

# Announcements for Thursday, 14NOV2024

- Replacement Grade Policy
  - See Canvas announcement from Nov 14 for details
- Exam 2 is now available for reviewing through ***Gradescope***
- Requests for Exam Question Regrades Now Open
  - Wednesday, 13NOV2024, 12:01 AM (EST) – Friday, 15NOV2024, 11:59 PM (EST)
  - MUST be submitted through ***Gradescope*** (do not email instructors)
  - see Canvas announcement from Nov 12 for regrading policies and procedure
  - after the deadline, Exam 2 grades will not be changed

**ANY GENERAL QUESTIONS?** Feel free to see me after class!

## Try This On Your Own

- A 1.40-L gaseous system absorbs 75 J of heat and expands its volume to 2.00 L against an external pressure of 1.02 atm. What is the change in internal energy for this process?  $1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$

$$\Delta V = V_{final} - V_{initial} = 2.00 \text{ L} - 1.40 \text{ L} = +0.60 \text{ L}$$

$$w = -P_{ext}\Delta V = -(1.02 \text{ atm})(0.60 \text{ L}) = -0.612 \text{ L}\cdot\text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L}\cdot\text{atm}} = -62.0 \text{ J}$$

**absorbs** 75 J of heat:  $q = +75 \text{ J}$

**expands its volume:**  $w = -62 \text{ J}$

$$\Delta E = q + w = (+75 \text{ J}) + (-62 \text{ J}) = +13 \text{ J}$$

## Try This On Your Own

- When **1.550 g** of liquid hexane ( $\text{C}_6\text{H}_{14}$ ) undergoes combustion in a bomb calorimeter, the temperature of the calorimeter rises from  $25.87^\circ\text{C}$  to  $38.13^\circ\text{C}$ . Find  $\Delta E_{\text{rxn}}$  for the combustion of **1 mole** of hexane in kJ. The heat capacity of the bomb calorimeter is  $5.73 \text{ kJ}/^\circ\text{C}$ .

2 frames of reference: the reaction (rxn) and the calorimeter, and we're monitoring energy transfer between them

*bomb calorimeter* = constant-**volume** calorimetry, so  $\Delta V = 0$  and no work being done by the reaction ( $w_{\text{rxn}} = 0$ )

$\Delta E_{\text{rxn}} = q_{\text{rxn}} + w \rightarrow \Delta E_{\text{rxn}} = q_{\text{rxn}}$  (change in internal energy due solely to transfer of heat of the reaction ( $q_{\text{rxn}}$ ))

$\Delta T$  of the calorimeter =  $38.13 - 25.87 = +12.26^\circ\text{C}$ ; the calorimeter is absorbing energy from the reaction and

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

$$q_{\text{calorimeter}} = (C_{\text{calorimeter}})(\Delta T_{\text{calorimeter}}) = (5.73 \text{ kJ}/^\circ\text{C})(12.26^\circ\text{C}) = 70.2 \text{ kJ}$$

$$q_{\text{rxn}} = -q_{\text{calorimeter}} = \mathbf{-70.2 \text{ kJ} = \Delta E_{\text{rxn}} \text{ for the combustion of 1.550 g hexane}}$$

$\Delta E$  for the combustion of **1 mole** hexane:

$$\frac{-70.2 \text{ kJ}}{1.550 \text{ g C}_6\text{H}_{14}} \times \frac{86.17 \text{ g C}_6\text{H}_{14}}{1 \text{ mol C}_6\text{H}_{14}} = \mathbf{-3.90 \times 10^3 \text{ kJ/mol C}_6\text{H}_{14}}$$

# Enthalpy (H)

- the enthalpy of a system is defined as the sum of a system's internal energy (E) and the product of its pressure and volume (PV)

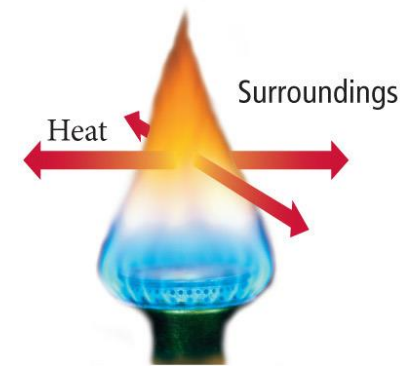
$$H = E + PV$$

$$\Delta H = \Delta E + P\Delta V$$

- essentially it's the heat of a reaction under ***constant pressure*** ( $q_p$ )
  - for this course, always assume reactions are at constant pressure unless explicitly stated
  - $q_p = \Delta H_{\text{rxn}}$
- absolute enthalpy values cannot be determined
  - $\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$  but only  $\Delta H$  can be measured directly

