

## Definitions

**System:** clearly defined part of space and whatever is within it. The rest, outside the defined boundaries, is called the **surroundings**.

A system is

**isolated** if neither energy nor matter is exchanged between system and surroundings,

**closed** if matter does not enter or leave,

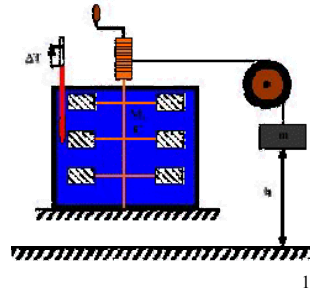
**open** if both energy and matter can be exchanged.

The **state** of a system determines all of its properties.

## BC3252y: Part II Heat, Work, and Energy



James  
Joule



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## Energy

**Kinetic:** associated with *motion*;  
involves velocities:

1D Cartesian coordinates:  $mv^2/2$

**Potential:** *stored*, involves positions:

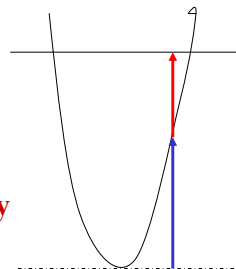
1D harmonic oscillator:  $kx^2/2$

Total internal energy of system

**U = sum of potential and kinetic energy**

The zero of U is arbitrary.

We can never measure U directly,  
measure only **changes** in U:  $\Delta U$ .



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## One way the energy of a system changes is through **work**

work = force acting through a distance.

work done **on** the system

= - work done **by** the system

The common sign convention in chemistry:

w is **positive** when work done **on** system

so w is negative when the system does work:

$$dw = -f dx \quad \text{or} \quad w = - \int f dx$$

**Work depends on the path**

**Example 1:** discharge of a car battery

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## Work of expansion and compression = "pV work"

$$dw = -f dx$$

f is the **external** force  
pressure = force/area

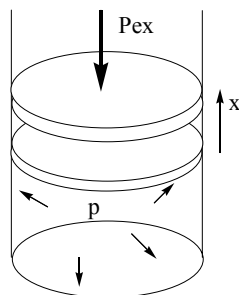
$$\text{so } f = p_{\text{ex}}A$$

A is the area of the piston

$$V = Ax, \text{ so } dV = A dx$$

$$dw = -(p_{\text{ex}} A) dx = -p_{\text{ex}} dV$$

$$\text{so } dw = -p_{\text{ex}} dV$$



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## Work depends on path. Example 2: isothermal expansion of an ideal gas

constants  $T = 298.15$  and  $n = 0.327$  mole

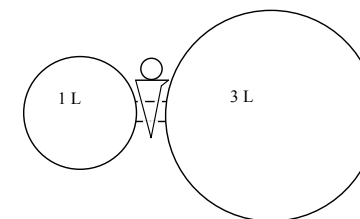
State 1:  $p_1 = 8$  atm,  $V_1 = 1$  L

State 2:  $p_2 = 2$  atm,  $V_2 = 4$  L

**Path 1:** expansion into a vacuum:

$$dw = -p_{\text{ex}} dV$$

$$p_{\text{ex}} = 0 \text{ so } w = 0$$



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## isothermal expansion of an ideal gas: Path 2: constant external pressure

$$p_{\text{ex}} = 2 \text{ atm}, w = -p_{\text{ex}} \Delta V$$

$$w = -(2 \text{ atm})(4 - 1) \text{ L} = -6 \text{ L-atm}$$

Work should be reported in joules.

