated ion size is more likely to interact with other competing ions in solution, decreasing the activity coefficient.

3. Aziridine (C_2NH_5) is a monobasic weak base with a pK_b of 5.96. Calculate the pH of a solution prepared by mixing 20.0 mL of 0.025 M HCl with 50.0 mL of 0.036 M aziridine and diluting the resulting solution to 100.0 mL. *Do not consider autoprotolysis or activities.*

Whenever you mix a strong acid with a weak base, they will react until one is completely consumed. Whatever remains after the reaction is complete will determine pH.

(6) What's left after HCl and aziridine react? (I'll call the aziridine "B")

| | | | | | | | |
|------------------|---------------|---|----------------------------|---|------------------------------|---|-----------------|
| | HCl | + | B | → | BH ⁺ | + | Cl ⁻ |
| Start (mmol) | 0.50 | | 1.8 | | 0 mmol | | 0 mmol |
| End (mmol) | 0.50-0.50 = 0 | | 1.8-0.5 = 1.3 | | 0.50 | | 0.50 |
| Concentration(M) | 0 | | 1.3mmol/100mL = 0.013 M | | 0.50mmol/100 mL = 0.0050M | | 0.0050 M |

(10) Now the equilibrium:

| | | | | | | | | |
|---|---------|---|------------------|---|-----------------|---|-----------------|---------------------------------------|
| | B | + | H ₂ O | ⇌ | BH ⁺ | + | OH ⁻ | $K_b = \frac{[BH^+][OH^-]}{[B]}$ |
| I | 0.013M | | -- | | 0.0050M | | 0 | |
| C | -x | | -- | | +x | | +x | $K_b = \frac{(0.0050+x)(x)}{0.013-x}$ |
| E | 0.013-x | | -- | | 0.0050+x | | x | |

After some algebra, $0 = x^2 + (0.0050+K_b)x - 0.013K_b$

Solving for x, we get $x = [OH^-] = 2.85 \times 10^{-6} \text{ M}$, $[H^+] = K_w/[OH^-] = 2.85 \times 10^{-9} \text{ M}$

$$pOH = 5.545$$

$$pH = 14 - pOH = 8.455$$

You can simplify the math a little if you realize this is a buffer solution and that we would not expect the equilibrium concentrations to vary much from their original concentrations, essentially assuming $x \ll 0.0050 \text{ M}$. In doing so, the K_b expression becomes:

$$K_b = \frac{0.0050x}{0.013}$$

Solving for x produces the same result as above since $2.85 \times 10^{-6} \ll 0.0050$

A third approach would be to recognize that, after reaction with HCl, a buffer solution is formed, and Henderson Hasselbach equation could be used:

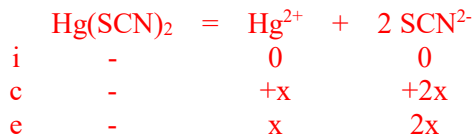
$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

$$pH = (14 - pK_b) + \log \frac{[B]}{[BH^+]}$$

$$pH = 8.04 + \log \frac{[0.013]}{[0.0050]} = 8.45$$

4. Using activities, find the mercury concentration of a solution of 0.025 M K_2SO_4 that is saturated with $Hg(SCN)_2$ (K_{sp} for $Hg(SCN)_2$ is 2.8×10^{-20}). Assume that all other salts are soluble. You may ignore the autoprotolysis of water and any acid-base character of sulfate and thiocyanate. Compare this result to that obtained if you were to ignore activities.

(4) Let's set up the system first:



$$K_{sp} = A_{Hg^{2+}}(A_{SCN^{-}})^2 = \gamma_{Hg^{2+}}[Hg^{2+}](\gamma_{SCN^{-}}[SCN^{-}])^2 = \gamma_{Hg^{2+}}(x)(\gamma_{SCN^{-}}(2x))^2 = 4(\gamma_{Hg^{2+}})(\gamma_{SCN^{-}})^2 x^3$$

$$x = [Hg^{2+}] = \left[\frac{K_{sp}}{4(\gamma_{Hg^{2+}})(\gamma_{SCN^{-}})^2} \right]^{1/3}$$

(4) To find activity coefficients, we need to calculate ionic strength:

$$[SO_4^{2-}] = 0.025 \text{ M}$$

$$[Li^+] = 2(0.025 \text{ M}) = 0.050 \text{ M}$$

$$\mu = 1/2([Li^+](+1)^2 + [SO_4^{2-}](-2)^2) = 1/2(0.050(1) + 0.025(4)) = 0.075 \text{ M}$$

