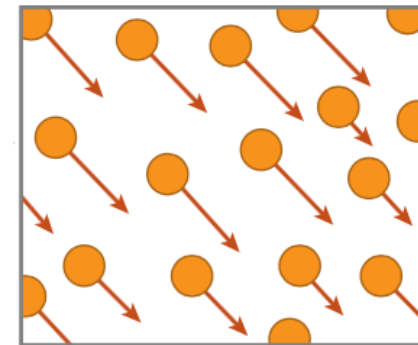
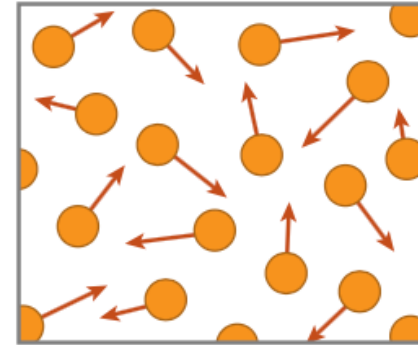


Unit 5 Review 1

FIRST LAW OF THERMODYNAMICS, HEATING CURVES, CALORIMETRY

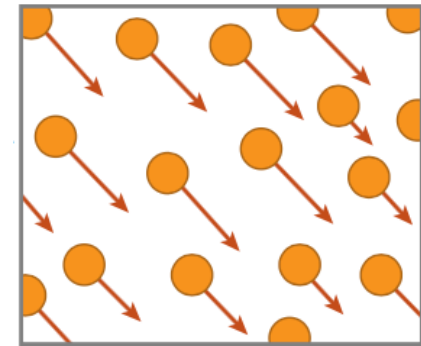
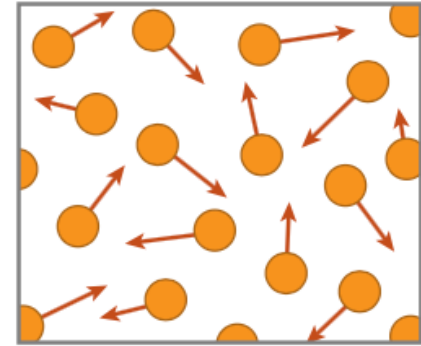
Thermodynamics Basic Definitions

- **Heat (q):** energy derived from random molecular motion (always travels from high T to low T)
- **Work (w):** the energy derived from organized molecular motion (in chemistry, mostly as a result of compression or expansion at constant pressure)
- **Internal Energy (U):** the total energy of a system, the surroundings, or the universe (depends on the subscript)
- **Enthalpy (H):** the heat content of a system (usually depicted as ΔH ; heat flow at constant pressure, q_p)



Thermodynamics Basic Definitions

- **Heat (q) = $mC_s\Delta T$**
- **Work (w) = $-P\Delta V$ ***
- **Change in Internal Energy (ΔU) = $q + w$**
- **Change in Enthalpy (ΔH) = q_p**



*Don't forget that this will give you L atm, but we almost always want work in joules

Heat Flow: System vs. Surroundings

- We define our environment in thermodynamics as the system and the surroundings. The system is the direct environment of the reaction and the surroundings is everything outside of this.

$q > 0$; endothermic (+), heat is absorbed

$q < 0$; exothermic (-), heat is released

$w > 0$; work energy in, work is done on the system (+)

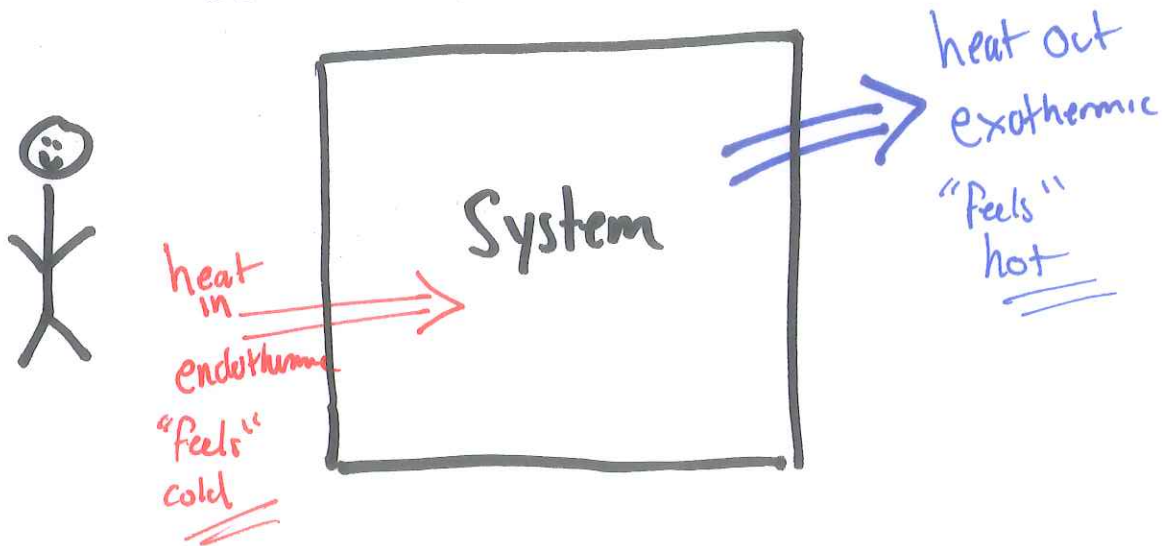
$w < 0$; work energy out, work is done by the system (-)

