

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

Part 0: Warmup. 4 points each

- Reactions with a positive ΔH° and a negative ΔS° are
 - spontaneous at all temperatures.
 - non-spontaneous at all temperatures.
 - spontaneous at low temperatures but non-spontaneous at high temperatures.
 - non-spontaneous at low temperatures but spontaneous at high temperatures.Answer **B**
- Which of the processes below DOES NOT result in an increase in entropy?
 - $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$
 - $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$ (The melting of ice.)
 - $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$ (The sublimation of dry ice.)
 - $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{N}_2\text{O}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$Answer **A**
- Consider the reaction below. If hydrogen chloride gas is being produced at 1.2 moles per liter per minute (M min^{-1}), at what rate is hydrogen gas being consumed?
$$2\text{ICl}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{I}_2(\text{g}) + 2\text{HCl}(\text{g})$$
 - 1.2 M min^{-1}
 - 0.60 M min^{-1}
 - 2.4 M min^{-1}
 - Not enough information to determine.Answer **B**

Part I: Complete all of problems 4-9

- Concisely discuss the validity of each of the following statements in a maximum of three sentences each. Clearly justify your reasoning. (12 points)
 - Reactions with a positive ΔH° and a positive ΔS° are always spontaneous.

Your answer should discuss how ΔH° , ΔS° and ΔG° are related. Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, as long as $T\Delta S^\circ$ is more positive than ΔH° , the reaction will be spontaneous. This occurs if ΔS° is very large or at increased temperature.

- Free energy changes provide a good indication of which reactions are favorable and fast, as well as those that are unfavorable and slow.

Free energy changes are thermodynamic quantities that tell us about the tendency for a reaction to proceed, they tell us nothing about the rate of the reaction. We need information about kinetics to do that.

5. If even a tiny spark is introduced into a mixture of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$, a highly explosive exothermic reaction occurs. Without the spark, the mixture remains unreacted indefinitely. Explain this observation in terms of the reaction thermodynamics and kinetics. A reaction coordinate diagram may be useful.(8 points)

The activation energy for the reaction of hydrogen with oxygen is quite high, too high, in fact, to be supplied by the energy ordinarily available in a mixture of the two gases at ambient temperatures. However, the spark supplies a suitably concentrated form of energy to overcome the activation barrier and initiate the reaction of at least a few molecules. Since the reaction is highly exothermic, the reaction of these first few molecules supplies sufficient energy for yet other molecules to react and the reaction proceeds to completion or to the elimination of the limiting reactant.

6. Consider a *first order* reaction: $\text{B} \rightarrow \text{Products}$. An experiment is performed and it is determined that with a starting $[\text{B}] = 0.100 \text{ M}$, it requires 56.2 seconds for the concentration to fall to 0.029 M. What is the rate constant for the reaction (with appropriate units)? How long would it take for the concentration to fall from 0.100 M to 0.0010 M? (14 points)

The integrated rate law for a first order reaction is helpful here: $\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$. From the problem, $[\text{A}]_t = 0.029 \text{ M}$, $[\text{A}]_0 = 0.100 \text{ M}$ and $t = 56.2 \text{ s}$

$$k = \frac{\ln[\text{A}]_t - \ln[\text{A}]_0}{-t} = \frac{\ln(0.029) - \ln(0.100)}{-56.2 \text{ s}} = \mathbf{0.022 \text{ s}^{-1} = k}$$

Now that we have k, we can use the integrated rate law to solve the second part of the problem:

$$t = \frac{\ln[\text{A}]_t - \ln[\text{A}]_0}{-k} = \frac{\ln(0.0010) - \ln(0.100)}{-0.022 \text{ s}^{-1}} = \mathbf{209 \text{ s} = 210 \text{ s (2 sig figs)}}$$

