

Announcements

Wednesday, October 28, 2009

Exam 2 is next Monday (Nov 2) covering chapters 4, 5, and 6 (thru today's lecture)

Ch 6 MasteringChemistry due NEXT Friday Nov 6. BUT you should still do appropriate problems for exam studying.

Thermochemistry lab report due a week from Monday (Nov 9).

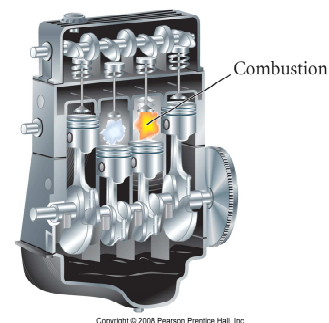
Reaction work

What if the system is a **chemical reaction** that gives off or absorbs heat?

$$\Delta E_{\text{rxn}} = q + w$$

internal energy heat transferred work

The most common work a chemical reaction does is expanding gases against an exterior pressure (pressure-volume work).



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$$w = -P\Delta V$$

But usually we are mostly interested in the heat exchanged with the surroundings

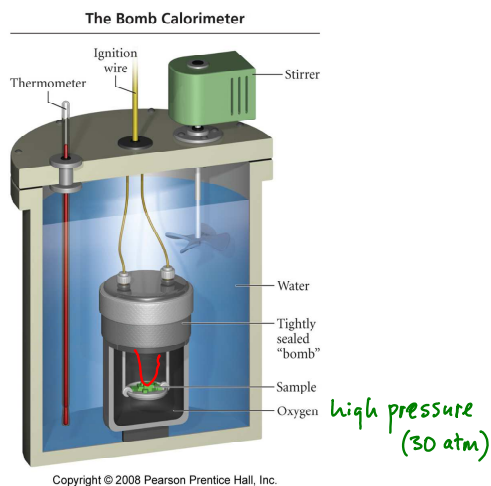
If $\Delta V = 0$, $w = 0$ and $\Delta E_{\text{rxn}} = q_v$ (constant volume) ^{no work}

If P is constant, we can use a different state function called enthalpy to only consider heat transferred.

Constant-volume calorimetry

Measurement of heat

A **bomb calorimeter** is used to measure ΔE_{rxn}



$$\Delta E_{\text{rxn}} = q + w$$

$$w = -P\Delta V$$

If $\Delta V = 0$, $w = 0$ and $\Delta E_{\text{rxn}} = q_V$ (constant volume)

- q is a measurable energy transfer for a certain experimental process
- State functions like ΔE are more general - they're given for a balanced chemical equation or per mole of a substance

$$q_{\text{cal}} = C_{\text{cal}} \Delta t \quad (C_{\text{cal}} \text{ is given}) \quad \text{heat capacity of calorimeter}$$

$$q_{\text{rxn}} = -q_{\text{cal}} \quad \text{sign change}$$

$$\Delta E_{\text{rxn}} = q_{\text{rxn}} / n \quad \text{moles}$$

Constant-volume calorimetry

$$q_{\text{cal}} = C_{\text{cal}} \Delta t \quad (C_{\text{cal}} \text{ is given})$$

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

$$\Delta E_{\text{rxn}} = (q_{\text{rxn}}) / n$$

2.14 g C_5H_{12} is combusted in a bomb calorimeter and the temperature rises from 25.50 °C to 41.23 °C. The heat capacity of the calorimeter is 6.23 kJ/°C. What is ΔE for the combustion of C_5H_{12} in kJ/mol?

$$\Delta t = 15.73^\circ\text{C}$$

$$q_{\text{cal}} = (6.23 \text{ kJ/}^\circ\text{C})(15.73^\circ\text{C}) = 97.9979 \text{ kJ}$$

$$q_{\text{rxn}} = -97.9979 \text{ kJ}$$

$$\Delta E = \frac{-97.9979}{0.02966 \text{ mol}} =$$

$$= \boxed{-3.31 \times 10^3 \text{ kJ/mol}}$$

$$2.14 \text{ g C}_5\text{H}_{12} \times \frac{\text{mol}}{72.146 \text{ g}} = 0.02966 \text{ mol C}_5\text{H}_{12}$$

ΔH , Change in enthalpy

It's more convenient to do a reaction open to the atmosphere, where pressure is constant.

The heat exchanged in a specific experiment is q_p and its related state function for a general process is ΔH : change in enthalpy.