- Important: we often measure chemical reactions from the perspective of the surroundings. Therefore, when a reaction produces heat, we are actually measuring the change in temperature of the surroundings – not the system

Systems vs. Surroundings

Solid $\xrightarrow{\text{endo}}$ Liquid \rightarrow Gas
 $\xleftarrow{\text{exo}}$

Surroundings



Process

Endo

Exo

Combustion Reaction

Solid dissolves & beaker feels cold

You heat copper
From 28°C to 35°C

Gas condenses into a liquid



The First Law of Thermodynamics

- The energy of the universe is always conserved
- The conclusions of this law are:
 1. The internal energy change of the system is the sum of the heat and work
 2. The internal energy loss of the system is the equal to energy gain of the surroundings
 3. The internal energy change of the universe is zero and there is no energy or matter leaving

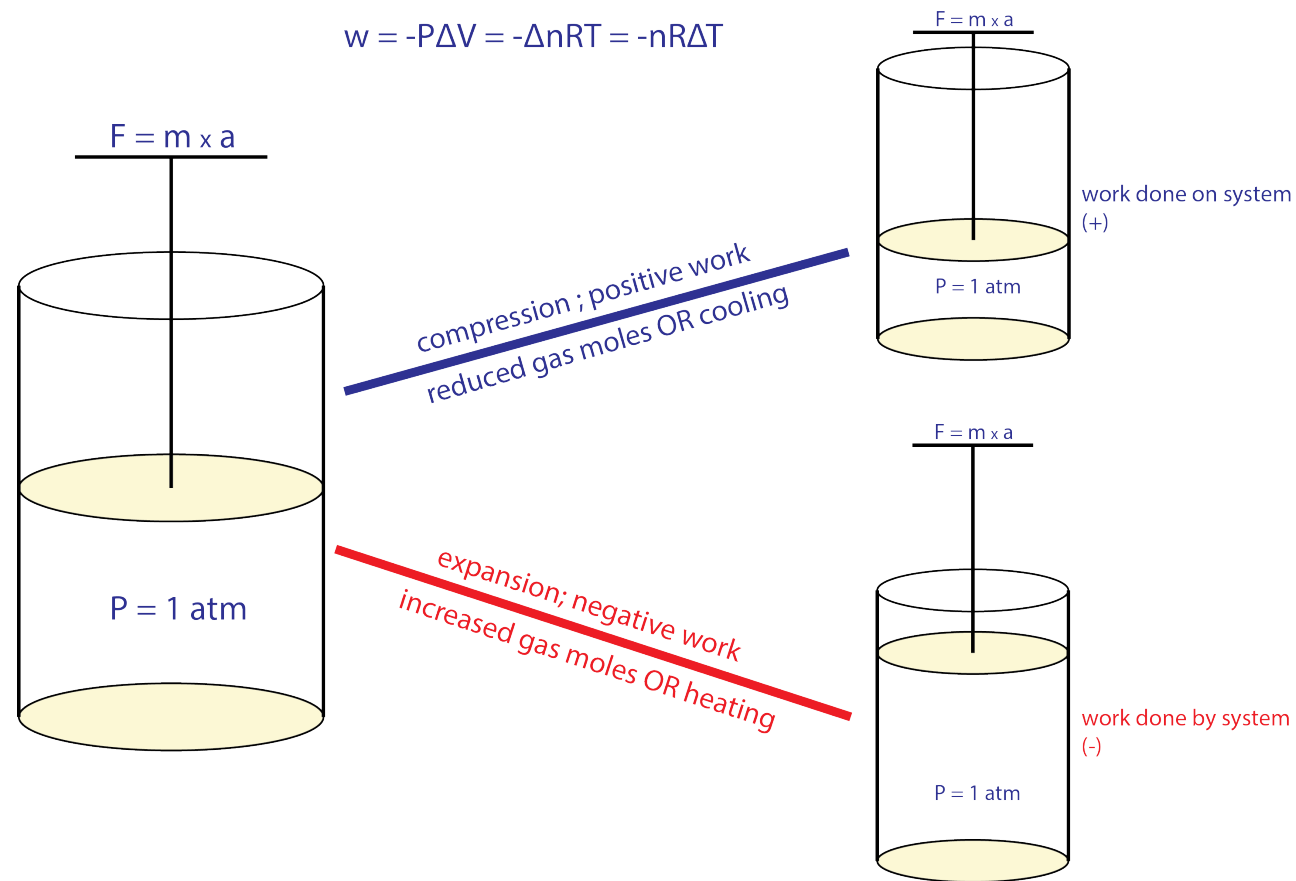
$$\Delta U_{universe} = 0$$

$$\Delta U_{sys} = q + w$$

$$\Delta U_{sys} = -\Delta U_{surr}$$

Visualizing Chemical Work

- Work in chemistry is most often related to what we call “PV” work, where $w = -P\Delta V$
- We often think of experiments measuring “PV” work in the context of using a piston
- Pistons exert a variable force to maintain a constant pressure. This pressure is used to determine the work done by or on the system
- When you are compressing your sample, you are doing work on the system (positive)
- When your sample expands, your system is doing work on the surroundings (the piston) to maintain the constant pressure (negative)



Basic Work Question

Consider a system where 2.50 L of ideal gas expands to 6.25 L against a constant external pressure of 330 torr. Calculate the work (w) for this system. Answer in joules.