Answer: Rate constant 0.022 s⁻¹ Time to 0.0010 M 210 s

7. How much heat energy is produced when 0.100 kg of gaseous ethane (C₂H₆) undergoes a combustion reaction with excess oxygen gas to produce gaseous carbon dioxide and liquid water? (14 points)

| Species | $\Delta H^\circ_f, \text{kJ mol}^{-1}$ | Species | $\Delta H^\circ_f, \text{kJ mol}^{-1}$ |
|--------------------|--|-----------------------------------|--|
| O(g) | +249.2 | H ₂ O(l) | -285.8 |
| O ₂ (g) | 0 | H ₂ O(g) | -241.8 |
| H(g) | +218.0 | C ₂ H ₆ (g) | -84.7 |
| H ₂ (g) | 0 | CO ₂ (g) | -393.5 |



$$\Delta H^\circ_{\text{rxn}} = (6\Delta H^\circ_{f, \text{H}_2\text{O}} + 4\Delta H^\circ_{f, \text{CO}_2}) - (2\Delta H^\circ_{f, \text{C}_2\text{H}_6} + 7\Delta H^\circ_{f, \text{O}_2})$$

$$\Delta H^\circ_{\text{rxn}} = (6(-285.8 \text{ kJ}) + 4(-393.5 \text{ kJ})) - (2(-84.7 \text{ kJ}) + 7(0 \text{ kJ}))$$

$$\Delta H^\circ_{\text{rxn}} = -3119 \text{ kJ}$$

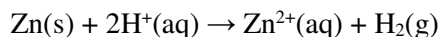
So, 3119 kJ of energy is released every time two moles of ethane is consumed.

$$100 \text{ g C}_2\text{H}_6 \times \frac{1 \text{ mol C}_2\text{H}_6}{30.07 \text{ g C}_2\text{H}_6} \times \frac{3119 \text{ kJ}}{2 \text{ mol C}_2\text{H}_6} = \mathbf{5188 \text{ kJ}}$$

Answer _____ **5190 kJ (3 s.f.)** _____

Part II. Answer three (3) of problems 8-11. Clearly mark the problem you do not want graded. 14 points each.

8. In a constant-pressure experiment, a coffee-cup calorimeter contains 100.0 mL of 0.300 M HCl at 20.3°C. When 1.82 g zinc metal also at 20.3°C is added and is allowed to react via the net ionic equation below, the temperature rises to 30.5°C. What is the heat of reaction (ΔH_{rxn}) per mole of Zn? Assume no heat is lost to the environment during the course of the reaction and that the heat capacity and the density of the solution is the same as that of pure water (1.00 g/mL and 4.184 J/g°C, respectively).



We first need to determine if all of the zinc will react. How many mL HCl will we need?

$$1.82 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{2 \text{ mol H}^+}{1 \text{ mol Zn}} \times \frac{1000 \text{ mL}}{0.300 \text{ mol H}^+} = 185 \text{ mL}$$

So, HCl is the limiting reagent:

$$q_{\text{reaction}} = -q_{\text{calorimeter}}$$

$$n_{\text{HCl}}\Delta H_{\text{rxn}} = -mc\Delta T$$

$$(0.100 \text{ L} \times 0.300 \text{ mol HCl/L})\Delta H_{\text{rxn}} = -(101.82 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(30.5^\circ\text{C} - 20.3^\circ\text{C})$$

$$\Delta H_{\text{rxn}} = \frac{-(101.82 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(10.2^\circ\text{C})}{(0.100 \text{ L} \times 0.300 \text{ mol HCl/L})} = \frac{144.8 \text{ kJ}}{\text{mol HCl}} \times \frac{2 \text{ mol HCl}}{1 \text{ mol Zn}} = \underline{\underline{-289.7 \text{ kJ/mol Zn}}}$$

(If you make the incorrect assumption that Zn is the limiting reagent, you find $\Delta H = -156 \text{ kJ/mol Zn}$.)