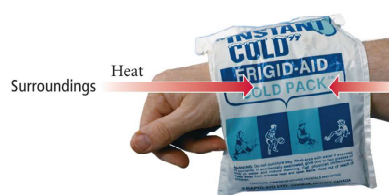
Since ΔH only involves the heat given off or absorbed, it has the same sign conventions as q :

Endothermic reaction: heat is transferred from surroundings to system (inwards) *feels cold*

ΔH is: positive
in system

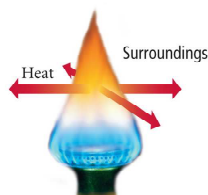
Exothermic reaction: heat is transferred from system to surroundings (outwards) *feels hot*

ΔH is: negative



Endothermic

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Exothermic

Thermochemical equations

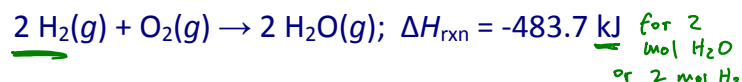
ΔH_{rxn} is always given per a balanced chemical equation.

extensive property: depends on amount of substance

Thermochemical equation:

- balanced chemical equation
- thermochemical state function (ΔH_{rxn})
- molar interpretation (coefficients = # moles)

for 2 mol H₂O



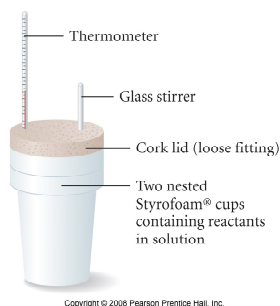
How much heat (in kJ) is given off when 20.0 g H₂ react with excess oxygen?

$$20.0 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \times \frac{-483.7 \text{ kJ}}{2 \text{ mol H}_2} = \boxed{-2.40 \times 10^3 \text{ kJ}}$$

Constant-pressure calorimetry

ΔH_{rxn} can be measured using a constant-pressure calorimeter

The Coffee-Cup Calorimeter



We assume all of the heat lost by the reaction is gained by the solution (or vice-versa), and since there is a varying amount of solution, we use its specific heat capacity (C_s or s)

$$q_{\text{soln}} = (m_{\text{soln}})(C_{s,\text{soln}})(\Delta t)$$

$$q_{\text{rxn}} = -m C_s \Delta t$$

will be given on exam →

$$q_{\text{surr}} = m C_s \Delta t$$

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

If the reaction is made only of dilute solutions, you can make these assumptions:

- $C_{s,\text{soln}} = C_{s,\text{water}} = 4.184 \text{ J/g}^\circ\text{C}$
- $m_{\text{solutions}} = m_{\text{water}}$
- $d_{\text{solutions}} = 1 \text{ g/mL}$

15 mL HCl(aq)
20 mL NaOH(aq)

$$m_{\text{soln}} \approx 35 \text{ g assumed.}$$

Constant-pressure calorimetry problem

50.0 mL of 0.500 M $\text{H}_2\text{SO}_4(\text{aq})$ were added to 20.0 mL of 0.500 M NaOH in a coffee-cup calorimeter. The temperature rose from 25.00 $^\circ\text{C}$ to 27.20 $^\circ\text{C}$. Assume $C_s = 4.184 \text{ J/g}^\circ\text{C}$. What is q_{rxn} in kJ?

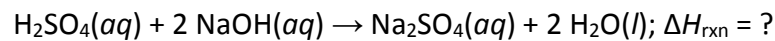
$$q_{\text{soln}} = (70.0 \text{ g}) (4.184 \text{ J/g}^\circ\text{C}) (2.20^\circ\text{C}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right)$$

assumed $d = 1 \text{ g/mL}$

$$= 0.644336 \text{ kJ}$$

$$q_{\text{rxn}} = -0.644336 \text{ kJ}$$

What is ΔH_{rxn} for the following balanced chemical equation?



Find the limiting reactant (LR):

$$50.0 \text{ mL H}_2\text{SO}_4 \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.500 \text{ mol H}_2\text{SO}_4}{1 \text{ L}} \times \frac{1 \text{ mol Na}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} = 0.025 \text{ mol Na}_2\text{SO}_4$$

$$20.0 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.500 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol Na}_2\text{SO}_4}{2 \text{ mol NaOH}} = 0.005 \text{ mol Na}_2\text{SO}_4$$

limiting reactant

What is n_{LR} for the reaction that was performed? 0.01 mol NaOH

$$\Delta H_{\text{rxn}} = \text{coefficient}_{\text{LR}} \times \frac{q_{\text{rxn}}}{n_{\text{LR}}}$$

eqn will be given on exam

$$(2 \text{ mol}) \left(\frac{-0.644336 \text{ kJ}}{0.01 \text{ mol}} \right) = -129 \text{ kJ}$$