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Enthalpy

Calorimetry of Chemistry

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Reaction Energies

In our earlier discussions of calorimetry, we used **physical** sources of heat (hot metal slug). It is also possible to use **chemical** sources of heat (like hot packs and cold packs).

The energy change associated with a chemical reaction is called the **enthalpy of reaction** and abbreviated ΔH .

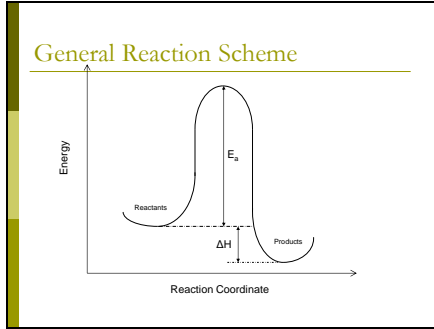
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Enthalpy of Reactions

There are actually a number of different types of enthalpies because enthalpy depends on conditions. THEY ARE ALL JUST SPECIFIC TYPES OF A GENERAL CONCEPT CALLED "ENTHALPY".

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

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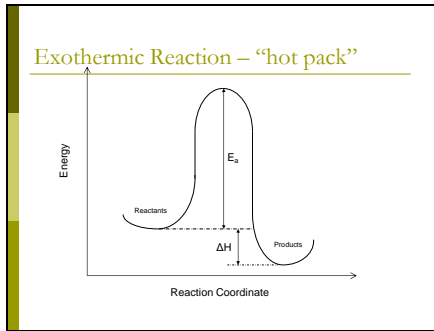
Reaction Coordinate

The "reaction coordinate" is actually complicated to determine, but easy to understand.

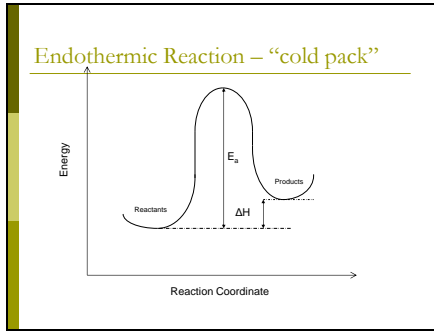
The actual energy profile of a reaction is a multi-dimensional curve with lots of different paths from reactants to products.

The **reaction coordinate** is simply the most common path that averages all of the different parameters: bond length, bond angle, collision frequency, etc.

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Where does the Energy go?

In the case of a chemical reaction, you need to keep the different types of energy separate in your mind:

- Bond energy – energy INSIDE the molecules
- Thermal energy (heat) – kinetic energy of the molecules
- Energy of the “bath” – kinetic energy of solvent or other molecules in the system

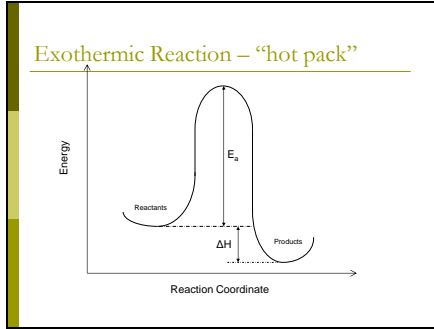
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Energy changes

ΔH represents the change in INTERNAL MOLECULAR ENERGY.

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

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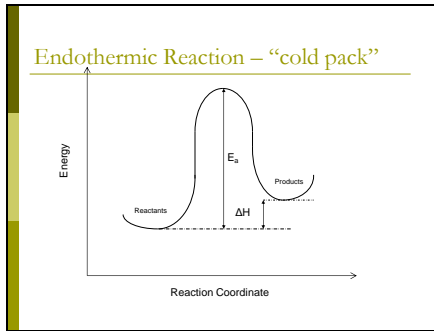
Exothermic energy changes

$\Delta H = H_{\text{final}} - H_{\text{initial}} < 0$

$H_{\text{initial}} > H_{\text{final}}$

This energy is internal to the molecule.
The excess gets absorbed by the rest of the system as heat causing the molecules to move faster (more kinetic energy) and the temperature to increase.

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Endothermic energy changes

$\Delta H = H_{\text{final}} - H_{\text{initial}} > 0$

$H_{\text{initial}} < H_{\text{final}}$

This energy is internal to the molecule and must come from somewhere.

The additional energy required by the system gets absorbed from the rest of the system as heat causing the molecules to move slower (less kinetic energy) and the temperature to decrease.

