

## Ch. 20 Nuclear Chemistry

1. Some rules for chemical reactions that do not apply to nuclear reactions:
  - a. Balanced reactions: the same atoms that go into a reaction come out
  - b. Conservation of mass (no mass is gained or lost)
  - c. Conservation of energy
2. In nuclear reactions:
  - a. Nuclei do change! ( $C \rightarrow N$ ,  $U \rightarrow Ba$ , etc.)
  - b. Mass does change (slightly)  $\Rightarrow$  large energy changes
  - c. Energy is not conserved: energy is produced
    - Mass is actually converted to energy via Einstein's  $E=mc^2$
    - The real conservation is of energy/mass, but in nuclear reactions mass can be converted into energy

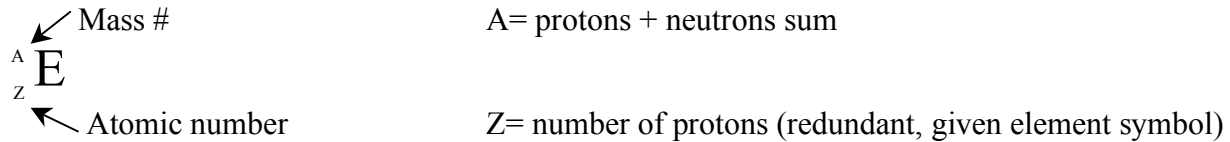
### Applications of Nuclear Energy (20.9)

1. Energy source
  - ~20% of US electricity, ~17% world-wide
  - cheap! Efficient
  - no greenhouse gases: environmentally 'clean', no acid rain, etc.
  - Currently, all the nuclear waste from one reactor can be stored in one barrel of "glass"
2. Medicinal
  - a) diagnostic tracers, "imaging"
    - PET: position emission tomography
    - thyroid, heart, tumors, bone studies, brain imaging, blood flow tracking
  - b) therapy: anti-cancer radiation therapy
3. Radioactive tracers, labelling
  - Incorporating radioactive nuclei into reactive molecules enables scientists to figure out which atoms go where in chemical and biochemical reactions
  - This enables researchers to unravel many biological pathways
4. Age dating
  - $^{14}C$  for archeological dates: recent several thousand years while people have been around (Carbon dating)
  - K/Ar dating for geological dates (dates for rocks, on the order of millions or billions rather than thousands of years)
5. Food irradiation: kill/retard Bacteria, molds, yeast (ala pasteurization)
6. Bombs!!
  - Fission: original WWII uranium bombs, in which big uranium nuclei break into smaller nuclei
  - Fusion (Hydrogen bomb): more powerful subsequent cold-war developed bombs that are much, much more destructive. Involve small hydrogen nuclei fusing into larger nuclei
7. Sun energy. All of the energy from the sun is produced by hydrogen and helium fusion.
  - All of the energy that we live on originally began with the sun
  - Plants harvest solar energy via photosynthesis
  - People and animals harvest energy by eating plants or by eating animals that ate plants
  - The solar energy harvested by plants also ends up being converted to fossil fuels and firewood

## 20.1 Radioactivity: Spontaneous Disintegration of Nucleus

- although spontaneous, this may still be very slow. Rates vary widely, which is good.

## A. Nuclear Review: Symbols for “Nuclide”



- Number of protons = Z (atomic number)
- Number of neutrons = A (mass number) – Z (number of protons)
- Number of electrons = Number of protons for a neutral atom
  - For an anion, negative charge means more electrons than protons
  - For a cation, the positive charge means fewer electrons than protons

“isotopes”: nuclei that have the same number of protons but differing number of neutrons

- $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{14}\text{C}$  all have six protons
- Stability often depends on the neutron/proton ratio, so frequently different isotopes will have different stability

“radioisotopes”: particular isotopes that spontaneously disintegrate and release radiation

Shorthands:  $^{12}_6\text{C} = {}^{12}\text{C} = \text{C}12 = 12\text{C}$

## B. Common “Particles” involved in Radioactivity and Nuclei (memorize these for test)



- Memorize names, symbols, constitution
- Crucial in balancing nuclear reactions
- The radiation emitted by radioactive elements is normally alpha, beta, or gamma. Positron emission and neutron emission is more rare.
  - Protons and neutrons are often involved when nuclei are being intentionally bombarded
- Different radiation has different penetrating power. (20.8) Biological impact depends on:
- The number or rays/particles that strike
- The energy and penetration depth of the rays
- Whether the radiation originates inside or outside the body