Answer -290 kJ/mol Zn

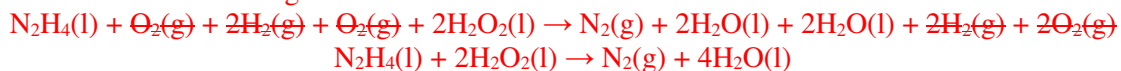
9. Determine ΔH° for the reaction $\text{N}_2\text{H}_4(\text{l}) + 2\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$ from these data:

| Reaction | ΔH° |
|--|------------------|
| $\text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ | -622.2 kJ |
| $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ | -285.8 kJ |
| $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$ | +173.1 kJ |
| $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l})$ | -187.8 kJ |

| | Reaction | ΔH° |
|------------------------------------|--|------------------|
| The first reaction is left alone: | $\text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ | -622.2 kJ |
| Double the second reaction: | $2(\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}))$ | 2(-285.8 kJ) |
| Reverse and double the fourth rxn: | $2(\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2(\text{g}) + \text{O}_2(\text{g}))$ | -2(-187.8 kJ) |

The third reaction is not used

Add the above reactions to get the overall reaction:



$$\Delta H^\circ = -622.2 \text{ kJ} + (2(-285.8 \text{ kJ})) + (-2(-187.8 \text{ kJ})) = \mathbf{-818.2 \text{ kJ}}$$

Answer -818.2 kJ

10. The reaction $\text{I}^-(\text{aq}) + \text{OCl}^-(\text{aq}) \rightarrow \text{IO}^-(\text{aq}) + \text{Cl}^-(\text{aq})$ was studied and the data below were obtained. Determine the rate law and the value of the rate constant for this reaction.

| $[\text{I}^-]_0(\text{mol/L})$ | $[\text{OCl}^-]_0(\text{mol/L})$ | Initial Rate (mol/Ls) |
|--------------------------------|----------------------------------|-----------------------|
| 0.12 | 0.18 | 0.00949 |
| 0.060 | 0.18 | 0.00237 |
| 0.030 | 0.090 | 0.000296 |
| 0.24 | 0.090 | 0.0190 |

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{I}^-]^x[\text{OCl}^-]^y}{k[\text{I}^-]^x[\text{OCl}^-]^y} = \frac{0.00949}{0.00237} = 4 = \frac{k[0.12]^x[0.18]^y}{k[0.06]^x[0.18]^y} = 2^x$$

So

$$4 = 2^x$$

Therefore $x = 2$ and the reaction is second order in I^-

Since there are no pairs of reactions in which only the OCl^- concentration changes the I^- concentration does not, we can use any of the pairs to determine the reaction order for OCl^- .

$$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{k[\text{I}^-]^x[\text{OCl}^-]^y}{k[\text{I}^-]^x[\text{OCl}^-]^y} = \frac{0.00237}{0.000296} = 8 = \frac{k[0.06]^2[0.18]^y}{k[0.03]^2[0.09]^y}$$

$$8 = \frac{[0.06]^2[0.18]^y}{[0.03]^2[0.09]^y}$$

$$8 = \frac{4[0.18]^y}{[0.09]^y}$$

$$2 = \frac{[0.18]^y}{[0.09]^y} = 2^y$$

Therefore, $y = 1$ and the reaction is first order in OCl^- . We can now use any of the data sets to find k .

$$\text{Rate} = k[\text{I}^-]^2[\text{OCl}^-] \quad k = \frac{\text{Rate}}{[\text{I}^-]^2[\text{OCl}^-]} = \frac{0.00949 \text{ M/s}}{(0.12 \text{ M})^2(0.18 \text{ M})} = 3.66 \text{ M}^{-2}\text{s}^{-1}$$

Answer Rate = $3.7\text{M}^{-2}\text{s}^{-1}[\text{I}^-]^2[\text{OCl}^-]$

11. Consider the reaction $\text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_4\text{NO}_3(\text{s})$ at 298K.

| Species | $\Delta\text{H}_f^\circ, \text{kJ mol}^{-1}$ | $\text{S}^\circ, \text{J mol}^{-1} \text{K}^{-1}$ | $\Delta\text{G}_f^\circ, \text{kJ mol}^{-1}$ |
|------------------------------------|--|---|--|
| $\text{O}_2(\text{g})$ | 0 | 205.1 | 0 |
| $\text{H}_2(\text{g})$ | 0 | 130.7 | 0 |
| $\text{NH}_4\text{NO}_3(\text{s})$ | -365.6 | 151.1 | -183.9 |
| $\text{N}_2\text{O}(\text{g})$ | 82.05 | 219.9 | 104.2 |
| $\text{H}_2\text{O}(\text{l})$ | -285.8 | 69.91 | -237.1 |
| $\text{H}_2\text{O}(\text{g})$ | -241.8 | 188.8 | -228.6 |