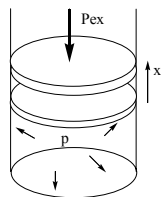
$$1 \text{ L-atm} = 101.325 \text{ J so}$$

$$w = (-6 \text{ L-atm})(101.325 \text{ J/L-atm}) = -607.9 \text{ J}$$

$w = -607.9 \text{ J}$  = work done on the gas

$w$  is negative: expanding system has done work  
on surroundings, pushing the piston up

{  $+607.9 \text{ J}$  = work done by the gas }



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## isothermal expansion of an ideal gas: path 3, reversible

$p_{\text{ex}} = p - dp$  where  $dp$  is **infinitesimal**

$$p_{\text{ex}} dV = p dV - dp dV$$

$dp dV$  is negligible compared with  $p dV$ : omit it

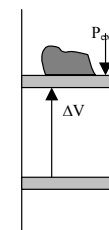
$$w_{\text{rev}} = -\int_{V_1}^{V_2} p_{\text{ex}} dV = -\int_{V_1}^{V_2} p dV$$

For an ideal gas,

$$w_{\text{rev}} = -\int_{V_1}^{V_2} \left(\frac{nRT}{V}\right) dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln V \Big|_{V_1}^{V_2} = -nRT \ln \frac{V_2}{V_1}$$

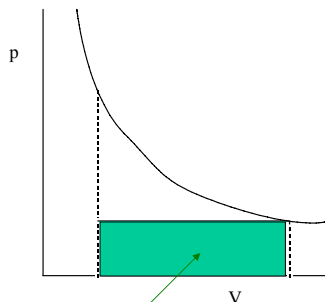
$$w_{\text{rev}} = - (0.327 \text{ mol})(8.3145 \text{ J/mol-K})(298.15 \text{ K}) \ln(4/1)$$

$$= - (0.327)(8.3145)(298.15)(1.3863) = -1124 \text{ J} = w$$



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Reversible work is **maximum** work that can be done by gas: if  $p_{\text{ex}}$  were any larger, gas would be compressed!



path #	1	2	3
process	$p_{\text{ex}} = 0$ vacuum	$p_{\text{ex}} = 2 \text{ atm}$	$p_{\text{ex}} \sim p$ reversible
work (J)	0	-607.9	-1124

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## expressions for pV work

General:  $dw = -p_{\text{ex}} dV$

If  $p_{\text{ex}}$  is constant:  $w = -p_{\text{ex}} \Delta V$

If the path is reversible,  $w = -\int p dV$

Ideal gas expanding reversibly at constant temperature

$$w_{\text{rev}} = -nRT \ln(V_2/V_1)$$

For an ideal gas, if  $dT = 0$ , then  $p_1 V_1 = p_2 V_2$ .

thus  $V_2/V_1 = p_1/p_2$

so  $w_{\text{rev}} = -nRT \ln(p_1/p_2) = +nRT \ln(p_2/p_1)$

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Another way to change the state of a system: **heat**

$q$  = heat absorbed by system

Like  $w$ ,  $q$  depends on the path

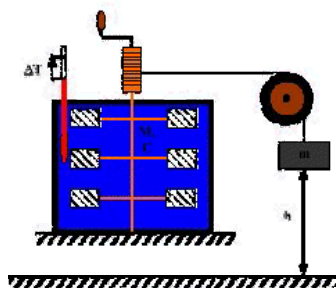
$dq$  is an **inexact** differential

Example: warming water,  $T$  rises

path 1: introduce heat ( $q > 0$ )

path 2: stir! ( $q = 0$ )

(Joule experiment)



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## The First Law of Thermodynamics

Pre-Einstein:

**Energy can be neither created nor destroyed.**

Today: *In a system of constant mass,*

**energy can be neither created nor destroyed.**

$$U_{\text{final}} - U_{\text{initial}} = \Delta U = q + w$$

$$dU = dq + dw$$

**No machine is possible that produces work without changing the state of some system.**

**Heat and work are the ways energy changes.**

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## The First Law of Thermodynamics

$$dU = dq + dw$$

While  $q$  and  $w$  depend on the path,  $U$  does not.

$U$  is a state function.

$dU$  is an **exact differential**  
(whereas  $dq$  and  $dw$  are inexact)

$\Delta U = 0$  over any **closed** cycle.