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Clicker Question

Consider the following reaction:
 $2 \text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{H}_2\text{O} (\text{g})$

If $\Delta H_{\text{rxn}} < 0$, it means:

- A) The products have less energy than the reactants – you could make a hot pack.
- B) The reactants have less energy than the products – you could make a cold pack.
- C) The products have less energy than the reactants – you could make a cold pack.
- D) The reactants have less energy than the products – you could make a hot pack.

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The hard part is getting over the hump.

The diagram is a reaction coordinate plot. The vertical axis is labeled 'Energy' and the horizontal axis is labeled 'Reaction Coordinate'. A curve starts at a point labeled 'Reactants', rises to a peak labeled 'E_‡', and then falls to a point labeled 'Products'. A dashed horizontal line extends from the reactant level to the right, and another dashed horizontal line extends from the product level to the left. A vertical double-headed arrow between these two dashed lines is labeled 'ΔH', indicating that the products are at a lower energy state than the reactants.

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$E_a = \text{Activation Energy}$

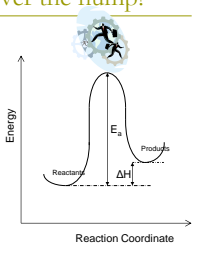
The tale of a reaction is not limited strictly to the identity and energetics of the products and reactants, there is a path (reaction coordinate) that must get followed.

The "hump" represents a hurdle that must be overcome to go from reactants to products.

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How do you get over the hump?

If you are at the top, it is easy to fall down into the valley (on either side), but how do you get to the top?

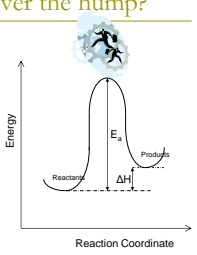


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How do you get over the hump?

The molecules acquire or lose energy the same way: by colliding with each other!

The energy comes from the "bath", the rest of the system.



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Types of ΔH

- ΔH – generic version
- ΔH_{rxn} – generic version
- ΔH° – enthalpy change under Standard Temperature and Pressure (298 K, 1 atm)
- ΔH_f – enthalpy of formation, refers to a specific reaction type
- ΔH_{comb} – enthalpy change of combustion
- ΔH_f° – enthalpy of formation at STP

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$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$

The enthalpy change involved in this reaction depends, to some extent, on conditions.

At STP, ΔH° will be known if it's ever been measured:

$\Delta H^\circ = -483.66 \text{ kJ}$

The enthalpy change must include some accounting for the amount (moles of the substance)

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$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$

This reaction is a very special type of reaction.

This is a **reaction of formation**.

A formation reaction creates a molecule from the most common elemental form of its constituent atoms

$\Delta H_f^\circ = -241.83 \text{ kJ/mol}$

We form 2 moles of H_2O in this reaction, so:
 $\Delta H_{\text{rxn}} = 2 \text{ mol} \cdot (-241.83 \text{ kJ/mol}) = -483.66 \text{ kJ}$

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Enthalpy is a "State Function"

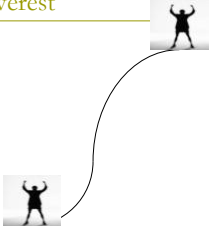
What's a "state function"?

A "state function" is a value that is a function only of the initial and final states of the system, not the path you take to get there!

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Climbing Mt. Everest

Suppose you start at Himalayan Base Camp #1, climb to the summit of Everest over the course of 3 weeks, then return to Himalayan Base Camp #1.

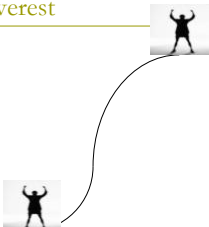


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Climbing Mt. Everest

Back at base camp, I figure out my altitude change. What is it?

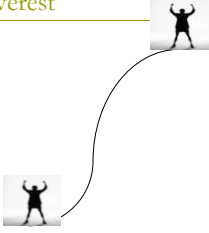
ZERO - I'm back where I started



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Climbing Mt. Everest

I did a lot of work along the way, but all that matters is I'm back where I started. The net change in altitude is NADA, ZERO, ZILCH!



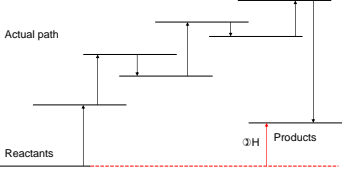
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Enthalpy as a State Function

Enthalpy is like that. It doesn't care how you got where you are going, it simply looks at the difference from where you started.

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Path doesn't matter!