$$w = -P \Delta V^*$$

(atm) (L)

$$J = - \left(\frac{330 \text{ torr}}{760 \frac{\text{torr}}{\text{atm}}} \right) (6.25 \text{ L} - 2.50 \text{ L})$$

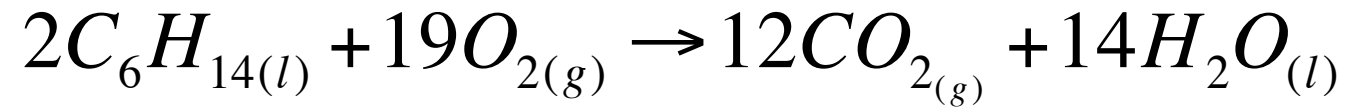
* $\times 101.325 \frac{\text{J}}{\text{L} \cdot \text{atm}}$

$$= -165 \text{ J}$$

$\Delta V (+) \Rightarrow$ expansion, $w (-)$

(-) work is work done by system

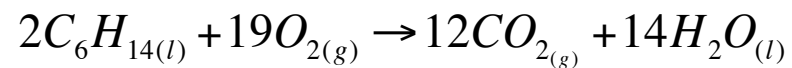
Chemical Work Question



Calculate the work in the combustion of hexane at standard conditions (298K and 1 atm). Is work done on or by the system?

Chemical Work Question

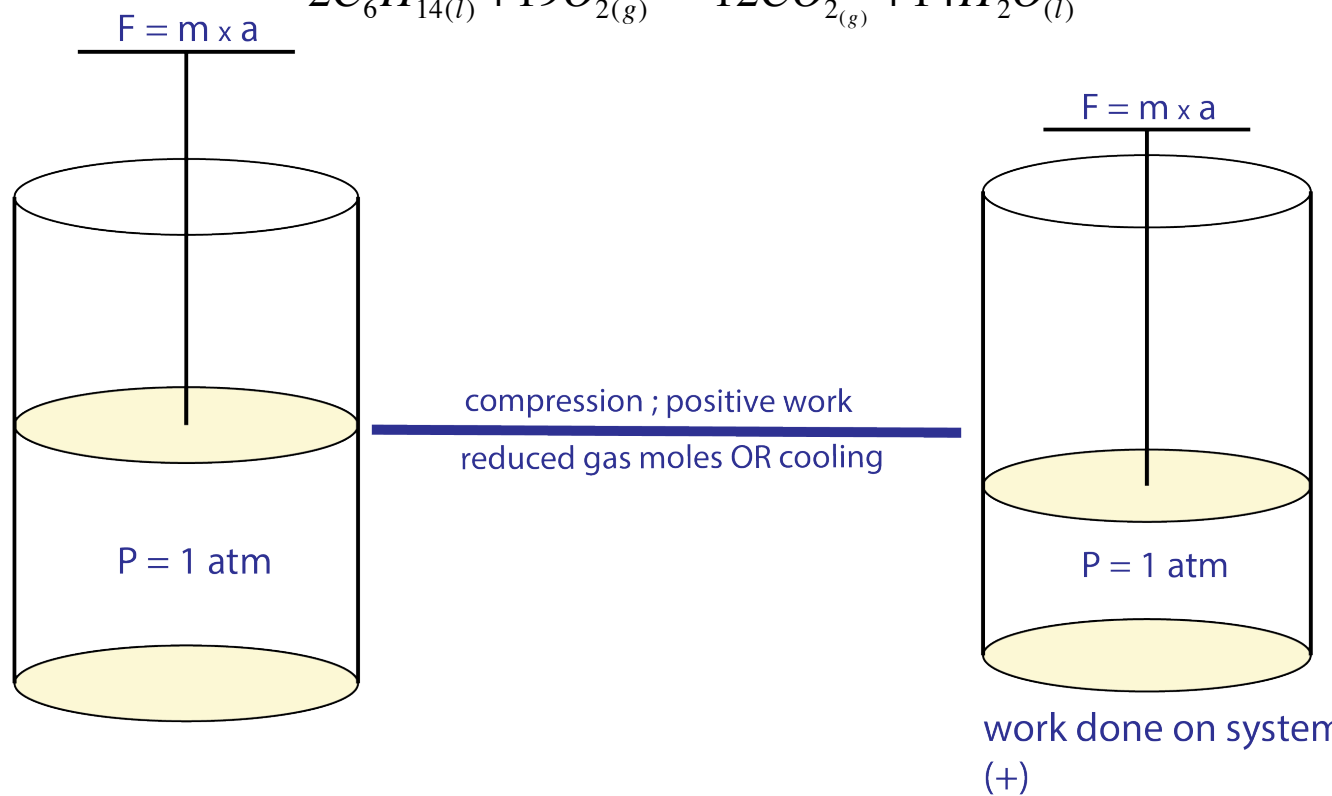
Calculate the work done in the combustion of hexane at RT and 1 atm.