**These are all alternate ways of stating the first law.**

**The first law has withstood the test of time:  
no reputable scientist believes that violations occur.**

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## WHAT'S NEW Robert L. Park (American Institute of Physics) Jan 2003

1. **FIRST LAW: SELF-POWERED FUEL-LESS GENERATOR AVAILABLE ON Ebay.** Machines that violate the First Law of Thermodynamics are not new, they are perpetual (WN 5 Apr 02). A sharp-eyed WN reader spotted a classic on Ebay. This fully-portable generator is described as a 3 cubic foot "black box" (what else?) with three standard 120-volt electrical outlets to plug home appliances into. It will generate 700 watts continuously...forever. Or so it says. This is not some wild claim about zero-point energy or anti-gravity; the device simply uses an electric motor to spin an alternator that supplies the power to drive the motor. I know, you're going to say the alternator can't possibly supply enough power to run the motor plus a bunch of appliances. But a schematic shows the inventor thought about that: a bicycle chain connects the motor to FIVE alternators.

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## WHAT'S NEW Robert L. Park (American Institute of Physics) Jan 2003

2. **MORE FIRST LAW: GENESIS PROJECT SHUNS "CONVENTIONAL THINKING."** Genesis World Energy (WN 13 Dec 02) proposes to free the world from fossil fuel dependence by "harnessing energy from the molecular structure of water". The idea is deceptively simple: use electrolysis to separate water into hydrogen and oxygen and then use a hydrogen fuel cell to generate electricity. I know, you're going to say it will take more electricity to split the water than the fuel cell can generate. We've got to think outside the black box. The Genesis people say they assembled a team of 400 top scientists. You think these guys never heard of the conservation of energy? "For security purposes," Genesis explains, "the Genesis Team has elected to disclose little about the science behind the technology. In the absence of detailed information, it is not possible to understand how Genesis' stated results were achieved. Therefore, the scientific community at large will analyze the Genesis Project based on conventional thinking." OK, I'm busted! I've been relying on the First Law of Thermodynamics, which is about as conventional as you can get.

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## What about "the hydrogen economy"?

There are good reasons to dream of hydrogen fuel cells powering future cars and other devices

**(The combustion product is clean water.)**

**ESSENTIAL QUESTION:**

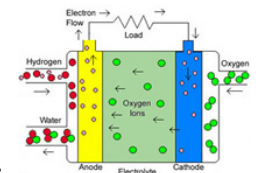
**Where does the hydrogen come from?**

**Water: the earth has an immense supply.**

**But...the energy to be released by the fuel cell must first be supplied to create the hydrogen:**

**Where does this energy come from?**

**Pay close attention to arguments for a hydrogen economy: some appear to neglect the first law!**



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## The heat of reaction at constant volume

If no work other than  $pV$  work is possible,  
then if  $V$  is constant ( $dV = 0$ ),  $w = 0$

so  $\Delta U = q$  or  $\Delta U = q_V$

**At constant volume,  
the heat absorbed by a system  
is equal to the change in its internal energy (U).**



**Bomb calorimeters** measure  $q$   
at fixed  $V$ , so they measure  $\Delta U$

What about measurements at **constant  $p$** ?  
(this is often much more convenient).

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## measurements at constant $p$

If  $p$  is constant and  $p = p_{\text{ex}}$ , then  $w = -p \Delta V$

$$\Delta U = q_p - p \Delta V$$

$$q_p = \Delta U + p \Delta V$$

Define a new quantity  $H \equiv U + pV$

$H$  is called **enthalpy**

If  $p$  is constant,  $\Delta H = \Delta U + p \Delta V = q_p$

**Therefore  $\Delta H = q_p$**

**At constant pressure, the heat absorbed by a  
system is equal to the change in its enthalpy (H).**

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## Facts about Enthalpy, $H$

**Definition  $H \equiv U + pV$**

units: energy

extensive, like  $U$  and  $V$

$$dH = dU + p dV + V dp$$

But  $dU = dq + dw$ , so

$$dH = dq + dw + p dV + V dp$$

For reversible  $pV$ -work only,  $dw = -p dV$  so

$$dH = dq + V dp$$

If  $dp = 0$ ,  $dH = dq$ , so  $\Delta H = q_p$

**Note that this is not limited to ideal gas (or any gas!)**

**Enthalpy of ...** often called **heat of ...**

(reaction, vaporization, combustion) since often  $dp = 0$ .

