# Chemistry 1142
# Spring 2013
# Exam 3a

**Name:** KEY

Take a deep breath, and relax! First, answer the questions you know how to do and then work on the more difficult problems. Don't forget to show all your work, so I can give you as much credit as possible.

Good Luck!

*Andy*

**Show all work to receive credit. Be sure to include units, and express answers to the correct number of significant figures / decimal places.**

Q1. [10 pts.] Calculate the pH of the following aqueous solutions at 25 °C. Show *all* work to receive credit!

a) 4.2 x $10^{-3}$ M $HNO_3$ $\xrightarrow{100\%}$ $H^+(aq) + NO_3^-(aq)$ ; $4.2\times10^{-3}$ M

$pH = -\log_{10}[H^+] = -\log_{10}[4.2\times10^{-3}]$

$= \boxed{2.38}$ (2dp)

b) 2.9 x $10^{-4}$ M KOH $\xrightarrow{100\%}$ $K^+(aq) + OH^-(aq)$ ; $2.9\times10^{-4}$ M

$pOH = -\log[OH^-] = -\log_{10}[2.9\times10^{-4}] = 3.538$ @25°C

$pH + pOH = 14.00$

$\Rightarrow pH = 14.00 - pOH = \boxed{10.46}$ (2dp)

c) 4.5 x $10^{-5}$ M $Sr(OH)_2$ $\longrightarrow Sr^{2+}(aq) + 2OH^-(aq)$ ; $9.0\times10^{-5}$ M ; $(2\times4.5\times10^{-5}$ M)

$pOH = -\log_{10}[9.0\times10^{-5}] = 4.046$ $\Rightarrow pH = 14.00 - pOH = \boxed{9.95}$ (2dp)

Q2. [12 pts.] State the Arrhenius, Brønsted, and Lewis definitions of an acid and a base:

| Theory | Acid | Base |
|---|---|---|
| **Arrhenius** | increases $[H_3O^+]$ in water | increases $[OH^-]$ in water |
| **Brønsted** | $H^+$ donor | $H^+$ acceptor |
| **Lewis** | $e^-$ pair acceptor | $e^-$ pair donor |

Q3. [10 pts.] Predict whether the following salts are acidic, basic, or neutral:

a) NaBr — neutral
b) LiF — basic
c) $KNO_2$ — basic
d) $Fe(NO_3)_2$ — acidic
e) $NaCH_3CO_2$ — basic

| CATIONS | ANIONS |
|---|---|
| $Li^+, Na^+, K^+, Rb^+, Cs^+, Ba^{2+}$ | $Cl^-, Br^-, I^-, NO_3^-, ClO_4^-$ |
| NEUTRAL | NEUTRAL |
| $H_3O^+$ | $OH^-$ |
| "all" others are acidic | "all" others are basic |

from strong acids ⇒ conj. base is neutral

from strong bases ⇒ conj. acid is neutral

unless they're from a polyprotic acid...

note: $H_2SO_4$ is diprotic

⇒ $HSO_4^-$ is acidic since it can lose 1 more proton

Q4. [10 pts.] Write the chemical reactions corresponding to $K_{a1}$ and $K_{a2}$ for carbonic acid, $H_2CO_3$.

$H_2O(l) + H_2CO_3(aq) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$ ; $K_{a1}$

$H_2O(l) + HCO_3^-(aq) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$ ; $K_{a2}$

- sequential loss of $H^+$

Q5. [15 pts.] Barbituric acid, $HC_4H_3N_2O_3$, is used to prepare various barbiturate drugs (used as sedatives). Calculate the concentrations of hydronium ion and barbiturate ion in a 0.25 M solution of the acid. The value of $K_a$ is $9.8 \times 10^{-5}$.

$K_a$ rxn: $H_2O(l) + HC_4H_3N_2O_3(aq) \rightleftharpoons H_3O^+(aq) + C_4H_3N_2O_3^-(aq)$

| | | | | |
|---|---|---|---|---|
| I | — | 0.25 M | ≈ 0 | 0 |
| C | — | $-x$ | $+x$ | $+x$ |
| E | — | $(0.25-x)$ | $(x)$ | $(x)$ |

$$K_a = \frac{[H_3O^+][C_4H_3N_2O_3^-]}{[HC_4H_3N_2O_3]_{eq}} \Rightarrow 9.8\times10^{-5} = \frac{(x)(x)}{0.25-x} \approx \frac{x^2}{0.25}$$

$$\Rightarrow x = \sqrt{9.8\times10^{-5} \times 0.25} = 4.95\times10^{-3}$$

5% rule? % ionization $= \frac{4.95\times10^{-3}}{0.25} \times 100 = 2.0\%$ ✓ OK!