(4) To find activity coefficients, we can either use the Debye-Huckel equation or interpolate from the tabulated values, since $\mu = 0.075 \text{ M}$ is not explicitly given on the table

After interpolation, for $\mu = 0.075 \text{ M}$, $\gamma_{Hg^{2+}} = 0.423$, $\gamma_{SCN^{-}} = 0.785$. If you use the D-H equation, you get $\gamma_{Hg^{2+}} = 0.412$, $\gamma_{SCN^{-}} = 0.783$

$$x = [Hg^{2+}] = \left[\frac{K_{sp}}{4(\gamma_{Hg^{2+}})(\gamma_{SCN^{-}})^2} \right]^{1/3} = \left[\frac{K_{sp}}{4(0.423)(0.785)^2} \right]^{1/3}$$

Substituting into the equation above gives $[Hg^{2+}] = 2.99 \times 10^{-7} \text{ M}$

(4) Ignoring activities,

$$[Hg^{2+}] = x = \left[\frac{K_{sp}}{4} \right]^{1/3}$$

Which gives $[Hg^{2+}] = 1.91 \times 10^{-7} \text{ M}$

5. Complete both parts a and b. (8 points each)

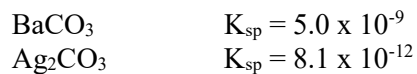
- a. A saturated solution of Ag_2CO_3 ($K_{\text{sp}} = 8.1 \times 10^{-12}$) that originally had a volume of 1.00 L is allowed to evaporate until the solution volume is 0.500 L. How does the new concentration of Ag^+ compare to the concentration in the original solution? Clearly justify your response. *Do not consider activities.*

Since the solution was initially saturated, a decrease in solution volume will force an increase in the concentrations of Ba^{2+} and SO_4^{2-} in solution, leading to supersaturation. This increase will cause the K_{sp} for barium sulfate to be exceeded, resulting in the precipitation of BaSO_4 , and a decrease in the concentration of Ba^{2+} and SO_4^{2-} back to their original values. Therefore, the $[\text{Ba}^{2+}]$ after evaporation will be the same as its initial concentration.

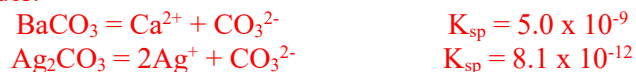
- b. In determining the pH of a solution that contains 0.10 M formic acid ($K_{\text{a}} = 1.8 \times 10^{-4}$) and 0.10 M HF ($K_{\text{a}} = 6.8 \times 10^{-4}$), why is the ICE table approach not a valid strategy to employ? What approach should be used instead? *Do not consider activities.*

Since we have two weak acids in solution, we must account for them simultaneously. That is, since H^+ appears in both equilibria and since there can only be one H^+ concentration in solution, that single concentration must satisfy both equilibrium constant expressions simultaneously. The ICE table approach only addresses one equilibrium at a time. Therefore, if you solve the ICE table for HF to determine $[\text{H}^+]$, the concentration you arrive at will not correspond to the equilibrium concentration for formic acid. You should use the systematic approach using mass and charge balance instead.

6. Is it possible to perform a 99.99 % complete separation of barium and silver by precipitation with carbonate if both Ba^{2+} and Ag^+ are present initially at 0.010 M? Justify your decision. *Do not consider activities.*



Two equilibria to consider:



1. What $[\text{CO}_3^{2-}]$ is needed to lower each ion's concentration to 0.01% of its initial value?
Target $[\text{Ba}^{2+}] = 0.0001(0.010\text{M}) = 1.0 \times 10^{-6}\text{M}$, Target $[\text{Ag}^+] = 1.0 \times 10^{-6}\text{M}$

$$\text{Ba}^{2+}: [\text{CO}_3^{2-}] = \frac{K_{\text{sp}}}{[\text{Ba}^{2+}]} = \frac{5.0 \times 10^{-9}}{1.0 \times 10^{-6}\text{M}} = \mathbf{0.0050\text{M CO}_3^{2-}}$$

$$\text{Ag}^+: [\text{CO}_3^{2-}] = \frac{K_{\text{sp}}}{[\text{Ag}^+]^2} = \frac{8.1 \times 10^{-12}}{(1.0 \times 10^{-6}\text{M})^2} = \mathbf{8.10\text{M CO}_3^{2-}}$$

So, Ba^{2+} will precipitate first.