# The Signs of $\Delta H$

- **exothermic reaction** = heat released by reaction =  $(-)\Delta H$ 
  - heat released into the surroundings
  - temperature of the surroundings increases and “it feels hot”
- **endothermic reaction** = heat absorbed by reaction =  $(+)\Delta H$ 
  - heat absorbed from the surroundings
  - temperature of the surroundings decreases and “it feels cold”
- $\Delta H_{\text{rxn}}$  can be measured by doing calorimetry under constant pressure



Exothermic

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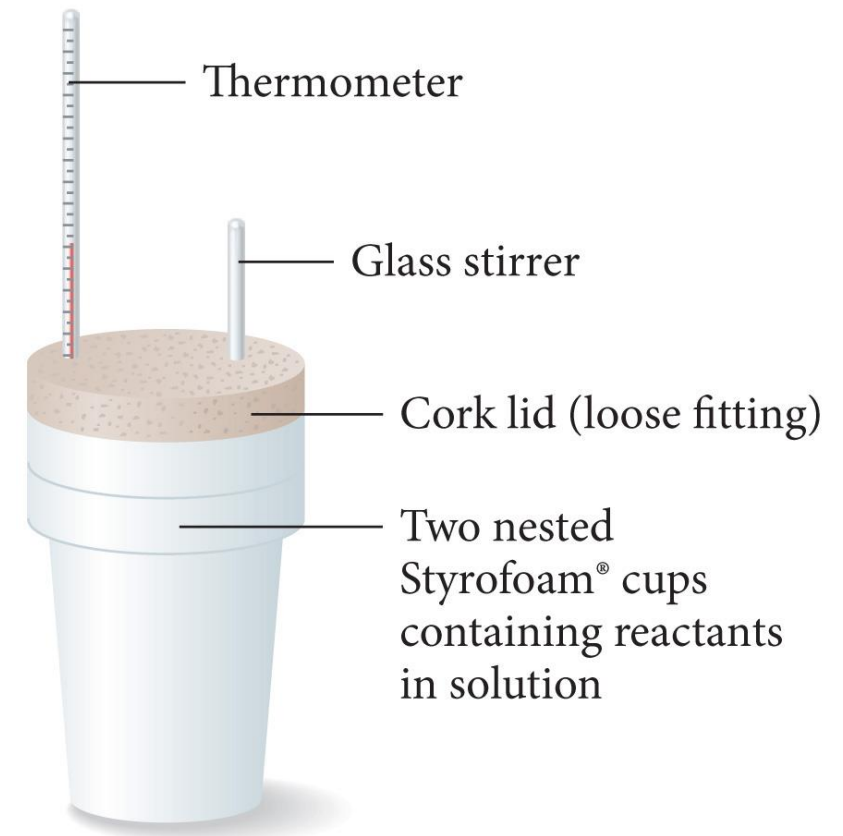
Endothermic

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# Constant-Pressure Calorimetry

- an experimental technique that allows the direct measurement of  $\Delta H$  for aqueous chemical reactions ( $\Delta H_{\text{rxn}}$ )
  - similar in concept to constant-volume calorimetry
  - reactions are run under constant pressure so that  $q_{\text{rxn}} = \Delta H_{\text{rxn}}$
- as with all calorimetry, temperature of the surroundings (the calorimeter and water) are measured to calculate  $q_{\text{solution}}$
- $-q_{\text{solution}} = q_{\text{rxn}} = \Delta H_{\text{rxn}}$

## The Coffee-Cup Calorimeter



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# Summary of Calorimetry

experimental conditions under which the reaction is taking place	property of reaction being directly measured by calorimeter	apparatus used to perform heat measurements	property of reaction being indirectly established
constant volume	$q_v$ (heat of reaction under constant volume)	bomb calorimeter	$\Delta E_{\text{rxn}}$
constant pressure	$q_p$ (heat of reaction under constant pressure)	coffee-cup calorimeter	$\Delta H_{\text{rxn}}$