$\gamma$ <b>Max damage, due to high energy, deep penetration</b>	$\beta$ Penetrate only a few mm	$\alpha$ Little penetration, only irritates outer skin. But bad if generated internally.
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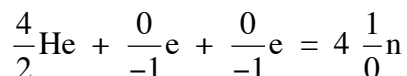
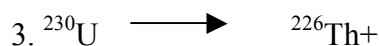
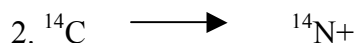
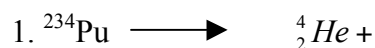
## 20.2 Nuclear Reactions: Equations and Balancing

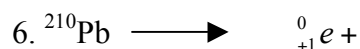
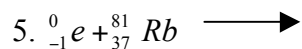
Keys: 1. balance mass sum (top) 2. balance charge sum (bottom)
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Five Types of Radioactive Reactions (Spontaneous)

	<u>Isotope Change</u>	<u>Effect on n/p ratio</u>	
1. Alpha emission	$\frac{A}{Z} \rightarrow \frac{4}{2}\text{He} + \frac{A-4}{Z-2}$ change	$\frac{n-2}{p-2}$	
2. Beta emission	$\frac{A}{Z} \rightarrow \frac{0}{-1}\text{e} + \frac{A}{Z+1}$ no change increase	$\frac{n-1}{p+1}$	Lower Neutron becomes a proton
3. Positron emission	$\frac{A}{Z} \rightarrow \frac{0}{+1}\text{e} + \frac{A}{Z-1}$ no change decrease	$\frac{n+1}{p-1}$	Higher Proton becomes a neutron
4. Electron capture	$\frac{0}{-1}\text{e} + \frac{A}{Z} \rightarrow \frac{A}{Z-1}$ no change decrease	$\frac{n+1}{p-1}$	Higher Proton becomes a neutron
5. Gamma emission	$\frac{A}{Z} \rightarrow \frac{0}{0}\gamma + \frac{A}{Z}$ no change no change	No change	

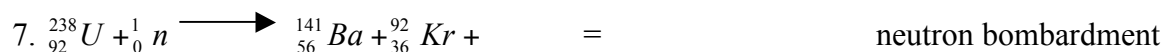
- Radioactive Series: many decays give unstable daughter nuclei, which then undergo subsequent serial decays
  - Show: **Brown Fig. 21.4**
- A very common sequence when the n/p ratio is too high is emission of one  $\alpha$  and two  $\beta$  particles (in any sequence)
- This results in the effective removal of 4 neutrons

Fill in the Holes, Name the process



20.5 Artificial Transmutations: The human-induced conversion of one nucleus into another by Bombardment with  ${}_0^1n$  or other nuclei

1. Key: reactions must still balance in the same way.
2. Often products are accompanied by production of side particles, often multiple neutrons
3. Few radioactive nuclei are still found in nature. Most fast-decay nuclei used for research or medicine are made by bombardment.



## 20.3 The Stability of Atomic Nuclei

## A. Physics background

## a. 3 fundamental forces

1. gravity
2. electrostatic attraction: opposite charges attract
3. “strong nuclear force”

b. **proton-proton repulsion destabilizes** all nuclei except hydrogen **BAD**

- This repulsion increases sharply with increasing number of protons
- In other words, as nuclei increase in atomic number, this destabilizing repulsion increases exponentially
- This is a destabilizing electrostatic force
- If proton-proton repulsion is destabilizing, why do nuclei exist at all for atoms other than hydrogen?

c. “**strong nuclear force**” between protons or neutrons **GOOD**

- This attracts nuclides, holds nucleus together
- Unknown how the strong nuclear force works. It’s existence and strength is really known by deduction!
- The neutron/proton ratio increases with larger nuclei.
  - This enables the strong nuclear force to increase at a pace that can balance the proliferating proton-proton repulsion
- Beyond atomic-number of 83, it becomes impossible for the nuclear force to keep up with the destabilizing proton-proton repulsion, so nuclei cease to be stable.

