Today:

Internal energy: $\Delta U = q + w$

Heating curves

Begin Calorimetry

$$\Delta U = q + w$$

There are three variables, you'll be given two of them.

You might not be given numbers. You might be given hints or clues instead.

exothermic means $q < 0$

endothermic means $q > 0$

ΔH_{rxn} might be (+) or (–) . That means q is (+) or (–).

expands or *expansion* means $w < 0$

contracts or *contraction* means $w > 0$

ΔH and q always have the same sign.

If you are given a chemical reaction:

more moles of gas in the products means expansion

$$CH_4(g) + H_2O(g) \rightarrow 3\ H_2(g) + CO(g)$$

$w < 0$

fewer moles of gas in the products means contraction

$$4\ FeO(s) + O_2(g) \rightarrow 2\ Fe_2O_3(s)$$

$w > 0$

$W = -P\Delta V$

If V increases, $w < 0$

If V decreases, $w > 0$

What is the sign on q, w, and ΔU for each of the reactions below:

$4\ XY(s) + \underline{Y_2(g)} \rightarrow 2\ X_2Y_3(s)$ $\Delta H = 350$ kJ/mol

1 mole gas

0 moles gas

$\Delta H > 0$ therefore $q > 0$

$\Delta n < 0$

$w = -\Delta nRT$

$w > 0$

Since $\Delta U = q + w$ and q and w are both (+), ΔU is (+).

$\underline{AC(g) + 3\ B_2(g)} \rightarrow \underline{AB_4(g) + B_2C(g)} + \underline{\text{heat}}$

4 moles of gas

2 moles of gas

exothermic - heat is given off. Therefore $q < 0$

$\Delta n = -2$, contraction, w is (+).

q is (−)

w is (+)

Can't say for sure if ΔU is (+) or (−), BUT...

q is generally way larger than w, so ΔU usually has the same sign as q.

$$\Delta U = q - P\Delta V$$

If ΔV is positive (the system volume is increasing against the surroundings) the system is doing work on the surroundings. $w < 0$.

(inflating balloon on the flask demo. $w<0$

If ΔV is negative (the system volume is decreasing against the surroundings) the surroundings are doing work on the system. $w > 0$.

collapsing bottle demo $w>0$

Question 4

1 pts

$w = +150$ kJ

A system had 150 kJ of work done on it and its internal energy increased by 60 kJ. How much energy did the system gain or lose as heat?

$\Delta U = +60$ kJ

- The system lost 210 kJ of energy as heat.
- The system gained 60 kJ of energy as heat.
- The system gained 210 kJ of energy as heat.
- ● The system lost 90 kJ of energy as heat.
- The system gained 90 kJ of energy as heat.

$\Delta U = q + w$

write the formula first, then fill in the variables you're given.

$60\text{ kJ} = q + 150\text{ kJ}$

$-90\text{ kJ} = q$

$\Delta U = q + w$

What is the change in internal energy if a 1 mol sample of helium gas at STP is heated with 2120 J of energy while expanding from 22.4 L to 30.6 L against 1 atm outside pressure?

(Warning - *units!* 1 L·atm = 101.325 J)

don't need this - it's left over from an earlier, harder problem I was going to give you.

$q = +2120\ J$

$w = -P\Delta V$

$w = -(1\ atm)(30.6 - 22.4)$

$w = -8.2\ L \cdot atm$

$(-8.2\ L \cdot atm)(101.325\ \frac{J}{L \cdot atm}) =$

$-830.87\ J$

$$\Delta U = q + w$$
$$= 2120\ J - 831\ J$$
$$\boxed{\Delta U = 1289\ J}$$

Want to try the harder problem? Gas Laws + Thermo = FUN!

Calculate ΔU when one mole of He is heated in a flexible-walled container from STP to 100°C.

$C_{He} = 5.30\ J/g°C$.