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$2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)$

We don't know exactly how this reaction occurs:

1. 2 H₂ collide forming 4 H fragments, then 1 H fragment collides with the O₂ creating an OH and an O, then the O collides with an H to make a second OH, then the two OH collide to make H₂O and another O which then collides with an H...
2. 2 H₂ and 1 O₂ all collide at the same time creating 2 H₂O molecules

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$2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)$

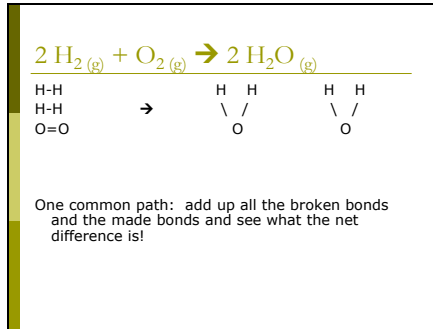
IT JUST
DOESN'T
MATTER

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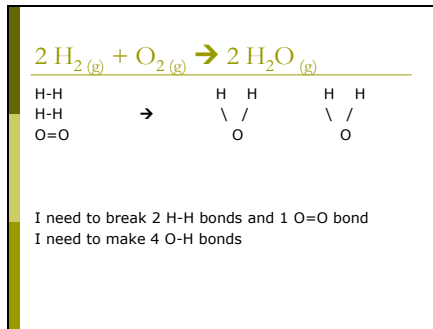
$2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)$

You can pick
whatever path you
want that makes it
easy to calculate.

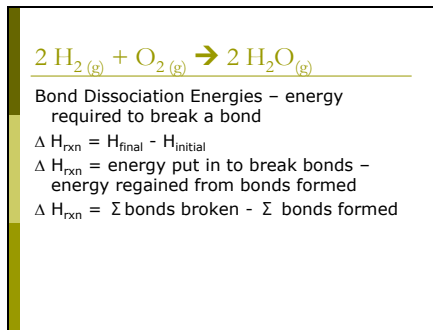
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$$\text{CH}_4(g) + 4 \text{Cl}_2(g) \rightarrow \text{CCl}_4(l) + 4 \text{HCl}(g)$$

This is not, itself, a formation reaction.

BUT remember ΔH is a STATE FUNCTION

What does that mean?

ΔH doesn't depend on the path, just the start and the end.

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$$\text{CH}_4(g) + 4 \text{Cl}_2(g) \rightarrow \text{CCl}_4(l) + 4 \text{HCl}(g)$$

All the elements known to mankind!

Slide 45

$$\text{CH}_4(g) + 4 \text{Cl}_2(g) \rightarrow \text{CCl}_4(l) + 4 \text{HCl}(g)$$

How does that help?

You can take the long road. Don't do the reaction as written, take a convenient path that you know the value of each step.

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$$\text{CH}_4(g) + 4 \text{Cl}_2(g) \rightarrow \text{CCl}_4(l) + 4 \text{HCl}(g)$$

Can you think of a path where you know the value of each step?

Make the products from elements (formation reactions). Make the reactants from elements (formation reactions). The difference between the ΔH_f° of the products and the reactants must be the $\Delta H^\circ_{\text{rxn}}$

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$$\text{CH}_4(g) + 4 \text{Cl}_2(g) \rightarrow \text{CCl}_4(l) + 4 \text{HCl}(g)$$

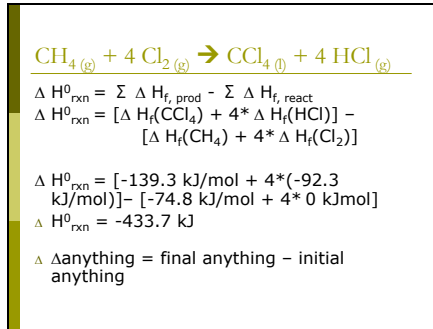
All the elements known to mankind!

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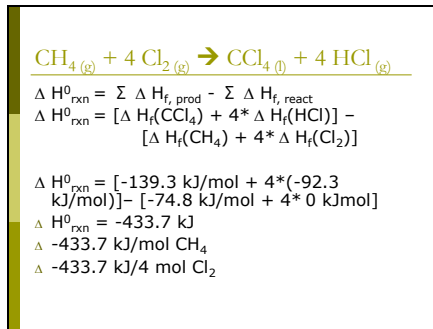
$$\text{CH}_4(g) + 4 \text{Cl}_2(g) \rightarrow \text{CCl}_4(l) + 4 \text{HCl}(g)$$

All the elements known to mankind!