**Fig. 20.2, 21.2 Brown**

B. Decay Patterns: The Band of Stability Target Ratio: A range of n/p ratios that appropriately balance the electrostatic repulsion and the nuclear attraction and give stable nuclei

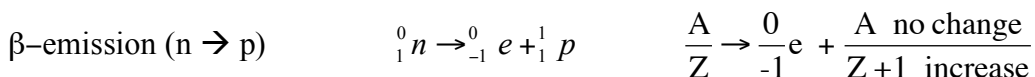
1. Rule of 83: Atoms/nuclei with atomic number of  $Z > 83$  are radioactive
  - nuclear force can’t keep up!
  - most elements  $Z < 83$  have at least one stable isotope ( ${}_{43}\text{Tc}$ ,  ${}_{61}\text{Pm}$ )
  - **$Z > 83$  emit  $\alpha$**  to reduce  $Z$

Normal solution: For unstable nuclei with  $Z > 83$ , **alpha emissions** normally occurs, to reduce the atomic number and move it toward stability

2. For atoms with  $Z < 83$ , but above the band of stability: **atoms whose n/p ratio is too high**

- Conversion of a neutron into a proton would help

Normal solution: For nuclei whose n/p ratio is too high, **beta emissions** normally occurs, to reduce the n/p ratio by converting a neutron into a proton



3. For atoms with  $Z < 83$ , but below the band of stability: **atoms whose n/p ratio is too low**

- Conversion of a proton into a neutron would help

Normal solution: For nuclei whose n/p ratio is too low, either **positron emission or electron capture** normally occurs, to increase the n/p ratio by converting a proton into a neutron

- Electron capture tends to be more likely for higher-Z elements

Positron emission  $\frac{A}{Z} \rightarrow \frac{0}{+1}e + \frac{A}{Z-1}$   $\frac{n+1}{p-1}$  Higher Proton becomes a neutron  
no change decrease

Electron capture  $\frac{0}{-1}e + \frac{A}{Z} \rightarrow \frac{A}{Z-1}$   $\frac{n+1}{p-1}$  Higher Proton becomes a neutron  
no change decrease

**Practical: How do I recognize whether a nucleus is likely to be stable or not? And if it isn't, how do I predict what it will do?**

1. **Check Z. Is  $Z > 83$ ?** If so, then **expect alpha emission**. If not, proceed to step two.
2. **Compare the n/p ratio to the ratio found in the periodic table for the same atom.**
3. If the **n/p ratio is similar**, it's probably a **stable** nucleus.
4. If the **n/p ratio is significantly higher** than in the periodic table, **expect beta emission**.
5. If the **n/p ratio is significantly lower** than in the periodic table, then **expect either positron emission or electron capture**.

- Note: There are some not-well-understood kind of stability pattern
- Pairing seems to be preferred, although it's not understood why
  - Even numbers of protons and even numbers of neutrons seem to be preferred, all else being equal

Problems: Predict how the following would decay by  $\alpha$ ,  $\beta$ , or positron emission, or by electron capture. Then draw the nuclide produced.

1.  $^{40}\text{Cl}$

2.  $^{134}\text{Ba}$

3.  $^{237}_{93}\text{Np}$

## C. Binding Energy

- the mass of an actual nucleus is always less than the sum of its component neutrons and protons
- The **missing mass ( $\Delta m$ ) is called the “mass deficit”**.

$$\Delta m = (\text{mass sum of protons} + \text{neutrons}) - \text{actual nuclear mass}$$

$${}^1_1\text{proton} \quad 1.00783 \quad {}^1_0\text{neutron} \quad 1.00867$$

- **The mass deficit ( $\Delta m$ ) equals the “nuclear binding energy” = “strong nuclear force”**

$$E = \Delta mc^2$$

$\Delta m$  in kg (convert from grams to kg)

E in J (convert to kJ)

- Get answers in either kJ/mol (of nucleus) or kJ/mole nucleon”
  - The number of “nucleons” is the sum of protons and neutrons

4. What is the binding energy in kJ/mol for  ${}^{16}_8\text{O}$ ?

$$\text{Given: } {}^{16}_8\text{O} \quad 15.978 \quad {}^1_1\text{proton} \quad 1.00783 \quad {}^1_0\text{neutron} \quad 1.00867$$