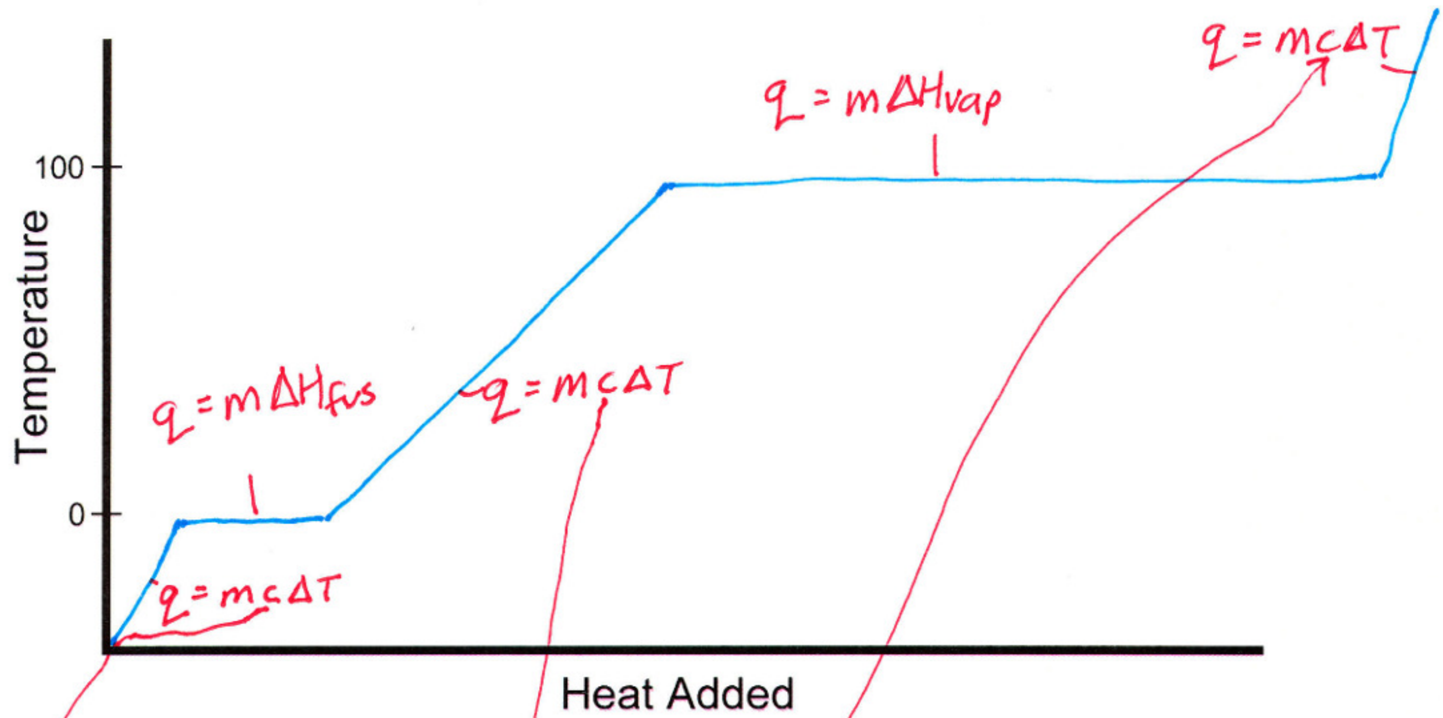
You can also calculate ΔU from ΔH using this relationship:

$$\Delta U = \Delta H - \Delta nRT$$

We'll talk more about that equation when we get to the second half of calorimetry.

Remember T is in Kelvins
and R = 8.314 J/mol·K

Heating curves



Specific heat capacity – how much energy is required to raise *1 gram of a substance* by *1 degree Celsius* (or kelvin)

The total heat required to heat a sample over a temperature range is just the specific heat capacity multiplied by the mass and the change in temperature:

$$q = mc\Delta T$$

ΔT – leave it in Celsius.

T – always in kelvins
by itself

$\boxed{c_{ice} = 2.09\ J/g^{\circ}C}$

$\boxed{c_{water} = 4.184\ J/g^{\circ}C}$

$\boxed{c_{vapor} = 2.03\ J/g^{\circ}C}$

This works on the parts of the heating curve where the temperature is changing. (Heat input becomes increasing KE.)

slopes are always $q = mc\Delta T$

Phase changes are physical changes and each one has its own Δ*H*. For water,

$\Delta H_{vaporization}$ = 2260 J/g

ΔH_{fusion} = 334 J/g

flats are always $q = m\Delta H$

per GRAM, so multiply by mass.

Notice it takes a *lot* more energy to boil a gram of water from liquid to gas than it does to melt a gram of ice from solid to liquid. You should know why this is the case.

ΔH is often given in kJ/mole, so in that case you multiply by moles.

For phase changes there is no temperature change. (Heat input becomes increasing PE.) To calculate the energy required for phase changes, multiply the mass by the Δ*H* for the process you're working with.

Each line segment on the heating curve is a separate calculation, !! then you add up all the *q* values for the process. If you are moving to the right on the heating curve, the heat values are all positive (heat is being absorbed by the system).

If you are moving to the left on the heating curve, the heat values are *negative* (heat is being released). The heats on the slopes will automatically come out negative if you use $\Delta T = T_{final} - T_{initial}$, but you'll have to remember to reverse the sign for condensation and for freezing.