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## $U$ and $H$ for isothermal processes involving fixed amounts of an ideal gas

$H = U + pV$ , so  $\Delta H = \Delta U + \Delta(pV)$

**For an ideal gas**,  $U$  depends on  $T$  only:

there are no forces, so no potential energy;

$T$  measures the average kinetic energy.

If  $T$  is constant for ideal gas,  $\Delta U = 0$

**Related fact for I.G.:**  $(\partial U / \partial V)_T = 0$ , to be proved later.

But  $pV = nRT$ , so  $\Delta H = \Delta U + \Delta(nRT)$

If  $T$  and  $n$  are constant,  $\Delta(nRT) = 0$

Thus  $\Delta H = 0$  also.

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## How are $\Delta H$ and $\Delta U$ related? *qualitative discussion*

Introduce a **fixed quantity of heat** into two systems with identical initial states. One system has fixed volume, the other fixed external pressure.

When  $dV = 0$ ,  $q = \Delta U$

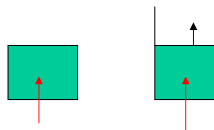
When  $dp = 0$ ,  $q = \Delta H$

Since  $T$  rises,  $p$  rises.

In the fixed  $p$  system, gas expands, doing work ( $w < 0$ ), so  $\Delta U = q + w$  is smaller than  $\Delta H = q$ .

$\Delta U < \Delta H$  (note that here the final states *differ*).

When some of the added heat is converted to work, the net change in internal energy  $U$  is less.



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## How are $\Delta H$ and $\Delta U$ related? Equations

$H = U + pV$ , so  $\Delta H = \Delta U + \Delta(pV)$

$\Delta H - \Delta U = \Delta(pV)$

(the *same* initial and final states)

note that this is  $\Delta(pV)$ , not  $p\Delta V$ !

$\Delta(pV)$  is often quite small (compared to  $\Delta U$ ),  
so  $\Delta H$  and  $\Delta U$  are often not very different.

Example: isothermal reactions among ideal gases:

$\Delta(pV) = \Delta(nRT) = RT\Delta n$

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## Digression: IUPAC notation

The International Union of Pure and Applied Chemistry (IUPAC) recommends a standard notation.

To indicate the specific process for  $\Delta X$  ( $X$  is any state function) they recommend appending a subscript to the  $\Delta$ .

For reaction, subscript is  $r$ :  $\Delta_r H$  is the **enthalpy of reaction**

Other subscripts below (more in Atkins Table 2.4)

<b>vap</b>	vaporization (liquid to gas)
<b>fus</b>	fusion (solid to liquid, i.e. melting)
<b>f</b>	formation from elements in standard state
<b>c</b>	combustion {making $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ }

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## $\Delta_r H$ and $\Delta_r U$ are often not very different Example: isothermal gas phase reactions

if gases are ideal  $\Delta_r(pV) = \Delta_r(nRT) = RT\Delta_r n$

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2 \text{HI}(\text{g}) \quad \Delta_r n = 0,$

so  $\Delta_r H = \Delta_r U$

$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta_r n = -\frac{1}{2}$

$\Delta_r H - \Delta_r U = -\frac{1}{2} RT = -1.24 \text{ kJ/mole at } 25^\circ\text{C}$

But  $\Delta_r H$  at  $25^\circ\text{C}$  is  **$-241.82 \text{ kJ/mole}$** ,

so  $\Delta_r U = \Delta_r H + \frac{1}{2} RT$  is  **$-240.58 \text{ kJ/mole}$**

**two values are not very different, but not identical.**

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$\Delta_r H$  and  $\Delta_r U$  are often not very different  
condensed phase reactions

If  $p$  is constant,  $\Delta_r(pV) = p \Delta_r V$

Molar volumes of solids and liquids are much smaller  
that those of gases.

Thus  $\Delta_r V$  values are small fractions of small numbers.