a. Is the forward reaction exothermic or endothermic? (5 points)

$$\Delta\text{H}_{\text{rxn}}^\circ = \Delta\text{H}_{f, \text{NH}_4\text{NO}_3}^\circ - (\Delta\text{H}_{f, \text{N}_2\text{O}}^\circ + 2\Delta\text{H}_{f, \text{H}_2\text{O}}^\circ)$$

$$\Delta\text{H}_{\text{rxn}}^\circ = -365.6 \text{ kJ} - (82.05 \text{ kJ} + 2(-285.8 \text{ kJ}))$$

$$\Delta\text{H}_{\text{rxn}}^\circ = +124 \text{ kJ}$$

Since ΔH° is positive, the reaction is endothermic

b. What is the value of ΔG° at 298 K? (5 points)

$$\Delta\text{S}_{\text{rxn}}^\circ = \text{S}_{f, \text{NH}_4\text{NO}_3}^\circ - (\text{S}_{f, \text{N}_2\text{O}}^\circ + 2\text{S}_{f, \text{H}_2\text{O}}^\circ)$$

$$\Delta\text{S}_{\text{rxn}}^\circ = 151.1 \text{ J/K} - (219.9 \text{ J/K} + 2(69.91 \text{ J/K}))$$

$$\Delta\text{S}_{\text{rxn}}^\circ = -209 \text{ J/K}$$

$$\Delta\text{G}_{\text{rxn}}^\circ = \Delta\text{H}_{\text{rxn}}^\circ - T\Delta\text{S}_{\text{rxn}}^\circ = +124 \text{ kJ} - 298 \text{ K}(0.209 \text{ kJ/K}) = +186 \text{ kJ}$$

Alternatively:

$$\Delta\text{G}_{\text{rxn}}^\circ = \Delta\text{G}_{f, \text{NH}_4\text{NO}_3}^\circ - (\Delta\text{G}_{f, \text{N}_2\text{O}}^\circ + 2\Delta\text{G}_{f, \text{H}_2\text{O}}^\circ)$$

$$\Delta\text{G}_{\text{rxn}}^\circ = -183.9 \text{ kJ} - (104.2 \text{ kJ} + 2(-237.1 \text{ kJ}))$$