2. Will Ag^+ precipitate if $[\text{CO}_3^{2-}] = 0.0050\text{M}$?
 $Q = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = (0.010\text{M})^2(0.0050\text{M}) = 5.0 \times 10^{-7}$

Since $Q > K_{\text{sp}}$ for Ag_2CO_3 , Ag^+ will precipitate before $[\text{Ba}^{2+}] = 1.0 \times 10^{-6}\text{M}$.
Separation is not feasible.

Possibly Useful Information

| | |
|---|--|
| $K_a K_b = K_w = 1.0 \times 10^{-14}$ | $\text{pH} = -\log [\text{H}^+]$ |
| $y = mx + b$ | $\text{pH} + \text{pOH} = 14$ |
| $\log \gamma = \frac{-0.51z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu} / 305)}$ (with α in pm) | $\mu = \frac{1}{2} \sum_i c_i z_i^2$ |
| $\Delta G = \Delta H - T\Delta S = -RT \ln K$ | $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ |

Activity coefficients for aqueous solutions at 25°C

| Ion | Ion size (α , pm) | Ionic strength (μ , M) | | | | |
|---|------------------------------|-----------------------------|-------|-------|-------|-------|
| | | 0.001 | 0.005 | 0.01 | 0.05 | 0.1 |
| CHARGE = ± 1 | | | | | | |
| H ⁺ | 900 | 0.967 | 0.933 | 0.914 | 0.86 | 0.83 |
| (C ₆ H ₅) ₂ CHCO ₂ ⁻ , (C ₃ H ₇) ₄ N ⁺ | 800 | 0.966 | 0.931 | 0.912 | 0.85 | 0.82 |
| (O ₂ N) ₃ C ₆ H ₂ O ⁻ , (C ₃ H ₇) ₃ NH ⁺ , CH ₃ OC ₆ H ₄ CO ₂ ⁻ | 700 | 0.965 | 0.930 | 0.909 | 0.845 | 0.81 |
| Li ⁺ , C ₆ H ₅ CO ₂ ⁻ , HOC ₆ H ₄ CO ₂ ⁻ , ClC ₆ H ₄ CO ₂ ⁻ , C ₆ H ₅ CH ₂ CO ₂ ⁻ , CH ₂ =CHCH ₂ CO ₂ ⁻ , (CH ₃) ₂ CHCH ₂ CO ₂ ⁻ , (CH ₃ CH ₂) ₄ N ⁺ , (C ₃ H ₇) ₂ NH ₂ ⁺ | 600 | 0.965 | 0.929 | 0.907 | 0.835 | 0.80 |
| Cl ₂ CHCO ₂ ⁻ , Cl ₃ CCO ₂ ⁻ , (CH ₃ CH ₂) ₃ NH ⁺ , (C ₃ H ₇)NH ₃ ⁺ | 500 | 0.964 | 0.928 | 0.904 | 0.83 | 0.79 |
| Na ⁺ , CdCl ⁺ , ClO ₂ ⁻ , IO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HSO ₃ ⁻ , H ₂ AsO ₄ ⁻ , Co(NH ₃) ₄ (NO ₂) ₂ ⁺ , CH ₃ CO ₂ ⁻ , ClCH ₂ CO ₂ ⁻ , (CH ₃) ₄ N ⁺ , (CH ₃ CH ₂) ₂ NH ₂ ⁺ , H ₂ NCH ₂ CO ₂ ⁻ | 450 | 0.964 | 0.928 | 0.902 | 0.82 | 0.775 |
| ⁺ H ₃ NCH ₂ CO ₂ H, (CH ₃) ₃ NH ⁺ , CH ₃ CH ₂ NH ₃ ⁺ | 400 | 0.964 | 0.927 | 0.901 | 0.815 | 0.77 |
| OH ⁻ , F ⁻ , SCN ⁻ , OCN ⁻ , HS ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , IO ₄ ⁻ , MnO ₄ ⁻ , HCO ₂ ⁻ , H ₂ citrate ⁻ , CH ₃ NH ₃ ⁺ , (CH ₃) ₂ NH ₂ ⁺ | 350 | 0.964 | 0.926 | 0.900 | 0.81 | 0.76 |
| K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , NO ₂ ⁻ , NO ₃ ⁻ | 300 | 0.964 | 0.925 | 0.899 | 0.805 | 0.755 |
| Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , TI ⁺ , Ag ⁺ | 250 | 0.964 | 0.924 | 0.898 | 0.80 | 0.75 |
| CHARGE = ± 2 | | | | | | |
| Mg ²⁺ , Be ²⁺ | 800 | 0.872 | 0.755 | 0.69 | 0.52 | 0.45 |
| CH ₂ (CH ₂ CH ₂ CO ₂ ⁻) ₂ , (CH ₂ CH ₂ CH ₂ CO ₂ ⁻) ₂ | 700 | 0.872 | 0.755 | 0.685 | 0.50 | 0.425 |
| Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺ , C ₆ H ₄ (CO ₂ ⁻) ₂ , H ₂ C(CH ₂ CO ₂ ⁻) ₂ , (CH ₂ CH ₂ CO ₂ ⁻) ₂ | 600 | 0.870 | 0.749 | 0.675 | 0.485 | 0.405 |
| Sr ²⁺ , Ba ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , S ₂ O ₄ ²⁻ , WO ₄ ²⁻ , H ₂ C(CO ₂ ⁻) ₂ , (CH ₂ CO ₂ ⁻) ₂ , (CHOHCO ₂ ⁻) ₂ | 500 | 0.868 | 0.744 | 0.67 | 0.465 | 0.38 |
| Pb ²⁺ , CO ₃ ²⁻ , SO ₃ ²⁻ , MoO ₄ ²⁻ , Co(NH ₃) ₅ Cl ²⁺ , Fe(CN) ₅ NO ²⁻ , C ₂ O ₄ ²⁻ , Hcitrate ²⁻ | 450 | 0.867 | 0.742 | 0.665 | 0.455 | 0.37 |
| Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , S ₂ O ₆ ²⁻ , S ₂ O ₈ ²⁻ , SeO ₄ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻ | 400 | 0.867 | 0.740 | 0.660 | 0.445 | 0.355 |
| CHARGE = ± 3 | | | | | | |
| Al ³⁺ , Fe ³⁺ , Cr ³⁺ , Sc ³⁺ , Y ³⁺ , In ³⁺ , lanthanides ^a | 900 | 0.738 | 0.54 | 0.445 | 0.245 | 0.18 |
| citrate ³⁻ | 500 | 0.728 | 0.51 | 0.405 | 0.18 | 0.115 |
| PO ₄ ³⁻ , Fe(CN) ₆ ³⁻ , Cr(NH ₃) ₆ ³⁺ , Co(NH ₃) ₆ ³⁺ , Co(NH ₃) ₅ H ₂ O ³⁺ | 400 | 0.725 | 0.505 | 0.395 | 0.16 | 0.095 |
| CHARGE = ± 4 | | | | | | |
| Th ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺ | 1 100 | 0.588 | 0.35 | 0.255 | 0.10 | 0.065 |
| Fe(CN) ₆ ⁴⁻ | 500 | 0.57 | 0.31 | 0.20 | 0.048 | 0.021 |