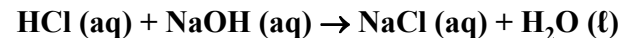
reaction	$\Delta_r V$ (mL/mole)
$\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(s)}$	-18.2
$\text{AgNO}_3\text{(s)} + \text{NaCl(s)} \rightarrow \text{AgCl(s)} + \text{NaNO}_3\text{(s)}$	-7.8
$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$	+21.3

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$\Delta_r H$  and  $\Delta_r U$  are often not very different  
condensed phase reactions, continued

With constant  $p$ ,  $\Delta_r(pV) = p\Delta_r V$

Calculate  $p\Delta_r V$  for the third reaction:



If  $p = 1 \text{ atm}$  and  $\Delta_r V = 0.0213 \text{ L/mole}$ ,

$$p \Delta_r V = 0.0213 \text{ L-atm/mole.}$$

Convert to joules: ( $101.325 \text{ J} = 1 \text{ L-atm}$ )

$$p \Delta_r V = 2.16 \text{ J/mole}$$

$\Delta_r H$  and  $\Delta_r U$  are typically in kJ/mole

$\Delta_r(pV)$  for condensed phase reactions is negligible.

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$\Delta_r H$  and  $\Delta_r U$  are often not very different  
reactions involving both gases and condensed phases

To an excellent approximation, **only gases undergo significant volume changes.**

Therefore in general  $\Delta_r(pV) = \Delta_r(pV)_{\text{gases}}$

If gases are ideal  $\Delta_r(pV) = \Delta_r(nRT) = RT\Delta_r n$

$$\text{so } \Delta_r H - \Delta_r U = \Delta_r(pV) = RT \Delta_r n_{\text{gas}}$$

**Units:** we usually use this in form  $\Delta_r H_m - \Delta_r U_m = RT \Delta_r n_{\text{gas}}$

$\Delta_r H_m$  is  $\Delta H$  per mole of reaction (as written).

$\Delta_r n_{\text{gas}}$  is dimensionless: change in moles of gas  
per mole of reaction (as written).

each term has units energy/mole

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Reactions with both gases and condensed phases

Examples	$\Delta n_{\text{gas}}$
$\text{C}_6\text{H}_5\text{CH}_3\text{(l)} + 9 \text{ O}_2\text{(g)} \rightarrow 7 \text{ CO}_2\text{(g)} + 4 \text{ H}_2\text{O(l)}$	-2
$\text{C(s)} + 4 \text{ O}_2\text{(g)} \rightarrow 4 \text{ CO}_2\text{(g)}$	0
$\text{C}_6\text{H}_6\text{(l)} \rightarrow \text{C}_6\text{H}_6\text{(g)}$	1

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## Hess' Law of Constant Heat Summation

Since H is a state function,  $\Delta H$  is independent of the path.

Hess' law: the total enthalpy of a reaction is the same whether you carry out that reaction in a single step or in a sequence of steps.

Therefore you can calculate  $\Delta_r H$  for a reaction by combining  $\Delta_f H$  values for **any sequence of steps** that combine to give the desired reaction.

**Thermodynamic cycles** used to analyze systems: in any complete cycle  $\Delta H = 0$ , so if  $\Delta H$ 's for all but one step are known, that step can be determined.

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## Standard enthalpies of formation

**Definition:**  $\Delta_f H^\circ$  is the enthalpy of reaction for the reaction at standard conditions in which **one mole** of the specified substance is formed from **elements in their standard state**.

Consequence:  $\Delta_f H^\circ$  is zero for **elements in their standard state**.

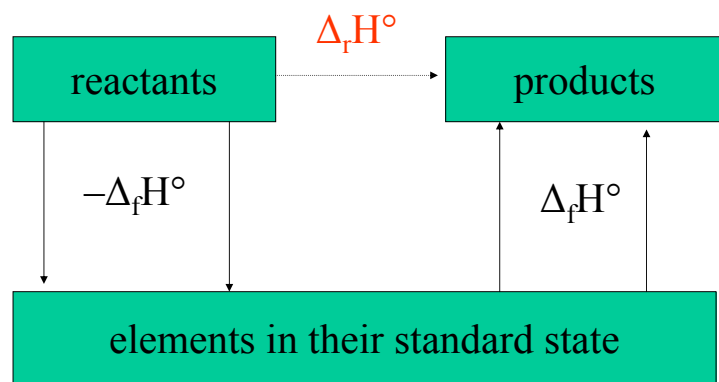
The standard state is the most stable form at 25°C and one atmosphere.