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$\Delta H_f(\text{CCl}_4) = -139.3 \text{ kJ/mol}$

If I make 1 mol CCl₄, I get/need 139.3 kJ?

A. Get
B. Need

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Clicker Question

$\text{CH}_4(\text{g}) + 4 \text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{l}) + 4 \text{HCl}(\text{g})$

$\Delta H^\circ_{\text{rxn}} = -433.7 \text{ kJ}$

If I want to heat 1000 g of water from 25 C to boiling. How much chlorine would I need to react (assuming I have infinite CH_4)?

A. 51.26 g
B. 0.723 g
C. 205.04 g

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Ways to determine ΔH

1. Find ΔH° in a table
2. Find ΔH_f° in a table
3. Calculate from Bond Energies
4. Calculate from ΔH_f°
5. Calculate from other ΔH that you already know (Hess's Law)

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Hess's Law

We already basically used Hess's Law when we added together the heats of formation

Hess's Law is simply the tools that go with enthalpy being a state function.

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Hess's Law

1. If you add two reactions together, ΔH adds together.
2. If you subtract two reactions, ΔH gets subtracted.
3. If you reverse a reaction, ΔH changes sign.
4. If you multiply or divide a reaction, ΔH gets multiplied or divided.

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Sample Hess's Law Problem

Calculate the enthalpy change for the reaction

$$\text{P}_4\text{O}_6(\text{s}) + 2 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})$$

given the following enthalpies of reaction:

$$\text{P}_4(\text{s}) + 3 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_6(\text{s}) \quad \Delta H = -1640.1 \text{ kJ}$$
$$\text{P}_4(\text{s}) + 5 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s}) \quad \Delta H = -2940.1 \text{ kJ}$$

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Sample Hess's Law Problem

$$\text{P}_4\text{O}_6(\text{s}) + 2 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})$$
$$\text{P}_4(\text{s}) + 3 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_6(\text{s}) \quad \Delta H = -1640.1 \text{ kJ}$$
$$\text{P}_4\text{O}_6(\text{s}) \rightarrow \text{P}_4(\text{s}) + 3 \text{O}_2(\text{g}) \quad \Delta H = +1640.1 \text{ kJ}$$
$$\text{P}_4\text{O}_6(\text{s}) + \text{P}_4(\text{s}) + 5 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s}) + \text{P}_4(\text{s}) + 3 \text{O}_2(\text{g}) + \text{P}_4\text{O}_{10}(\text{s})$$
$$\text{P}_4\text{O}_6(\text{s}) + \text{P}_4(\text{s}) + 5 \text{O}_2(\text{g}) \rightarrow \text{P}_4(\text{s}) + 3 \text{O}_2(\text{g}) + \text{P}_4\text{O}_{10}(\text{s})$$
$$\Delta H = -1300 \text{ kJ}$$

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Enthalpy & Calorimetry

You can combine the enthalpies of reaction with the calorimetry we discussed earlier, using the reactions to generate the heat.

This is nothing new, just a combination of the two concepts we already discussed and a few things we knew from before.

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A bomb calorimeter is a water calorimeter with a small chamber inside in which combustion reactions can be executed. If I put 1 mole of hydrogen and 1 mole of oxygen in a bomb calorimeter containing 1 L of water at 25 °C, what will the temperature of the water be after ignition? The empty (no water) calorimeter has a specific heat capacity of 145.1 J/°C.

$$q_{\text{H}_2\text{O}} = m c \Delta T$$
$$q_{\text{calorimeter}} = m c \Delta T$$
$$Q = S_0 \Delta T$$

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$$q_{\text{rxn}} = -(q_{\text{bomb}} + q_{\text{water}})$$
$$1 \text{ mol O}_2 * (2 \text{ mol H}_2) / 1 \text{ mol O}_2 = 2 \text{ mol H}_2\text{O}$$

Hydrogen is the limiting reagent.
 $1 \text{ mol H}_2 * \frac{2 \text{ mol H}_2\text{O}}{2 \text{ mol H}_2} = 1 \text{ mol H}_2\text{O}$

$$\Delta H_f^\circ = -241.83 \text{ kJ/mol}$$

$$\Delta H_{\text{rxn}} = -241.83 \text{ kJ/mol} * 1 \text{ mol} = -241.83 \text{ kJ}$$

$$1 \text{ L H}_2\text{O} * \frac{1000 \text{ mL}}{1 \text{ L}} * \frac{1 \text{ g H}_2\text{O}}{1 \text{ mL H}_2\text{O}} = 1000 \text{ g H}_2\text{O}$$