The molar heat of fusion of sodium metal is 2.6 kJ/mol. How much heat is required to melt a 5.0 g chunk of solid sodium metal?

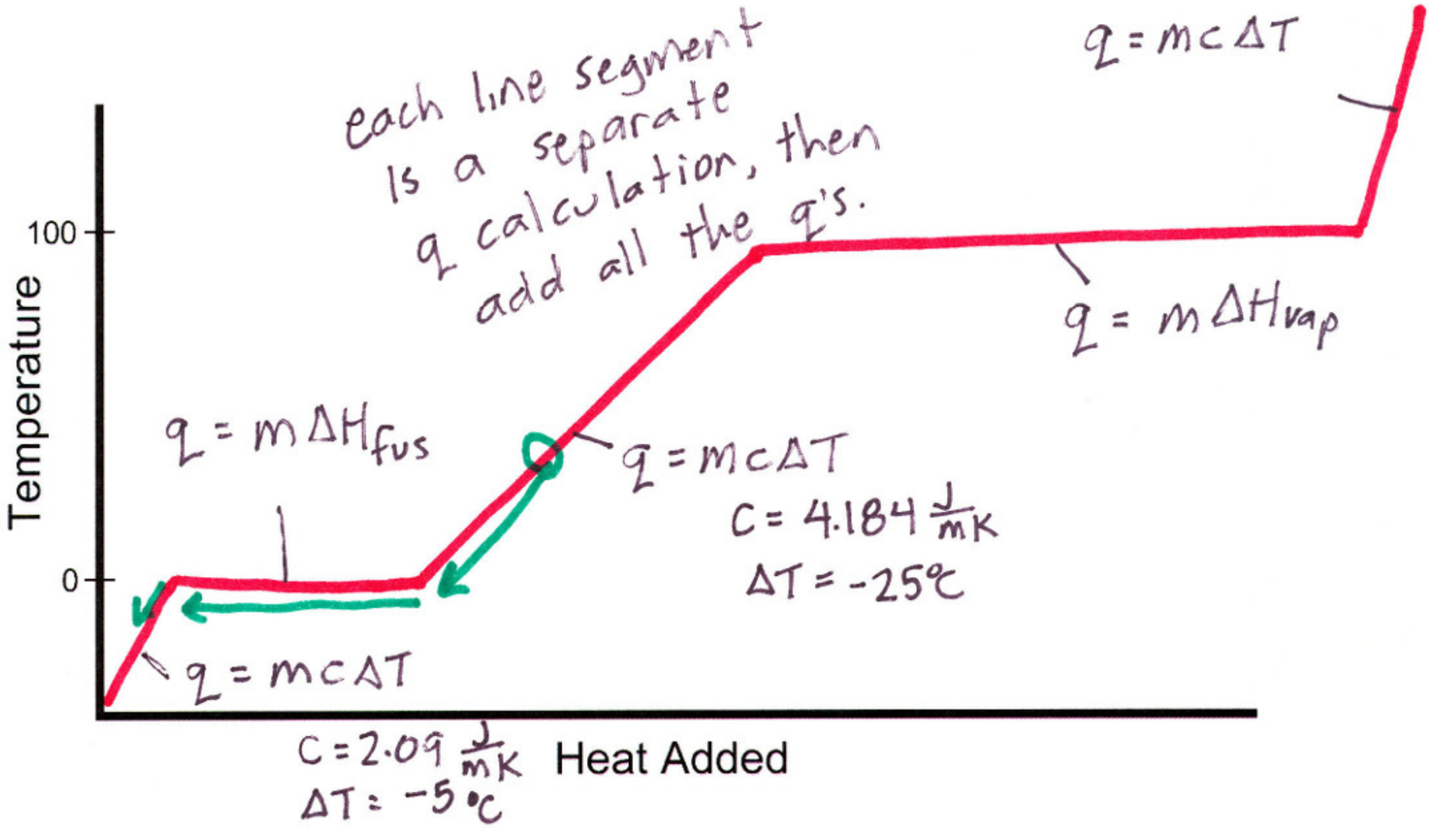
ΔH_{fusion} = 2.6 kJ/mol

molar mass of Na = 22.99 g/mol

$$5.0\text{g Na} \times \frac{1 \text{ mole}}{22.99\text{g}} = 0.2175 \text{ mol}$$

$$0.2175 \text{ mol} \times \frac{2.6 \text{ kJ}}{1 \text{ mol}} = 0.5655 \text{ kJ}$$