# Stoichiometry and $\Delta H$

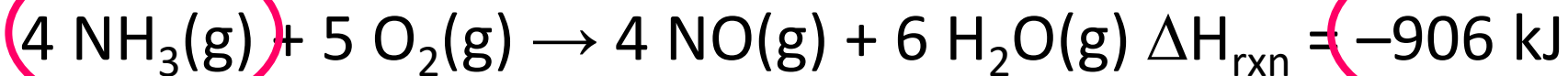
- the  $\Delta H$  of a reaction can be used as a conversion factor to convert amount product/reactant  $\leftrightarrow$  amount of energy
  - all the previous “rules” and procedures of stoichiometry still apply
- the  $\Delta H$  of a reaction is for the amounts of reactants/products specified by the balanced reaction coefficients

for example:  $4 \text{ NH}_3(\text{g}) + 5 \text{ O}_2(\text{g}) \rightarrow 4 \text{ NO}(\text{g}) + 6 \text{ H}_2\text{O}(\text{g}) \quad \Delta H_{\text{rxn}} = -906 \text{ kJ}$

- 906 kJ **released** for every 4 moles of  $\text{NH}_3$  consumed
- 906 kJ **released** for every 5 moles of  $\text{O}_2$  consumed
- 906 kJ **released** for every 4 moles of  $\text{NO}$  produced
- 906 kJ **released** for every 6 moles of  $\text{H}_2\text{O}$  produced



## Stoichiometry and $\Delta H$ (continued)



What mass of  $\text{NH}_3$  (MM = 17.03 g/mol) needs to be reacted with excess oxygen to produce 255 kJ?

$$-255 \text{ kJ} \times \frac{4 \text{ mol NH}_3}{-906 \text{ kJ}} \times \frac{17.03 \text{ g NH}_3}{1 \text{ mol NH}_3} = \mathbf{19.2 \text{ g NH}_3}$$

## Try This On Your Own

- The enthalpy of combustion for 1 mole of propane ( $\text{C}_3\text{H}_8$ ) is  $-2044 \text{ kJ}$ . What is the minimum mass of propane needed to react in excess oxygen to generate enough heat to raise the temperature of 10.0 moles of silver by  $25.0 \text{ }^\circ\text{C}$ ? The specific heat of silver is  $0.235 \text{ J/g}\cdot^\circ\text{C}$ .

## Try This On Your Own

250.0 mL of 1.00 M HCl(aq) was added to 250.0 mL of 1.00 M NaOH(aq) in a coffee-cup calorimeter. Both solutions initially are at 20.00 °C. Upon mixing, the temperature of the mixture increases to 26.84 °C. Using this data, calculate the enthalpy change for the following reaction:



Assume that the density and heat capacity of the mixture are 1.00 g/mL and 4.18 J/g·°C, respectively.

### Some questions to consider:

Why is the temperature of the mixture increasing?

Where is the heat that warms the mixture coming from?

What can we deduce about the sign of  $\Delta H_{\text{rxn}}$ ?

How does  $\Delta H_{\text{rxn}}$  relate to  $q_{\text{solution}}$ ?

What amounts of HCl and NaOH are actually reacting?

What amounts of HCl and NaOH are being depicted in the reaction?

# Methods to Determine $\Delta H_{\text{rxn}}$

directly by doing *calorimetry* at constant pressure

- may not be practical to do especially if side-reactions are possible

indirectly by doing **calculations**

- $\Delta H$  is a **state function** and the path to get from reactants to products doesn't matter

1. Hess's law

2. using Bond Energies

$$\Delta H_{\text{rxn}} = \sum (\Delta H \text{'s bonds broken}) + \sum (\Delta H \text{'s bonds formed})$$

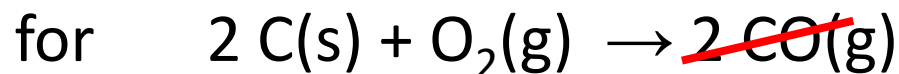
3. using Standard Enthalpies of Formation

$$\Delta H_{\text{rxn}}^{\circ} = \sum n_{\text{p}} \Delta H_{\text{f}}^{\circ} (\text{products}) - \sum n_{\text{r}} \Delta H_{\text{f}}^{\circ} (\text{reactants})$$

# Hess's Law

- a **computational approach** to determine enthalpy changes for reactions that are not easily studied by calorimetry
- based on the fact that the change in enthalpy for a stepwise process is the sum of the enthalpy changes of each step
  - the number of steps is unimportant
  - what ultimately matters is that the individual steps “add up” to the reaction you are concerned with (i.e., the reaction of interest)
- the purpose of Hess's law is to manipulate “helper reactions” (and their associated  $\Delta H$  values) such that when you “add” the helper reactions (and their  $\Delta H$ s) up, you are left with a reaction of interest (and its  $\Delta H$ ).