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$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$

$q_{\text{rxn}} = -(q_{\text{bomb}} + q_{\text{water}})$
 $-241.83 \text{ kJ} = -(S_{\text{bomb}} \Delta T + m_{\text{H}_2\text{O}} c_{\text{H}_2\text{O}} \Delta T)$
 $-241.83 \text{ kJ} = -(145.1 \text{ J/}^\circ\text{C} \Delta T + 1000 \text{ g} \cdot 4.18 \text{ J/g}^\circ\text{C} \Delta T)$
 $-241.83 \text{ kJ} = -(4325.1 \text{ J/}^\circ\text{C} \Delta T)$
 $-241.83 \times 10^3 \text{ J} = -4325.1 \text{ J/}^\circ\text{C} \Delta T$
 $55.9 = \Delta T = T_f - T_i = T_f - 25^\circ\text{C}$
 $T_f = 80.9^\circ\text{C}$

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Clicker Question

Given the following:
 $2 \text{Fe}(\text{s}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s}) \Delta H = -824.2 \text{ kJ}$
 $\text{CO}(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \Delta H = -282.7 \text{ kJ}$
What is the ΔH_{rxn} for the following reaction:
 $\text{Fe}_2\text{O}_3(\text{s}) + 3 \text{CO}(\text{g}) \rightarrow 2 \text{Fe}(\text{s}) + 3 \text{CO}_2$

A. -1106.9 kJ
B. -541.5 kJ
C. -1672.3 kJ
D. -23.90 kJ
E. 541.5 kJ

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Clicker Question

Iron can be reacted with nitrogen to yield iron nitride in the reaction:
 $3 \text{Fe}(\text{s}) + \text{N}_2(\text{g}) \rightarrow \text{Fe}_3\text{N}_2(\text{s})$

10.0 g Fe and 2.00 g N₂ are placed in a calorimeter at 25.0°C and the reaction triggered. The heat capacity of the calorimeter (INCLUDING WATER) is 14.7 kJ/°C. If the final temperature of the calorimeter is 21.2°C, what is the ΔH of the reaction?

A. 55.9 kJ/mol
B. -55.9 kJ/mol
C. 782. kJ/mol
D. 936 kJ/mol
E. -936 kJ/mol

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Clicker Question

Iron can be reacted with nitrogen to yield iron nitride in the reaction:
 $3 \text{Fe (s)} + \text{N}_2(\text{g}) \rightarrow \text{Fe}_3\text{N}_2(\text{s})$

10.0 g Fe and 2.00 g N_2 are placed in a 2.00 L flask that was initially at STP (before adding the reactants). The reaction was initiated. If the final temperature of the flask is 25°C, what is the final pressure in the flask?

A. 0.14 atm
B. 1.14 atm
C. 1.23 atm
D. 1.8 atm
E. 0.8 atm

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Clicker Question

10.0g Fe (1 mol/55.85 g) = 0.179 mol
2.00 g N_2 (1 mol/28.014 g) = 0.0714 mol

$3 \text{Fe (s)} + \text{N}_2(\text{g}) \rightarrow \text{Fe}_3\text{N}_2(\text{s})$

I	0.179 mol	0.0714 mol	0
C	-3x	-x	+x
E			

0.179 mol - 3x = 0
x = 0.0597

0.0714 - x = 0
x = 0.0714

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Clicker Question

10.0g Fe (1 mol/55.85 g) = 0.179 mol
2.00 g N_2 (1 mol/28.014 g) = 0.0714 mol

$3 \text{Fe (s)} + \text{N}_2(\text{g}) \rightarrow \text{Fe}_3\text{N}_2(\text{s})$

I	0.179 mol	0.0714 mol	0
C	-3x	-0.0597	+0.0597
E	0	0.0117	0.0597

Only the N_2 causes pressure

$P = nRT/V = 0.0117 \text{ mol} * 0.08206 * 298\text{K} / 2$
 $P = 0.143 \text{ atm}$

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$$P/T = nR/V = \text{constant}$$
$$1 \text{ atm}/273 \text{ K} = x \text{ atm}/298\text{K}$$
$$x = 1.09 \text{ atm}$$
$$\text{Total pressure} = 1.09 \text{ atm} + 0.14 \text{ atm}$$
$$= 1.23 \text{ atm}$$