For carbon, this is **graphite**, not **diamond**.

**What does the ° denote?** Reaction is at standard conditions: pressure is 1 atm (or 1 bar), dissolved species are at 1 molar concentration.

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## Using standard enthalpies of formation



example of a thermodynamic cycle

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## Using standard enthalpies of formation

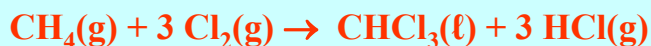
What is  $\Delta_r H_m^\circ$  at 25°C for the reaction



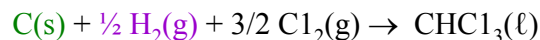
Enthalpies of formation from tables:

formation reaction	$\Delta_f H_m^\circ$ (kJ/mol)
$\text{C}(\text{s}) + \frac{1}{2} \text{H}_2(\text{g}) + \frac{3}{2} \text{Cl}_2(\text{g}) \rightarrow \text{CHCl}_3(\text{l})$	-134.47
$\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$	-74.81
$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g})$	-92.307

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net reaction = rxn (1) + 3 rxn (3) – Eq. (2):



$$\Delta_r H_m^\circ = \Delta_f H_m^\circ(\text{CHCl}_3, \ell) + 3 \Delta_f H_m^\circ(\text{HCl}, \text{g}) - \Delta_f H_m^\circ(\text{CH}_4, \text{g})$$

$$= -134.47 + 3(-92.307) - (-74.81) = -336.58 \text{ kJ/mole}$$

using parentheses including all signs explicitly, recommended!

#	formation reaction	$\Delta_f H^\circ$ (kJ/mol)
1	$\text{C}(\text{s}) + \frac{1}{2} \text{H}_2(\text{g}) + 3/2 \text{Cl}_2(\text{g}) \rightarrow \text{CHCl}_3(\ell)$	-134.47
2	$\text{C}(\text{s}) + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$	-74.81
3	$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g})$	-92.307 <sub>33</sub>

## General equation



$$\Delta_r H_m^\circ = \gamma \Delta_f H_m^\circ(\text{C}) + \delta \Delta_f H_m^\circ(\text{D})$$

$$- \alpha \Delta_f H_m^\circ(\text{A}) - \beta \Delta_f H_m^\circ(\text{B})$$

**units:**  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  are **dimensionless**:

they specify (moles substance)/(moles reaction)

$\Delta_r H_m^\circ$  and  $\Delta_f H_m^\circ$  values have same units: kJ/mole

the mole in the denominator is moles of reaction

as written (this is why the reaction must appear)!

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## Heats (enthalpies) of combustion

Enthalpies of formation difficult to measure directly.

For **hydrocarbons** (compounds with C, H, and O), combustion reactions generally occur cleanly.

**Combustion** combines the specified molecule with  $\text{O}_2(\text{g})$  to form  $\text{H}_2\text{O}$  and  $\text{CO}_2$

Enthalpies of combustion often measured directly; tabulated enthalpies of formation determined from them!

**Enthalpies of combustion (in tables) can also be used directly to determine reaction enthalpies.**

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## Heats (enthalpies) of combustion

### Definition:

The enthalpy of combustion,  $\Delta_{\text{comb}} H^\circ$  or  $\Delta_c H^\circ$ , is  $\Delta_r H^\circ$  for the reaction in which **one mole** of the specified substance combines with  $\text{O}_2(\text{g})$ , forming  **$\text{H}_2\text{O}(\ell)$  and  $\text{CO}_2(\text{g})$** .

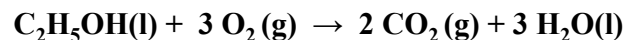
Note that by convention, **liquid** water is the product, unless stated otherwise.

Why liquid? It is the stable form at 25°C.