You fill an ice cube tray with 250 g of water at 25 °C and put it in the freezer. How much heat must the water in the ice cube tray lose to become ice cubes at –5 °C?



c_{ice} = 2.09 J/g°C

c_{water} = 4.184 J/g°C

ΔH_{fusion} = 334 J/g

Cool the water

$q = mc\Delta T$

$= (250g)(4.184\frac{J}{g°C})(-25°C)$

$= -26150 J$

Freeze the water

$q = -m\Delta H_{fus}$ make it negative because the water is giving up heat as it freezes

$= -(250g)(\cancel{2.09}\ 334\frac{J}{g})$

$= -83,500 J$

Cool the ice

$q = mc\Delta T$

$= (250g)(2.09\frac{J}{g°C})(-5°C)$

$= -2613 J$

total = −26,150
−83,500
− 2613 / −112 kJ

Calorimetry

In calorimetry typically something hot is added to something cold. If no heat is lost to the surroundings, then according to the First Law of Thermodynamics:

heat lost by the hot = heat gained by the cold

heat lost by the hot: $q = -m_H c_H \Delta T_H$

heat gained by the cold: $q = m_C c_C \Delta T_C$

Suppose we add a piece of hot metal to some cold water.

heat lost by the metal: $q = -m_H c_H \Delta T_H$

heat gained by the water: $q = m_C c_C \Delta T_C$

Since q is the same amount of heat in both equations,

$$-m_H c_H \Delta T_H = m_C c_C \Delta T_C$$

Be careful! The m, c, and ΔT values are different on each side.

$$\Delta T_H = (T_{\text{final}} - T_{\text{metal}}) \qquad \Delta T_C = (T_{\text{final}} - T_{\text{water}})$$

The calorimetry equation actually has *SEVEN* variables in it!

3 on the hot side, 3 on the cold side, and one final temperature that appears on both sides of the equation.

You will always be given six of them and will be solving for the seventh.

Question 10

1 pts

A piece of metal with a mass of 22 g at 92 °C is placed in a calorimeter containing 53.7 g of water at 21 °C. The final temperature of the mixture is 55.3 °C. What is the specific heat capacity of the metal? Assume that there is no energy lost to the surroundings.

- $-9.5\ J\ g^{-1}\ {}^{\circ}C^{-1}$
- $-1.3 \times 10^4\ J\ g^{-1}\ {}^{\circ}C^{-1}$
- $1.3 \times 10^4\ J\ g^{-1}\ {}^{\circ}C^{-1}$
- ● $9.5\ J\ g^{-1}\ {}^{\circ}C^{-1}$

Specific heat capacity is always positive. If you get a negative number you probably forgot the minus sign on the Hot side of the calorimetry equation.

$$-m_H c_H \Delta T_H = m_c C_c \Delta T_c$$

$$-(22g)\,C_H\,(55.3 - 92\,°C) = (53.7g)(4.184\tfrac{J}{g°C})(55.3 - 21°C)$$

$$C_H = \frac{7{,}706.6\ J}{807.4\ g°C}$$

$$C_H = 9.54\ J/g°C$$

This answer is unrealistic but is the correct answer.

A mad scientist wants a glass of cold water (5°C), but all he has in the lab is a water bottle at room temperature (500 g of water at 25°C), and no ice. He realizes he has some dry ice (–78.5 °C) and some copper pellets, so he decides to put the copper pellets on dry ice until they reach –78.5 °C and then add them to his water to chill it to 5 °C. How many grams of copper will he need?

(Be careful – this time the metal is not the hot side of the equation!)

c_{Cu} = 0.345 J/g°C

$$-m_H C_H \Delta T_H = m_c C_c \Delta T_c$$

Water is the hot side, metal is the cold side.

$$-(500g)(4.184 \tfrac{J}{g°C})(5-25°C) = m_c(.345 \tfrac{J}{g°C})(25 - -78.5)$$

$$\frac{41,840 \text{ J}}{35.7075 \text{ J/g}} = m_c = 1,172 \text{g Cu.}$$

probably not a feasible plan.

Next time in calorimetry:

These calculations assume the calorimeter does not absorb any heat. How do you tweak the equation to include the calorimeter if it does?

Hint: add it to the cold side:

$$-m_H c_H \Delta T_H = m_C c_C \Delta T_C + C_{cal} \Delta T_C$$

Also: instead of adding something hot to something cold, measure the heat given off by a chemical reaction. Hint: the hot side of the equation simply becomes the heat given off by the reaction:

$$q = m_C c_C \Delta T_C$$

Then if you divide the heat given off by the reaction by the number of moles of reactant, you get ΔH for the reaction (kJ/mol).