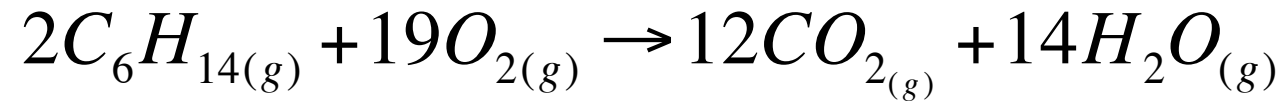
$$w = -\Delta nRT$$

$$w = -(-7 \text{ moles}) \left(8.314 \frac{\text{J}}{\text{molK}} \right) (298.15 \text{ K})$$

$$w = 17351 \text{ J} = 17 \text{ kJ}$$



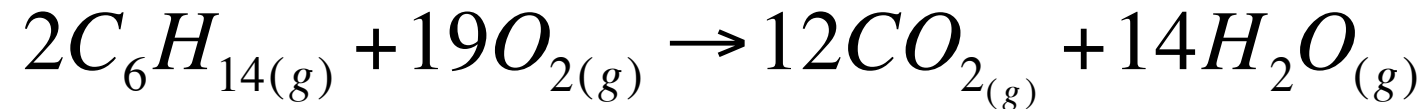
Chemical Work Question



Calculate the work in the combustion of hexane at 100°C. Is work done on or by the system?

Chemical Work Question

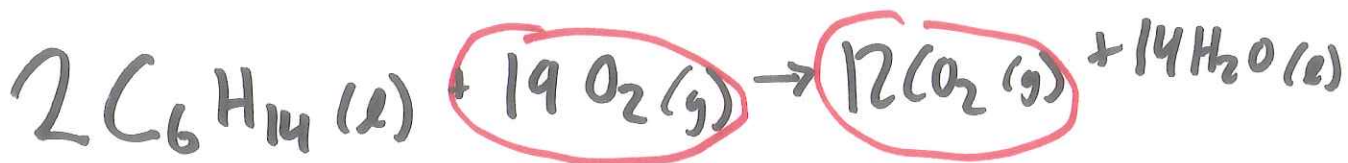
Calculate the work in the combustion of hexane at 100°C.



$$w = -\Delta nRT$$

$$w = -(5 \text{ moles}) \left(8.314 \frac{\text{J}}{\text{molK}} \right) (373.15 \text{ K})$$

$$w = -15511 \text{ J} = -15.5 \text{ kJ}$$



$$w = -\Delta nRT$$

↳ gas only

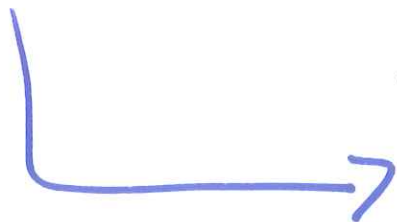
$$\Delta n = 12 - 19 = -7$$

work is done on the system ($w > 0$)

$$R = 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$T = 298\text{K}$$

$$+17351\text{J} = -(-7 \text{ moles}) \left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (298\text{K})$$



17.35 KJ For this balanced chemical reaction

Heat Flow: Heating Curves

Suppose you are melting a 10g ice cube from -10°C to 110°C at constant pressure (1 atm). How can we use what we know about thermodynamics to quantify the total heat of this change?

- We must understand that heat flow can apply to a temperature change or no temperature change and **these are calculated differently**

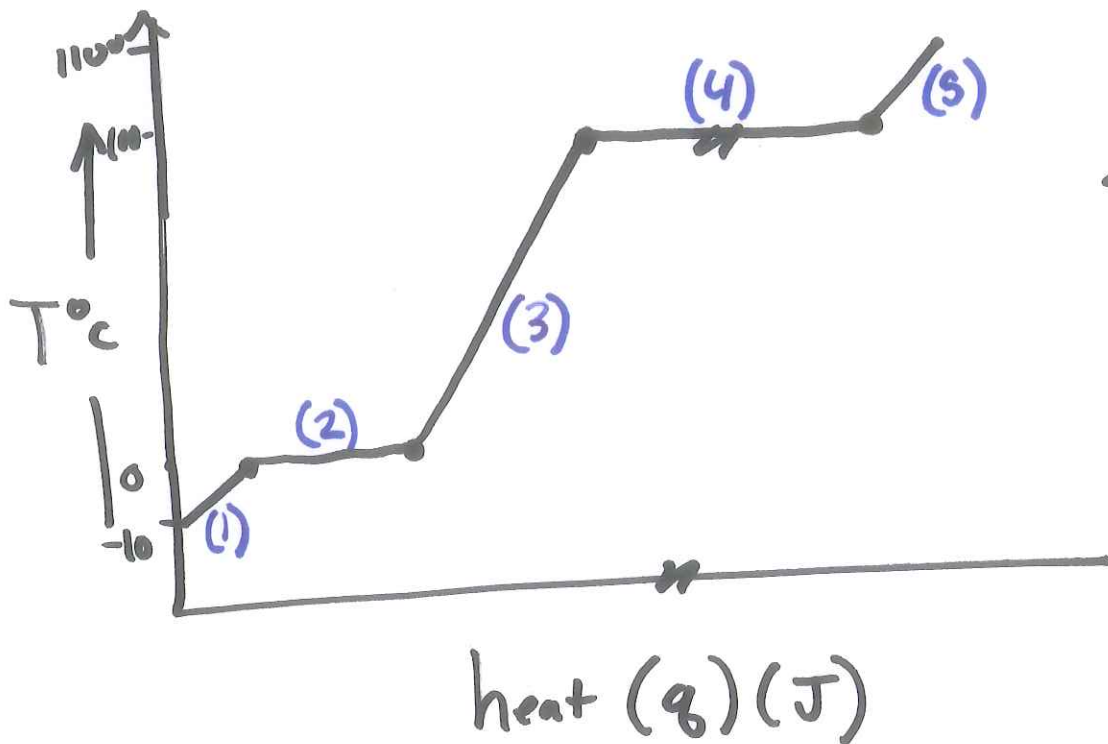
$$\text{H}_2\text{O (s)} = 2.09 \text{ J/g}\cdot^{\circ}\text{C}$$

$$\text{H}_2\text{O (l)} = 4.18 \text{ J/g}\cdot^{\circ}\text{C}$$

$$\text{H}_2\text{O (g)} = 2.03 \text{ J/g}\cdot^{\circ}\text{C}$$

The heat of fusion for water is 334 J/g and its heat of vaporization is 2260 J/g.