$$\Delta\text{G}_{\text{rxn}}^\circ = +186 \text{ kJ}$$

Answer +186 kJ

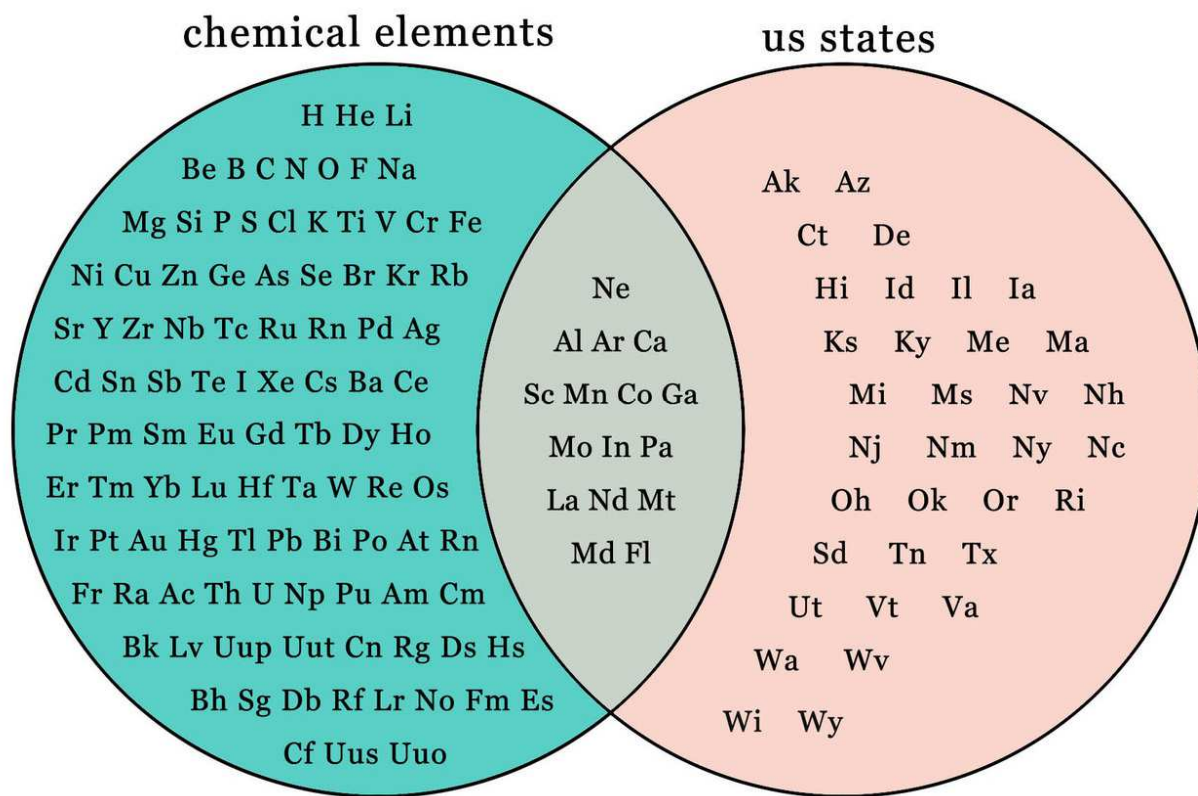
c. Does the reaction occur spontaneously at high temperatures, low temperatures, all temperatures or no temperatures? Justify your answer. (4 points)

Since $\Delta\text{H}_{\text{rxn}}^\circ$ is positive, and $\Delta\text{S}_{\text{rxn}}^\circ$ is negative, $\Delta\text{G}_{\text{rxn}}^\circ$ will be positive at all temperatures, since $\Delta\text{G}_{\text{rxn}}^\circ = \Delta\text{H}_{\text{rxn}}^\circ - T\Delta\text{S}_{\text{rxn}}^\circ = (+) - (+)(+) = (+)$ regardless of temperature. So, the reaction is non-spontaneous at all temperatures.

(NOTE: If you did not calculate $\Delta\text{S}_{\text{rxn}}^\circ$ in part b, you can infer that it is negative by looking at the reaction. Since there are fewer moles of gas on the products side of the reaction compared to the reactants, we expect $\Delta\text{S}_{\text{rxn}}^\circ$ to be negative.)

Possibly Useful Information

| | | |
|--|---|--|
| $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ | $K = ^\circ\text{C} + 273.15$ | $q_{\text{released}} = -q_{\text{absorbed}}$ |
| $q = mc\Delta T$ | $q = n_{\text{LR}}\Delta H_{\text{rxn}}$ | $q = m\Delta H$ |
| $\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta S_{\text{surr}}$ | $\Delta G = \Delta H - T\Delta S$ | $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$ |
| $\text{rate} = k[\text{A}]^0$ | $[\text{A}]_t = -kt + [\text{A}]_0$ | $t_{1/2} = [\text{A}]_0/2k$ |
| $\text{rate} = k[\text{A}]^1$ | $\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$ | $t_{1/2} = 0.693/k$ |
| $\text{rate} = k[\text{A}]^2$ | $\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$ | $t_{1/2} = 1/(k[\text{A}]_0)$ |
| $k = Ae^{-(E_a/RT)}$ | $\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$ | $\text{slope} = m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1}$ |



<http://mentalfloss.com/article/61102/12-funny-and-delicious-venn-diagrams>

To save some calculation time, you may round all atomic masses to two (2) decimal points.