5. For the above, what is the binding energy in kJ/mol **nucleons**?

**Miscellaneous**

1. Fe-56 is the most stable of all nuclei, has the greatest binding energy per nucleon
2. In nuclear reactions, the great amounts of energy are provided by nuclear “binding energy” that is released

**Fig. 20.3**

3. Fission reactions (Section 20.6): large nuclei fragment into smaller nuclei
4. Fusion reactions (20.7): small nuclei combine to give bigger nuclei
5. Both fission and fusion occurs to draw nearer the maximum stability of Fe-56

## 20.4 Rates of Radioactive Decay

A. Nuclear half-life: radioisotope decay with 1<sup>st</sup> order rate laws, have characteristic half-lives ( $t_{1/2}$ )

Isotope	Half-Life	Notes
$^{238}_{92}\text{U}$	$5 * 10^9$ years (5 billion years)	Slow enough so that plenty is still left from when earth was made
$^{40}\text{K}$	$1 * 10^9$ years (1 billion years)	<ul style="list-style-type: none"> <li>• Daughter nucleus is <math>^{40}\text{Ar}</math>.</li> <li>• Used to date old rocks. The ratio of <math>^{40}\text{Ar}</math> to <math>^{40}\text{K}</math> reflects how much time has passed.</li> </ul>
$^{14}\text{C}$	5730 years	Medium half life, used to measure the ages of artifacts used during human history
$^{131}\text{I}$	8 days	Short, used in medical imaging
$^{24}\text{Na}$	15 hours	Short, used in medical imaging
$^{99}\text{Tc}$	6 hours	Short, used in medical imaging

Notes:

- For radioactive nuclei to be around, they must either have:
  - Long half-lives so that there hasn't been enough time for the original stuff to decay away. ( $^{238}\text{U}$  and  $^{40}\text{K}$ )
  - Have some source by which they have been made more recently.
    - $^{14}\text{C}$  is continuously made in the atmosphere as result of cosmic rays acting on  $^{14}\text{N}$
    - Radioactive nuclei used in medical imaging techniques ( $^{131}\text{I}$ ,  $^{24}\text{Na}$ ,  $^{99}\text{Tc}$ ) must be made fresh by laboratory techniques.
- Radioactive nuclei used in medical imaging techniques or in chemotherapy must have relatively short life times.
  - You want them radiating so the doctors can detect whether the solution is going where it should.
  - But once the analysis is completed, you'd like the body to be free from them as soon as possible. (Rather than irradiating your DNA for weeks for no reason.)

## B. Radioactive Decay Math

- Radioactive nuclei decay via first-order rate laws
- Formulas for First Order Reactions:  $kt = \ln ([A_o]/[A_t])$        $kt_{1/2} = 0.693$

$\ln (A_o/A_t) = 0.693 \cdot t / t_{1/2}$	When solving for the amount of material left after a given time, given the half life
$t = (t_{1/2}/0.693) \ln (A_o/A_t)$	When solving for time, given half life and quantities of material

$$t_{1/2} \cdot \ln (A_o/A_t) = 0.693 \cdot t$$

Rearranged version when solving for  $t_{1/2}$ 

- $A_o$  = original amount of material
- $A_t$  = amount after time  $t$ 
  - Amounts can be in mass, or in emission rate, or activity, or 100%  $\rightarrow$  percent.
- $t_{1/2}$  = half life, the time for half of the material to decay
- Boxed formulas are the ones you'll be given on the test
- Handling "ln  $y = x$ " on calculator, when you know "x" but want to solve for "y": enter "x", then hit your "e<sup>x</sup>" button.

1.  $^{99}\text{Tc}$  is used for brain imaging scan. The half-life for  $^{99}\text{Tc} = 6.0$  hours. What percentage of a dose of  $^{99}\text{Tc}$  is left after 24 hours?

2.  $^{131}\text{I}$  has a half-life = 8.0 days. How long will it take to decay for a sample to decay so that only 10% of the original  $^{131}\text{I}$  survives?

3.  $^{90}\text{Sr}$   $t_{1/2} = 28.8$  g If 42 g of  $^{90}\text{Sr}$  is buried, how much is left after 120 years?