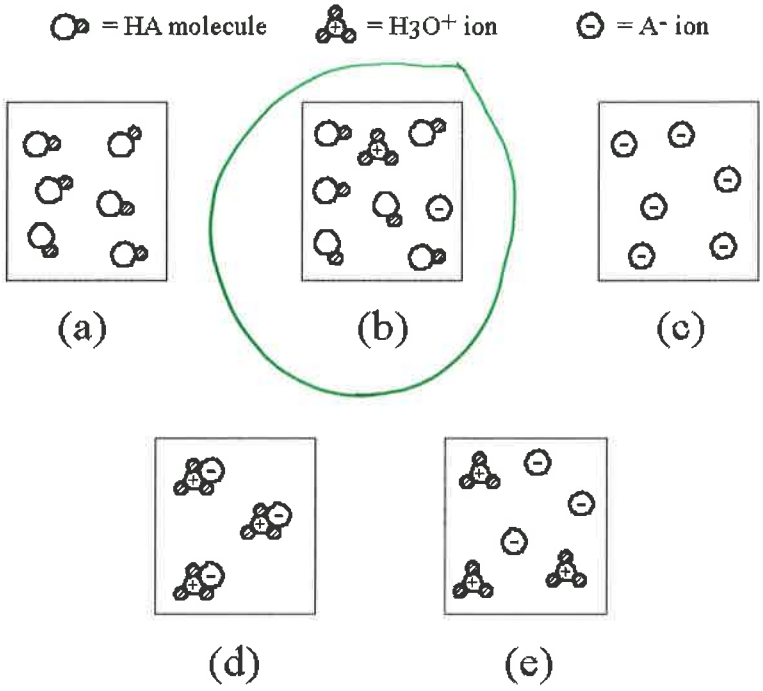
$[H_3O^+]_{eq} = [C_4H_3N_2O_3^-]_{eq} = x = 4.95\times10^{-3}\ M$

$= \boxed{5.0\times10^{-3}\ M}$ or $5.0\ mM$

Q6. [5 pts.] Which of the following diagrams represents a snapshot of a very small portion of a beaker containing a weak acid, HA, dissolved in water? (Circle the best response.)

$HA(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

Note that the solvent molecules (i.e., $H_2O$) are not shown for clarity.




weak acids undergo <100% ionization
⇒ mostly HA @ eq$^m$
only small amount of $H_3O^+$ and $A^-$

Q7. [12 pts.] Calculate the molar solubility of silver carbonate in an aqueous solution of 0.10 M sodium carbonate. $K_{sp}(Ag_2CO_3) = 8.1 \times 10^{-12}$.

$Na_2CO_3(aq) \xrightarrow{100\%} 2Na^+(aq) + CO_3^{2-}(aq)$
0.10M 0.20M 0.10M
common ion!

$K_{sp}$ rxn: $Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$

| | | | |
|---|---|---|---|
| I | ___ | 0 | 0.10 |
| C | "−s" | +2s | +s |
| E | ___ | (2s) | (0.10+s) |

$K_{sp} = [Ag^+]^2[CO_3^{2-}]_{eq} \Rightarrow 8.1\times10^{-12} = (2s)^2(0.10+s) \approx (2s)^2(0.10)$

$\Rightarrow 8.1\times10^{-12} \cong 4s^2 \times 0.10 \Rightarrow s = \sqrt{\frac{8.1\times10^{-12}}{4\times0.10}} = \boxed{4.5\times10^{-6}\,M}$

Q8. [12 pts.] Solutions of lead(II) nitrate and sodium iodide are mixed together in a test-tube. Upon mixing, $[Pb^{2+}] = 2.4 \times 10^{-3}$ M and $[I^-] = 1.8 \times 10^{-2}$ M. Will a precipitate of lead(II) iodide form? $K_{sp}(PbI_2) = 1.4 \times 10^{-8}$. *Show all work.*

$K_{sp}$ rxn: $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

$Q_{sp} = [Pb^{2+}]_i [I^-]_i^2 = [2.4 \times 10^{-3}][1.8 \times 10^{-2}]^2 = 7.8 \times 10^{-7}$

Since $Q_{sp} > K_{sp}$, eqm will shift to LHS + form a ppt

$Q \sim \frac{P\downarrow}{RT\uparrow}$

Q9. [14pts.] A buffer is prepared by adding 45.0 mL of 0.18 M NaF to 35.0 mL of 0.12 M HF. What is the pH of the final solution? $K_a$ for HF is $6.8 \times 10^{-4}$.