1) Heat of ΔT

$$q = m \underline{C} \Delta T$$

2) Heat of phase change (no ΔT)

$$q = m \underline{\Delta H}_{\text{phase}}$$

1. Heat from -10 to 0°C

$$q = (10\text{g}) \left(2.09 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (10^\circ\text{C}) = 209 \text{ J}$$

2. Convert $\text{H}_2\text{O}(\text{s})$ to $\text{H}_2\text{O}(\text{l})$ @ 0°C

$$q = (10\text{g}) \left(334 \frac{\text{J}}{\text{g}} \right) = 3340 \text{ J}$$

3. Heat from 0°C to 100°C

$$q = (10\text{g}) \left(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (100^\circ\text{C}) = 4184 \text{ J}$$

4. Boil $\text{H}_2\text{O}(\text{l})$ to $\text{H}_2\text{O}(\text{g})$ @ 100°C

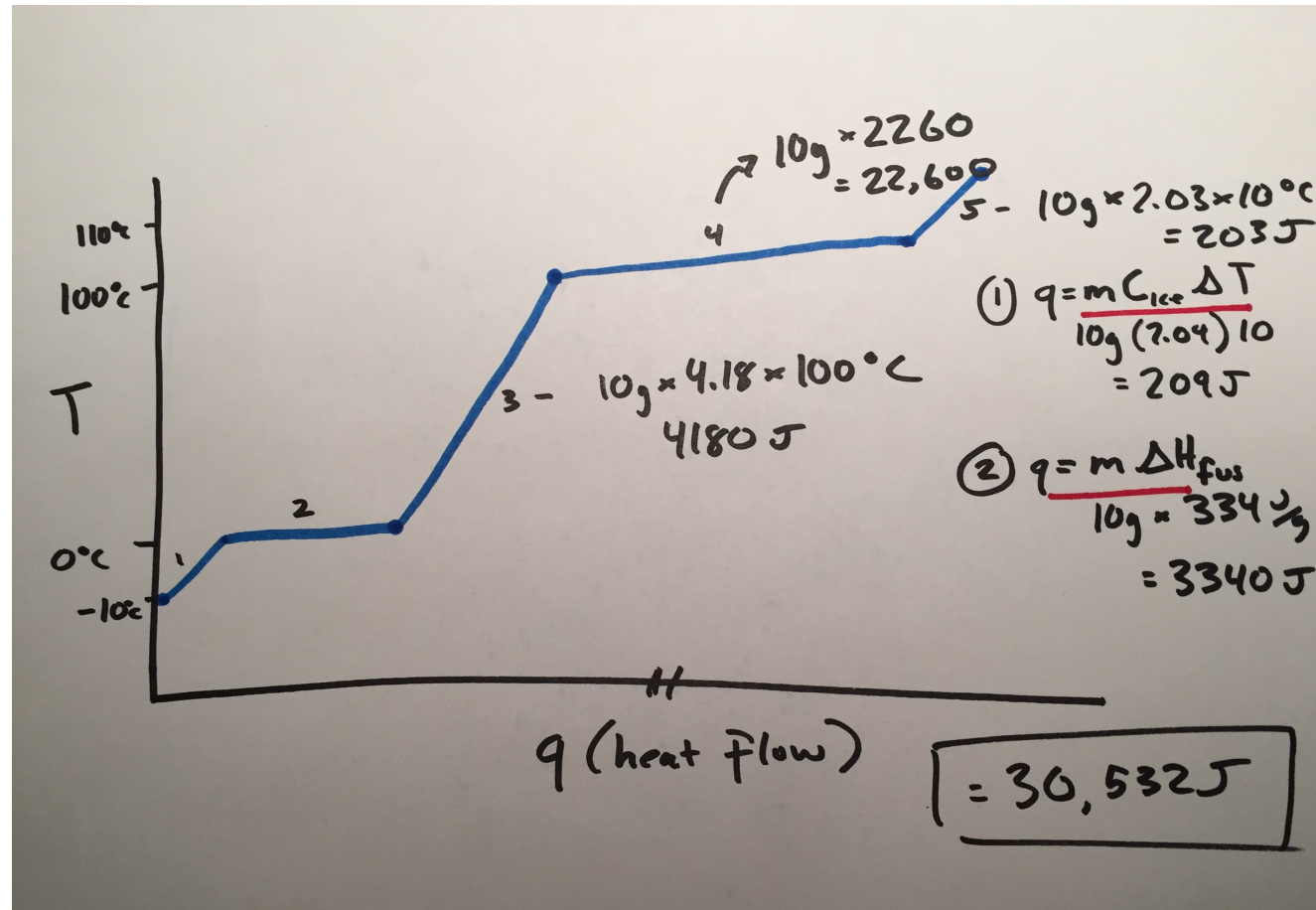
$$q = (10\text{g}) \left(2260 \frac{\text{J}}{\text{g}} \right) = 22600 \text{ J}$$