## C. C-14 and Carbon Age Dating: Measurement of Human History Dates.

- carbon-14 is a very small, low abundance isotope of carbon. C-12 is the major isotope, C-13 next. But the C-14 is good for finding human history dates.
- $^{14}\text{C}$   $t_{1/2} = 5730$  years
- Since most of human history has been within the last few thousand years, the half-life for carbon-14 ends up being pretty appropriate.

The logic of Carbon dating:

1. A steady state percentage of  $\text{CO}_2$  in the air is radioactive  $^{14}\text{CO}_2$ .
  - a. The  $^{14}\text{CO}_2$  in the air is produced from  $^{14}\text{N}$  as the result of cosmic rays
  - b. Plants take in  $^{14}\text{CO}_2$  directly from the air via photosynthesis.
  - c. Animals and humans take in  $^{14}\text{C}$  indirectly, either by eating plants that have  $^{14}\text{C}$  or by eating animals that ate the plants with the  $^{14}\text{C}$ .
2. All living things (plant or animal) have a known steady state percentage of  $^{14}\text{C}$  relative to total carbon
  - This results in a known  $^{14}\text{C}$  radioactivity rate, relative to total carbon
  - $A_0$  is known
3. Once a living thing dies, it stops incorporating  $^{14}\text{C}$ .
  - Plants stop photosynthesizing, people and animals stop eating
4. After death, the radioactive  $^{14}\text{C}$  decays at  $t_{1/2}$  rate, and the  $^{14}\text{C}$  radioactivity rate declines, relative to total carbon
5. By looking at the  $^{14}\text{C}$  activity, you can determine approximately how long it's been since something that was formerly alive has died
  - Wood, cloth, anything ex-biological...
  - After a couple of half lives, the amount of  $^{14}\text{C}$  radiation gets too low to allow much accuracy

Problem.  $^{14}\text{C}$  has a half-life = 5730 years. "Live" carbon has activity of 15.3. A shirt is claimed to be Jesus's, but is found to have carbon activity of 14.0. How old is the shirt, and can the claim be true?

Rock dating similar:

- When lead is formed by sources other than  $^{238}\text{U}$  decay, isotopes other than just  $^{206}\text{Pb}$  are formed, so you can tell that the  $^{206}\text{Pb}$  came from the  $^{238}\text{U}$ .
- By measuring the ratio of  $^{40}\text{K}$  to ( $^{40}\text{K} + ^{40}\text{Ar}$ ), or  $^{238}\text{U}$  to ( $^{238}\text{U} + ^{206}\text{Pb}$ ), you can determine what fraction of the original  $^{40}\text{K}$  or  $^{238}\text{U}$  is left, figure out how many half-lives have passed, and figure out how long ago a rock formed.

## 20.6 Nuclear Fission

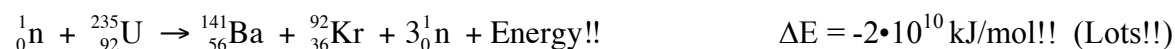


Fig. 20.6

**Keys**

1. Fission: When a larger nucleus breaks to give smaller nuclei
2. Humongous energy release!!
3. Fact: neutron bombardment doesn't always result in the same fission. Sometimes the  ${}^{235}\text{U}$  fragments in other ways to produce other daughter nuclei. Fig. 20.7
4. Neutron: both a reactant and a product!!
  - more neutrons are produced than are absorbed!
5. Branching and the uranium fission "chain reaction" Fig. 20.7
  - more neutrons produced than absorbed  $\Rightarrow$  more neutrons can strike other uraniums and cause more fission reaction  $\Rightarrow$  more neutrons  $\Rightarrow$  more fissions (and energy), etc..
  - Proliferating neutrons  $\rightarrow$  proliferating fissions  $\rightarrow$  proliferating energy, proliferating chain reaction (and maybe a uranium fission bomb, WWII Japan...)
6. "Critical Mass": enough  ${}^{235}\text{U}$  is required to support chain
  - "subcritical"- There isn't a large enough block of  ${}^{235}\text{U}$  to absorb the neutrons. While a given fission may absorb only one neutron and produce several neutrons, most of those neutrons produced just escape, rather than hitting another  ${}^{235}\text{U}$ , causing another fission reaction, and propagating/proliferating the chain
  - "supercritical": more than enough  ${}^{235}\text{U}$  so that more than enough of the neutrons produced bump into another  ${}^{235}\text{U}$ , cause another fission, and propagate/proliferate the chain.
  - Nuclear fission bomb: 2 subcritical masses are smashed together to achieve supercritical mass. The chain reaction then propagates/proliferates!!
    - A chemical bomb is actually used to propels one mass into the other!