$NaF(aq) \longrightarrow Na^+(aq) + F^-(aq)$

$F^-$ = conj. base of HF

Vol change upon mixing, so let's work w/ #mol

$\#mol\ F^- = 0.0450L \times \frac{0.18mol}{L} = 8.1 \times 10^{-3}\ mol$

$\#mol\ HF = 0.0350L \times \frac{0.12mol}{L} = 4.2 \times 10^{-3}\ mol$

$tot.\ vol = 45.0mL + 35.0mL = 80.0mL = 0.0800L$

Since we have a buffer, let's use the Henderson-Hasselbalch equation!

$pH = pK_a + \log \frac{[base]}{[acid]}$, $pK_a = -\log K_a = -\log(6.8 \times 10^{-4}) = 3.167$

$\Rightarrow pH = 3.167 + \log_{10}\left(\frac{8.1 \times 10^{-3}\ mol / 0.0800L}{4.2 \times 10^{-3}\ mol / 0.0800L}\right)$

$= 3.167 + 0.285$

$= \boxed{3.45}$ (2dp)

$HA \rightleftharpoons H^+ + A^-$

$K_a \sim \frac{Prods}{Reacts}$ $\Rightarrow$ $K_a \uparrow$ as % dissoc $\uparrow$

**BONUS Questions. Circle the best response:**

Q. Given three separate solutions containing equal concentrations of formic acid ($K_a = 1.7 \times 10^{-4}$), phenol ($K_a = 1.3 \times 10^{-10}$), and acetic acid ($K_a = 1.8 \times 10^{-5}$), select the response below that has the acids arranged in order of increasing percent dissociation at equilibrium.

a) formic < phenol < acetic
b) formic < acetic < phenol
c) acetic < formic < phenol
d) phenol < acetic < formic
e) No response is correct.

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Q. Why is it necessary to take the acid-base properties of water into account when computing the hydronium ion concentration of very dilute solutions of strong acids?

a) The hydroxide ion produced from the dissociation of water reacts with most of the hydronium ion produced from the acid.
b) The dissociation constant for water is larger in dilute rather than in concentrated solutions of acids.
c) The acids do not dissociate completely in dilute solutions.
d) The amount of hydronium ion produced by the dissociation of water is significant compared to that produced by the acid.
e) The conjugate base of the strong acid reacts with the hydroxide ion produced from the dissociation of water.

normally we assume $[H^+]_i \approx 0$ but if acid is really dilute, have to use actual $[H^+]_i = 1.0 \times 10^{-7} M$

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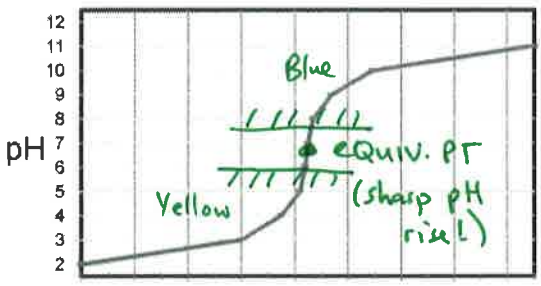
Q. Given the following pH titration curve, which acid-base indicator should be used to determine the end-point?




| Indicator | Color In Acid | Color In Base | pH Range* |
|---|---|---|---|
| Thymol blue | Red | Yellow | 1.2–2.8 |
| Bromophenol blue | Yellow | Bluish purple | 3.0–4.6 |
| Methyl orange | Orange | Yellow | 3.1–4.4 |
| Methyl red | Red | Yellow | 4.2–6.3 |
| Chlorophenol blue | Yellow | Red | 4.8–6.4 |
| Bromothymol blue | Yellow | Blue | 6.0–7.6 |
| Cresol red | Yellow | Red | 7.2–8.8 |
| Phenolphthalein | Colorless | Reddish pink | 8.3–10.0 |

*The pH range is defined as the range over which the indicator changes from the acid color to the base color.

a) Thymol blue
b) Methyl orange
c) Bromothymol blue
d) Phenolphthalein

color changes going from pH 6.0 → 7.6 which is close to equiv. point (end-point)

# Chemistry 1142
# Spring 2013
# Exam 3b

**Name:** KEY

Take a deep breath, and relax! First, answer the questions you know how to do and then work on the more difficult problems. Don't forget to show all your work, so I can give you as much credit as possible.