5. Heat from 100°C to 110°C

$$q = (10)(2.03)(10^\circ\text{C}) = 203 \text{ J}$$

30,532 J

Heat Flow: Heating Curves



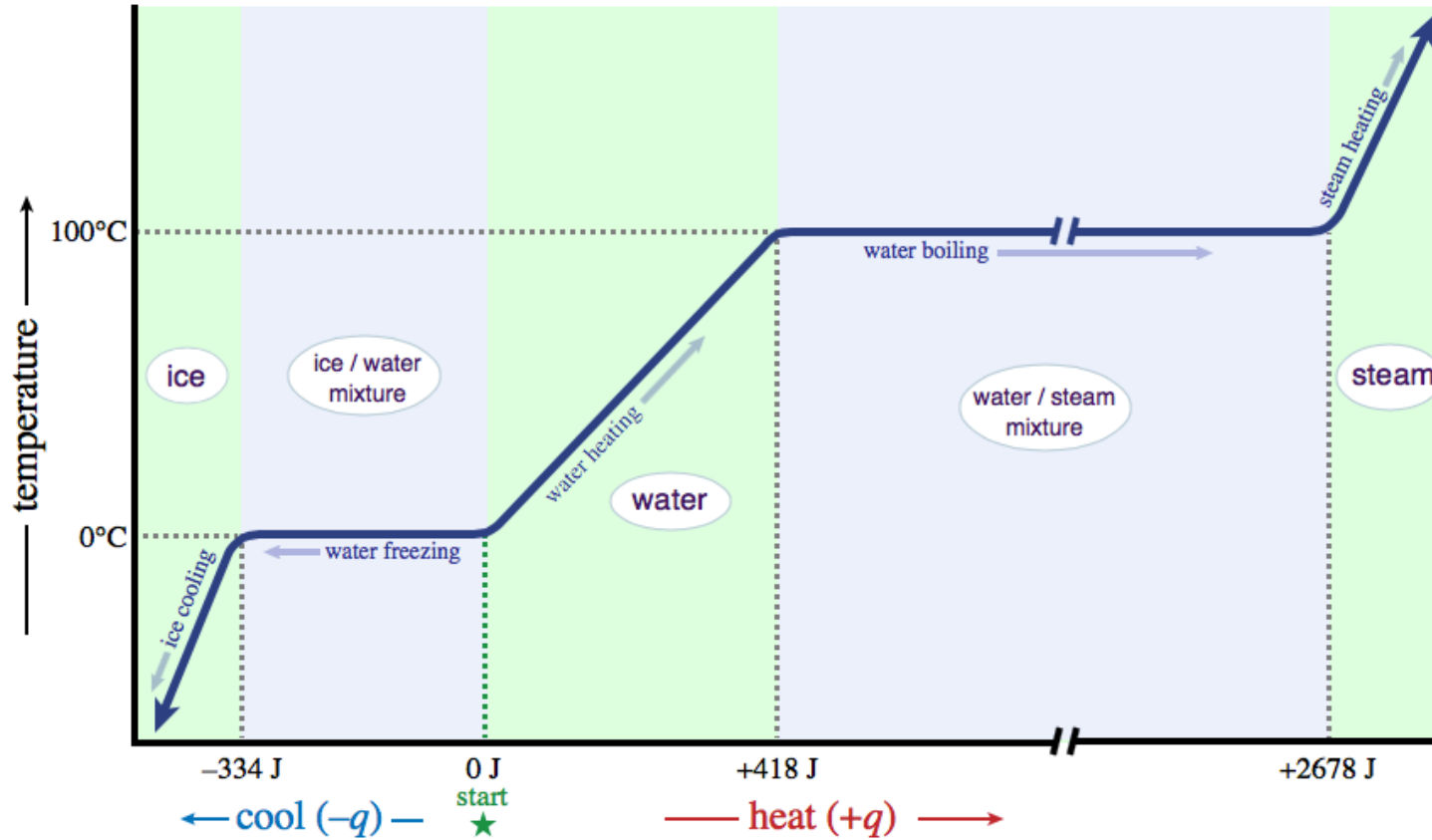
Heat of a Temperature Change

$$q = mC\Delta T$$

Heat of a Phase Change

$$q = m\Delta H_{\text{phase-change}}$$

Heat Flow: Heating Curves



Heat of a Temperature Change

$$q = mC\Delta T$$

Heat of a Phase Change

$$q = m\Delta H_{\text{phase-change}}$$



Calorimetry

- There are two types of calorimetry:
 1. **Coffee cup calorimetry measures heat at constant pressure ($q_p = \Delta H$) in an insulated, open-air container**

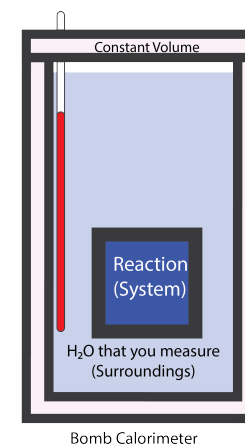
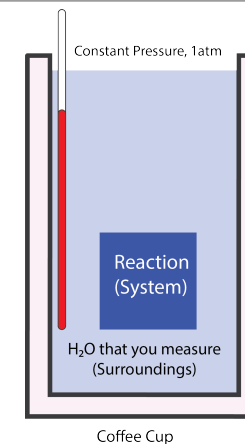
$$q_{cal} = m_{water} C_{water} \Delta T = -q_{p,sys}$$

$$q_{p,sys} = \Delta H_{sys}$$

2. **Bomb calorimetry measures heat at constant volume ($q_v = \Delta U$) in a rigid, isolated container**

$$q_{cal} = C_{hardware} \Delta T + m_{water} C_{water} \Delta T = -q_{v,sys}$$

$$q_{v,sys} = \Delta U_{sys}$$



Definition of Enthalpy

- **Enthalpy (H):** a state function that describes the heat content of a system, given by the equation:

$$H = U + PV$$

- **However, in chemistry we are more concerned with the change in enthalpy, ΔH , which is simply the heat flow at constant pressure, q_p**

$$\Delta H = q_p$$

Change in enthalpy derivation at constant pressure:

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = (q - \cancel{P\Delta V}) + \cancel{P\Delta V} + \Delta PV$$

$$\Delta P = 0$$

$$\Delta H = q$$

PS: if you want to think of reactions in our environment as occurring at constant pressure, change in enthalpy is a great term for determining the heat flow of reactions “IRL”

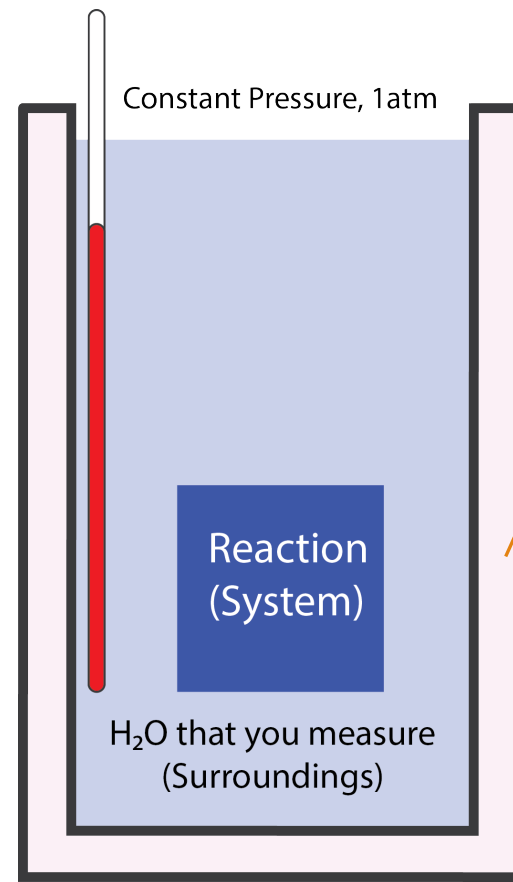
Coffee Cup Calorimetry

Coffee Cup: **the goal here is to measure heat at constant pressure. This directly gives us the enthalpy (ΔH) for a reaction.**

$$q_{cal} = m_{water} C_{water} \Delta T = -q_{p,sys}$$

$$q_{p,sys} = \Delta H_{sys}$$

The sign switches to get the heat flow for the system

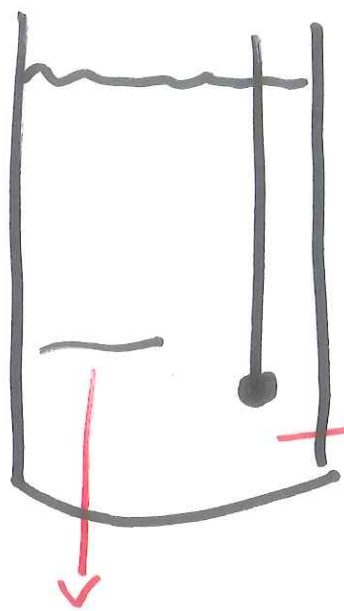


Insulated hardware does not absorb heat, so we don't care about the $C\Delta T$ term for the calorimeter

Chemical Work Question

A 100g sample of hot copper is placed in a coffee cup calorimeter containing 100 grams of water at room temperature. After some time the temperature of the water and the copper become a constant at 50°C. Calculate the initial temperature of the copper piece.

The specific heat of copper is 0.385 J/g°C. The specific heat of liquid water is 4.184 J/g°C.



Cu wire = system

$$\underbrace{-mC\Delta T}_{\text{sys}} = \underbrace{mC\Delta T}_{\text{sur}}$$

$$\underline{q_{\text{sys}}} = -\underline{q_{\text{surr}}}$$

$$q_{\text{cal}} = \underbrace{mC\Delta T}_{\text{H}_2\text{O}}$$

$$q_{\text{sys}} = \underbrace{mC\Delta T}_{\text{Copper wire}}$$

$$q_{\text{cal}} = (100\text{g}) \left(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (50^\circ\text{C} - 25^\circ\text{C})$$

$$= \underline{10,460 \text{ J}} = -q_{\text{sys}} = \underbrace{-mC\Delta T}_{\text{sys}}$$

$$-10,460 \text{ J} = (100\text{g}) \left(0.385 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (50^\circ\text{C} - T_i)$$