Nuclear Reactors: Major Components (Brown 21.20)

1.  **${}^{235}\text{U}$  fuel rods** (last for years)
  - subcritical: can't explode
  - these are not pure natural uranium; rather they are enriched in  ${}^{235}\text{U}$
2. **Cadmium control rods** to control the rate of reaction and provide emergency security
  - a. The control rods are adjustable and are suspended in between the fuel rods
  - b. The control rods absorb neutrons.**
  - c. They can block the spray of neutrons from one fuel rod to another and prevent chain reaction.
  - d. The rate of chain reaction is controlled by raising the control rods just high enough so that enough neutrons can get through and sustain the chain reaction.
  - e. As a fuel rod ages and becomes less active, it needs more neutron hits to sustain the chain reaction, so the fuel rods get raised higher and higher.
  - f. Many automatic controls are in place to drop the control rods and stifle chain reaction in case of any emergency
3. **A coolant (water) absorbs energy**, produces steam that drives turbine $\Rightarrow$ electricity

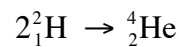
Concern: what do with spent fuel rods, still with some radioactive content?

- Current process: “vitrifications”
  - Fuel rods get “melted” and dissolved in liquid glass;
  - The liquid glass gets poured into a steel can, cools, and glasses over.
  - For one year plant: only one barrel gets produced!!

“Breeder Reactors”  $^{238}\text{U} + {}^1_0\text{n} \Rightarrow {}^{239}\text{Pu}$

- Active Plutonium is “bred” from relatively inactive  $^{238}\text{U}$  by bombardment with high-speed neutrons

### 20.7 Nuclear Fusion



- Solar process, hydrogen and deuterium fusion is how the sun produces it’s energy!
- Ideal energy dream: no radioactive byproducts, huge energy, cheap  $\text{H}_2\text{O}$  provides lots of hydrogen (and a good amount of deuterium) for fuel!!
- Problem: huge temperatures are needed (to overcome nuclear repulsion) in order to push Hydrogens together in order for them to fuse
  - Materials that can contain and support such high temperatures are not currently practical
- Hydrogen-bomb (cold war, never used in actual wars): a uranium fission bomb is used to provide the heat needed to support fusion!



## Chapter 20 Nuclear Chemistry Math Summary

### Particles Involved in Nuclear Reactions, either as Nucleons, Emitted particles or Particles that React with a Nucleus and Induce a Decay

(Memorize these for Test)

-the first three, alpha, beta, and positrons are the crucial ones for balancing radioactive nuclear decay reactions

$\frac{4}{2}\text{He}$ $\alpha$ -particle (alpha)	$\frac{0}{0}\gamma$ gamma
$\frac{0}{-1}\text{e}$ $\beta$ -particle (beta), electron	$\frac{1}{0}\text{n}$ neutron
$\frac{0}{+1}\text{e}$ positron	$\frac{1}{1}\text{H}$ proton

### Radioactive Decay Math

$t = (t_{1/2}/0.693) \ln (A_0/A_t)$  When solving for time, given half life and quantities of material

$\ln (A_0/A_t) = 0.693 (t /t_{1/2})$  When solving for the amount of material left after a given time, given the half life

Handling “ $\ln y = x$ ” on calculator, when you know “ $x$ ” but want to solve for “ $y$ ”: enter “ $x$ ”, then hit your “ $e^x$ ” button.

### Mass Defect/Binding Energy Math

Proton mass: 1.00783

Neutron mass: 1.00867

$E = \Delta mc^2$   $\Delta m = (\text{sum mass of protons plus neutrons}) - \text{actual mass}$

- The binding energy will depend on the  $\Delta m$  difference between the summed weight of the protons and neutrons minus the actual mass of the nucleus.
- $\Delta m$  in terms of kilograms (you’ll normally need to convert from grams to kg)
- The energy answer from the formula comes out in terms of Joules, not kJ; you’ll routinely need to convert from J to kJ to fit the answers.