| | | | | | | | | | | | | | | | | | | | | | |
|---------------------|---------------------|----------------------|--------------------|---------------------|---------------------|---------------------|--------------------|---------------------|--------------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------------------|--------------------|---------------------|--------------------|--|--|--|
| 1 1A | | | | | | | | | | | 18 8A | | | | | | | | | | |
| 1 H 1.00794 | 2 2A | | | | | | | | | | 13 3A | 14 4A | 15 5A | 16 6A | 17 7A | 2 He 4.00260 | | | | | |
| 3 Li 6.941 | 4 Be 9.01218 | | | | | | | | | | | 5 B 10.811 | 6 C 12.011 | 7 N 14.0067 | 8 O 15.9994 | 9 F 18.9984 | 10 Ne 20.1797 | | | | |
| 11 Na 22.9898 | 12 Mg 24.3050 | 3 3B | 4 4B | 5 5B | 6 6B | 7 7B | 8 8B | | 9 9B | 10 10B | 11 11B | 12 12B | 13 Al 26.9815 | 14 Si 28.0855 | 15 P 30.9738 | 16 S 32.066 | 17 Cl 35.4527 | 18 Ar 39.948 | | | |
| 19 K 39.0983 | 20 Ca 40.078 | 21 Sc 44.9559 | 22 Ti 47.88 | 23 V 50.9415 | 24 Cr 51.9961 | 25 Mn 54.9381 | 26 Fe 55.847 | 27 Co 58.9332 | 28 Ni 58.693 | 29 Cu 63.546 | 30 Zn 65.39 | 31 Ga 69.723 | 32 Ge 72.61 | 33 As 74.9216 | 34 Se 78.96 | 35 Br 79.904 | 36 Kr 83.80 | | | | |
| 37 Rb 85.4678 | 38 Sr 87.62 | 39 Y 88.9059 | 40 Zr 91.224 | 41 Nb 92.9064 | 42 Mo 95.94 | 43 Tc (98) | 44 Ru 101.07 | 45 Rh 102.906 | 46 Pd 106.42 | 47 Ag 107.868 | 48 Cd 112.411 | 49 In 114.818 | 50 Sn 118.710 | 51 Sb 121.757 | 52 Te 127.60 | 53 I 126.904 | 54 Xe 131.29 | | | | |
| 55 Cs 132.905 | 56 Ba 137.327 | 57 *La 138.906 | 72 Hf 178.49 | 73 Ta 180.948 | 74 W 183.84 | 75 Re 186.207 | 76 Os 190.23 | 77 Ir 192.22 | 78 Pt 195.08 | 79 Au 196.967 | 80 Hg 200.59 | 81 Tl 204.383 | 82 Pb 207.2 | 83 Bi 208.980 | 84 Po (209) | 85 At (210) | 86 Rn (222) | | | | |
| 87 Fr (223) | 88 Ra 226.025 | 89 †Ac 227.028 | 104 Rf (261) | 105 Db (262) | 106 Sg (266) | 107 Bh (264) | 108 Hs (277) | 109 Mt (268) | 110 Ds (271) | 111 Rg (272) | | | | | | | | | | | |

| | | | | | | | | | | | | | | |
|--------------------|---------------------|---------------------|--------------------|---------------------|--------------------|---------------------|--------------------|---------------------|--------------------|---------------------|--------------------|---------------------|--------------------|---------------------|
| *Lanthanide series | 58 Ce 140.115 | 59 Pr 140.908 | 60 Nd 144.24 | 61 Pm (145) | 62 Sm 150.36 | 63 Eu 151.965 | 64 Gd 157.25 | 65 Tb 158.925 | 66 Dy 162.50 | 67 Ho 164.930 | 68 Er 167.26 | 69 Tm 168.934 | 70 Yb 173.04 | 71 Lu 174.967 |
| †Actinide series | 90 Th 232.038 | 91 Pa 231.036 | 92 U 238.029 | 93 Np 237.048 | 94 Pu (244) | 95 Am (243) | 96 Cm (247) | 97 Bk (247) | 98 Cf (251) | 99 Es (252) | 100 Fm (257) | 101 Md (258) | 102 No (259) | 103 Lr (262) |