$$= \underline{\hspace{2cm}}^\circ\text{C}$$

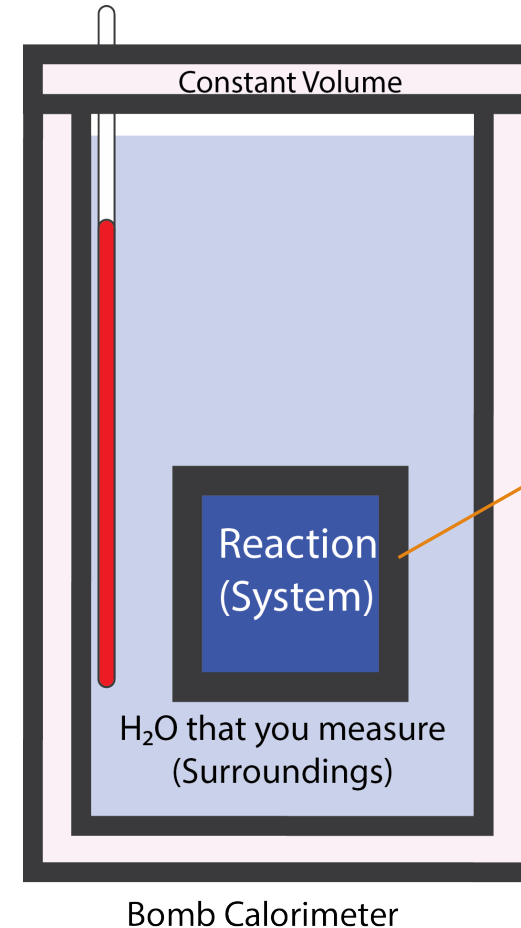
Bomb Calorimetry

Bomb Calorimetry: **the goal is to get the internal energy change (ΔU) of a combustion reaction by measuring the ΔT of both the surrounding water and the hardware of the calorimeter**

$$q_{cal} = C_{hardware} \Delta T + m_{water} C_{water} \Delta T = -q_{v,sys}$$

$$q_{v,sys} = \Delta U_{sys}$$

The sign switches to get the heat flow for the system



Bomb Calorimetry – ΔU to ΔH

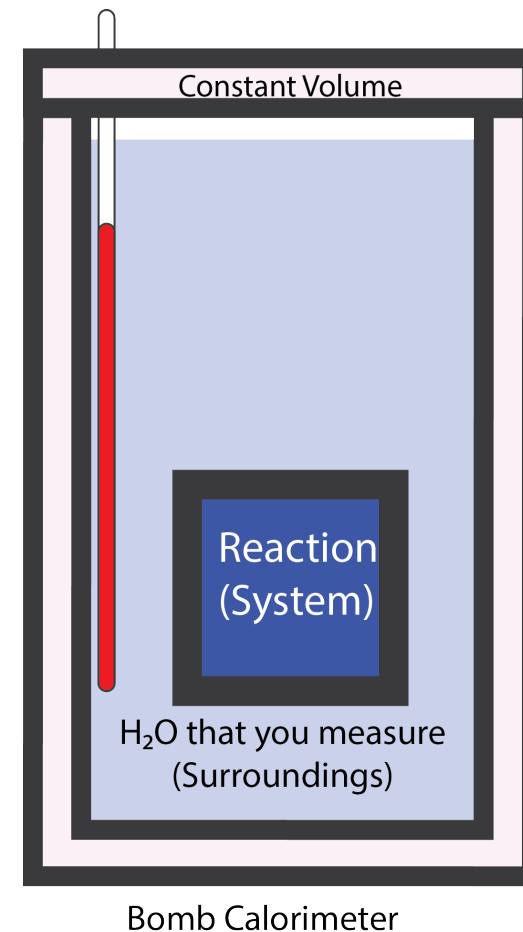
If we are interested in finding the ΔH° of the combustion reaction, two additional steps are necessary.

$\Delta U = q + w$; remember that at standard conditions and constant pressure:

$$q = \Delta H^\circ \text{ and } w = - \Delta nRT$$

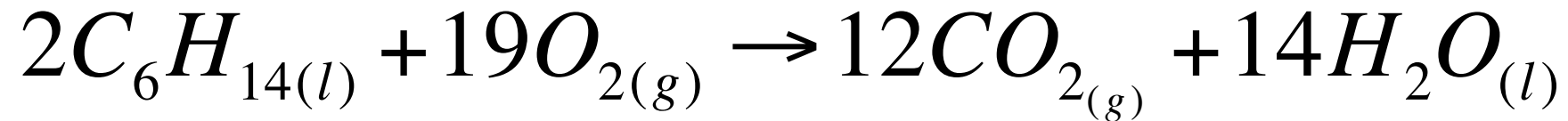
If you can write out your balanced combustion reaction, you can easily solve for ΔH°

$$\Delta U + \Delta nRT = \Delta H^\circ$$



Chemical Work Question

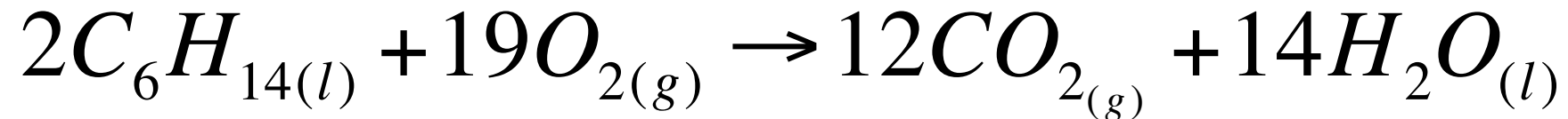
If the enthalpy of combustion of hexane is -4163kJ/mol, what is the change in internal energy for this process at RT?



$$w = 17351J = 17kJ$$

Chemical Work Question

If the enthalpy of combustion of hexane is -4163kJ/mol , what is the change in internal energy for this process at RT ?



$$w = 17351\text{J} = 17\text{kJ}$$

$$\Delta U = q + w = q - \Delta nRT$$

$$\Delta U = -4163\text{kJ} + 17\text{kJ} = -4146\text{kJ}$$