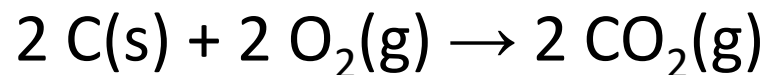
What is  $\Delta H$  for  $2\text{C(s)} + 2\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$ ?



$$\Delta H = -221.0 \text{ kJ}$$



$$\Delta H = -566.0 \text{ kJ}$$



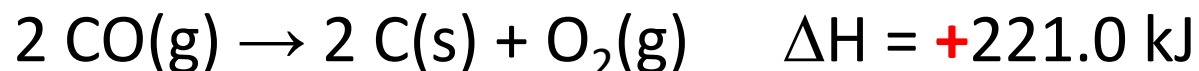
$$\Delta H = (-221.0) + (-566.0) = -787.0 \text{ kJ}$$

# Hess's Law – Manipulating the Helpers

helper reactions can be manipulated by:

1. changing the direction of the reaction

- this changes the sign of  $\Delta H_{\text{rxn}}$



2. multiplying the coefficients of the reaction by a certain factor

- since enthalpy is an extensive property,  $\Delta H_{\text{rxn}}$  gets multiplied by the same factor



when adding up the helper reactions, like species on opposite sides of the arrow cancel, and the reaction of interest should be left over

- adding up the adjusted  $\Delta H$  values gives the  $\Delta H$  of the reaction of interest

## Hess's Law – Example

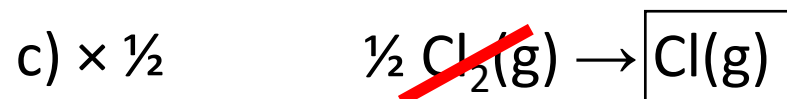
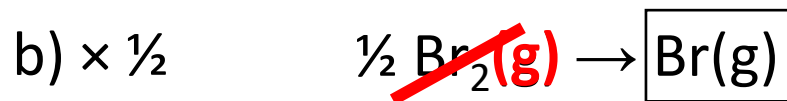
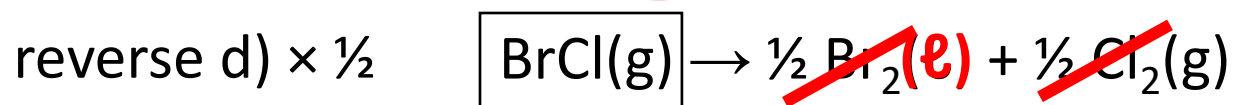
Calculate the enthalpy change for the following reaction

Reaction of Interest:



$$\Delta H = +219.0 \text{ kJ}$$

given the following data

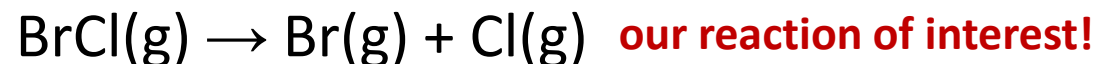


$$\Delta H = \frac{-29.2}{2} = -14.6 \text{ kJ}$$

$$\Delta H = \frac{+192.9}{2} = +96.45 \text{ kJ}$$

$$\Delta H = \frac{+243.4}{2} = +121.7 \text{ kJ}$$

$$\Delta H = \frac{+30.90}{2} = +15.45 \text{ kJ}$$



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$$+219.0 \text{ kJ}$$

## Try This On Your Own

Calculate the enthalpy change for the following reaction



given the following data

- a)  $\text{C}_2\text{H}_4(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\ell) \quad \Delta\text{H} = -1410.9 \text{ kJ}$
- b)  $2 \text{C}_2\text{H}_6(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 4 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\ell) \quad \Delta\text{H} = -3119.4 \text{ kJ}$
- c)  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\ell) \quad \Delta\text{H} = -571.6 \text{ kJ}$