a. Lanthanides are elements 57–71 in the periodic table. SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937**, *59*, 1675.

Periodic Table of the Elements

| | | | | | | | | | | | | | | | | | | | |
|----------------------------|-----|--|------|-----|--------|-----|------|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|------------|--|
| | | | | | | | | | | | | | | | | | | VIIA 8A | |
| 1A | | | | | | | | | VIII | | | | | | | | | | |
| 1 | 2 | | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | |
| IA | | | IIIB | IVB | VB | VIB | VIIB | 8 | 9 | 10 | 11B | 12B | 3A | 4A | 5A | 6A | 7A | 8A | |
| H Hydrogen 1.008 | | | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | |
| 2 | 3 | | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | |
| IIA | | | IIIB | IVB | VB | VIB | VIIB | 8 | 9 | 10 | 11B | 12B | 3A | 4A | 5A | 6A | 7A | 8A | |
| Li Lithium 6.941 | 4 | | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | |
| Be Beryllium 9.012 | 3 | | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | |
| Na Sodium 22.990 | 12 | | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | |
| Mg Magnesium 24.305 | 3 | | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | |
| Ca Calcium 40.078 | 20 | | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | |
| K Potassium 39.098 | 19 | | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | |
| Ar Argon 39.948 | 18 | | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | |
| Kr Krypton 83.798 | 36 | | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | |
| Xe Xenon 131.294 | 54 | | 55 | 56 | 57-71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | |
| Rn Radon 222.018 | 86 | | 87 | 88 | 89-103 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | |
| Og Oganesson [294] | 118 | | 119 | 120 | 121 | 122 | 123 | 124 | 125 | 126 | 127 | 128 | 129 | 130 | 131 | 132 | 133 | 134 | |
| Lu Lutetium 174.967 | 71 | | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | |
| Yb Ytterbium 173.055 | 70 | | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | |
| Lu Lutetium 174.967 | 71 | | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | |
| No Nobelium 259.101 | 103 | | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | 119 | |
| Lr Lawrencium [262] | 103 | | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | 119 | |

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