Good Luck!

*Andy*

See version 3A for details...

**Show all work to receive credit. Be sure to include units, and express answers to the correct number of significant figures / decimal places.**

Q1. [10 pts.] Calculate the pH of the following aqueous solutions at 25 °C. Show *all* work to receive credit!

a) $1.9 \times 10^{-2}$ M $HNO_3$

1.72

b) $2.9 \times 10^{-4}$ M LiOH

10.46

c) $3.2 \times 10^{-5}$ M $Sr(OH)_2$

9.81

Q2. [12 pts.] State the Arrhenius, Brønsted, and Lewis definitions of an acid and a base:

| Theory | Acid | Base |
|---|---|---|
| **Arrhenius** | See 3A | |
| **Brønsted** | | |
| **Lewis** | | |

Q3. [10 pts.] Predict whether the following salts are acidic, basic, or neutral:

a) NaF Basic
b) LiBr Neutral
c) $KNO_2$ Basic
d) $Al(NO_3)_3$ Acidic
e) $CH_3CO_2Na$ Basic

Q4. [10 pts.] Write the chemical reactions corresponding to $K_{a1}$ and $K_{a2}$ for oxalic acid, $H_2C_2O_4$.

$$H_2O(l) + H_2C_2O_4(aq) \rightleftharpoons H_3O^+(aq) + HC_2O_4^-(aq)$$

$$H_2O(l) + HC_2O_4^-(aq) \rightleftharpoons H_3O^+(aq) + C_2O_4^{2-}(aq)$$

Q5. [15 pts.] Barbituric acid, $HC_4H_3N_2O_3$, is used to prepare various barbiturate drugs (used as sedatives). Calculate the concentrations of hydronium ion and barbiturate ion in a 0.35 M solution of the acid. The value of $K_a$ is $9.8 \times 10^{-5}$.

$5.9 \times 10^{-3}$ M (See Exam 3A)

Q6. [5 pts.] Which of the following diagrams represents a snapshot of a very small portion of a beaker containing a weak acid, HA, dissolved in water? (Circle the best response.)

$HA(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

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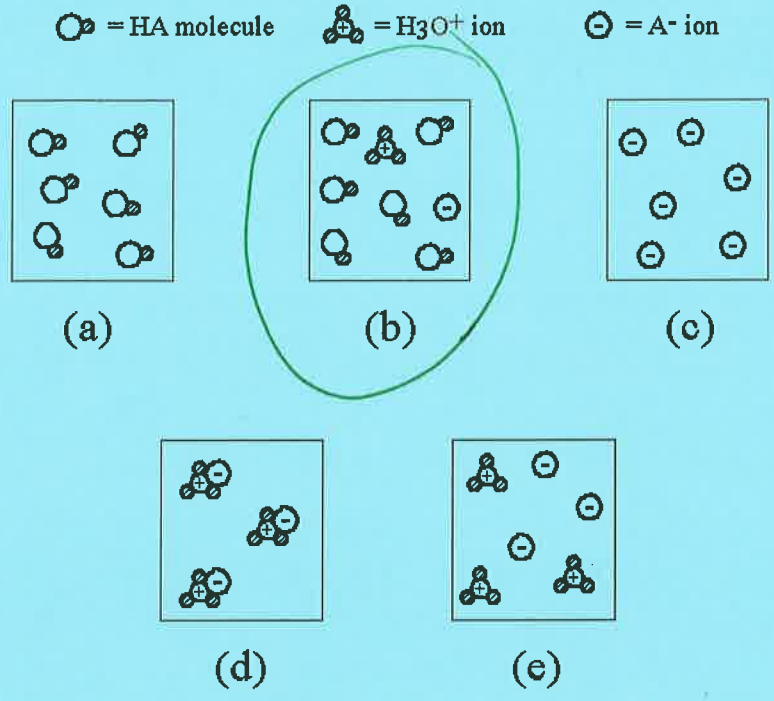


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$1.4 \times 10^{-6}$ M

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$$Q_{sp} = [Pb^{2+}]_i [I^-]_i^2 = 9.2 \times 10^{-8}$$

$$Q_{sp} > K_{sp} \Rightarrow \text{will ppt.}$$

Q9. [14pts.] A buffer is prepared by adding 15.0 mL of 0.48 M NaF to 75.0 mL of 0.12 M HF. What is the pH of the final solution? $K_a$ for HF is $6.8 \times 10^{-4}$.

3.07

**BONUS Questions. Circle the best response:**

Q. Given three separate solutions containing equal concentrations of formic acid ($K_a = 1.7 \times 10^{-4}$), phenol ($K_a = 1.3 \times 10^{-10}$), and acetic acid ($K_a = 1.8 \times 10^{-5}$), select the response below that has the acids arranged in order of increasing percent dissociation at equilibrium.

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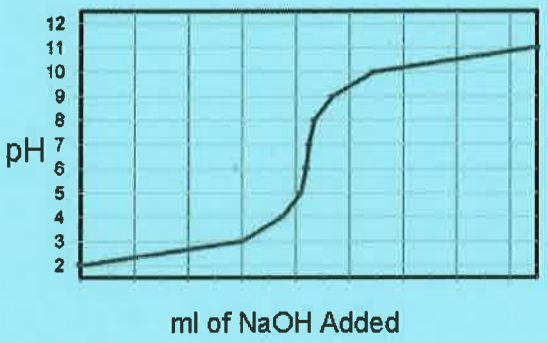


| Indicator | Color In Acid | Color In Base | pH Range* |
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| Cresol red | Yellow | Red | 7.2–8.8 |
| Phenolphthalein | Colorless | Reddish pink | 8.3–10.0 |

*The pH range is defined as the range over which the indicator changes from the acid color to the base color.

a) Thymol blue  b) Methyl orange  c) Bromothymol blue  d) Phenolphthalein

# Useful Information

$N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$

Given: $ax^2 + bx + c$, then $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ at 25 °C.

$pH = -\log[H_3O^+]$

$pH + pOH = 14.00$ (at 25 °C)

$K_aK_b = K_w$

$R = 8.3145\ \text{J/mol·K} = 0.08206\ \text{L·atm/mol·K}$

$$pH = pK_a + \log\frac{[\text{Base}]}{[\text{Acid}]}$$

$M_1V_1 = M_2V_2$

## Periodic Table of the Elements

| IA | IIA | | | | | | | | | | | IIIA | IVA | VA | VIA | VIIA | VIIIA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | | | | | | | | | 2 |
| H | | | | | | | | | | | | | | | | | He |
| 1.01 | 2 | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 4.00 |
| 3 | 4 | | | | | | | | | | | 5 | 6 | 7 | 8 | 9 | 10 |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 6.94 | 9.01 | | | | | | | | | | | 10.81 | 12.01 | 14.01 | 16.00 | 19.00 | 20.18 |
| 11 | 12 | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| 22.99 | 24.31 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 26.98 | 28.09 | 30.97 | 32.07 | 35.45 | 39.95 |
| 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 39.10 | 40.08 | 44.96 | 47.87 | 50.94 | 52.00 | 54.94 | 55.85 | 58.93 | 58.69 | 63.55 | 65.39 | 69.72 | 72.61 | 74.92160 | 78.96 | 79.90 | 83.80 |
| 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| 85.47 | 87.62 | 88.91 | 91.22 | 92.91 | 95.94 | [98] | 101.07 | 102.91 | 106.42 | 107.87 | 112.41 | 114.82 | 118.71 | 121.76 | 127.60 | 126.90 | 131.29 |
| 55 | 56 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 |
| Cs | Ba* | Lu | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 132.91 | 137.33 | 174.97 | 178.49 | 180.95 | 183.84 | 186.21 | 190.23 | 192.22 | 195.08 | 196.97 | 200.59 | 204.38 | 207.20 | 208.98 | [210] | [210] | [222] |
| 87 | 88 | 103 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 |
| Fr | Ra** | Lr | Rf | Db | Sg | Bh | Hs | Mt | | | | | | | | | |
| [223] | [226] | [262] | [261] | [262] | [266] | [264] | [265] | [268] | [269] | [272] | [277] | | [285] | | [289] | | [293] |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| * | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 |
| | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb |
| | 138.91 | 140.12 | 140.91 | 144.24 | [145] | 150.36 | 151.96 | 157.25 | 158.93 | 162.50 | 164.93 | 167.26 | 168.93 | 173.04 |
| ** | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 |
| | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No |
| | [227] | 232.04 | 231.04 | 238.03 | [237] | [244] | [243] | [247] | [247] | [251] | [252] | [257] | [258] | [259] |