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## Heats (enthalpies) of combustion

Example: combustion of **ethanol**



Burn ethanol in a calorimeter, measure  $\Delta_c H^\circ$ :

$$\Delta_c H^\circ\{\text{EtOH}(\text{l})\} = -1366.82 \text{ kJ/mole}$$

Large negative energy: ethanol is a good fuel.

From this, calculate enthalpy of formation of ethanol:

$$\Delta_c H^\circ(\text{EtOH}) = 2 \Delta_f H^\circ(\text{CO}_2) + 3 \Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_f H^\circ(\text{EtOH})$$

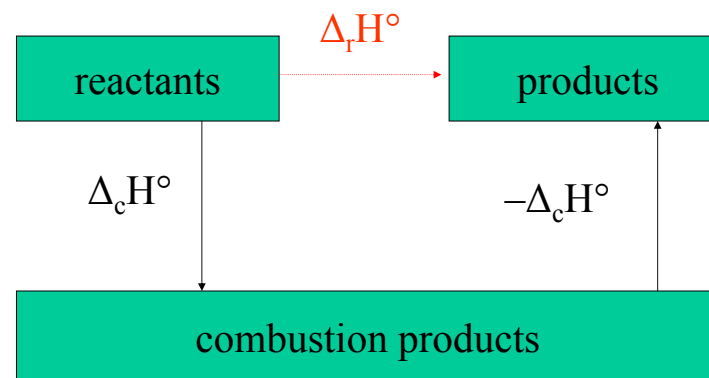
(phases omitted to save writing, but use the correct data!)

$$\Delta_f H^\circ(\text{EtOH}) = 2 \Delta_f H^\circ(\text{CO}_2) + 3 \Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_c H^\circ(\text{EtOH})$$

$$= -277.69 \text{ kJ/mole}$$

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## Using standard enthalpies of combustion



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Suppose we want  $\Delta_r H$  for  
 $\text{C}_6\text{H}_{14}(\text{l}) \rightarrow 2 \text{C}_2\text{H}_4(\text{g}) + \text{C}_2\text{H}_6(\text{g})$

Consider the combustion of each	$\Delta_c H$ (kJ/mole)
$\text{C}_2\text{H}_4(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	-1410.94
$\text{C}_2\text{H}_6(\text{g}) + 7/2 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l})$	-1559.9
$\text{C}_6\text{H}_{14}(\text{l}) + 19/2 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 7 \text{H}_2\text{O}(\text{l})$	-4163

Net reaction is Eq. (3) – Eq. (2) – 2{Eq. (1)}

$$\Delta_r H^\circ = \Delta_c H^\circ(\text{C}_6\text{H}_{14}) - \Delta_c H^\circ(\text{C}_2\text{H}_6) - 2 \Delta_c H^\circ(\text{C}_2\text{H}_4)$$

[subscripts m omitted, but implied, on all terms]

$$= +(-4163) - (-1559.9) - 2(-1410.94) = +219 \text{ kJ/mole}$$

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## Bond dissociation energy

The bond dissociation energy (enthalpy) ( $D_0$ ) of a **diatomic** molecule is well-defined:



Reactants and products are all gases.

Values are typically a few hundred kJ/mole

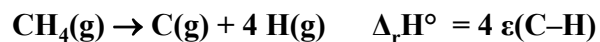
$\text{H}_2(\text{g}) \rightarrow 2 \text{H}(\text{g})$	$D_0(\text{H}_2) = 2 \Delta_f H^\circ[\text{H}(\text{g})] = 435.93 \text{ kJ/mol}$
$\text{O}_2(\text{g}) \rightarrow 2 \text{O}(\text{g})$	$D_0(\text{O}_2) = 2 \Delta_f H^\circ[\text{O}(\text{g})] = 495.0 \text{ kJ/mol}$

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## Bond energies in polyatomics

What is the bond dissociation energy of an O–H bond in H<sub>2</sub>O, or of a C–H bond in CH<sub>4</sub>?

We can define an **average bond energy**:



These are **atomization** reactions: we are taking the gaseous molecule and breaking all bonds, making atoms.

There is no standard notation for average bond energies;

I will use the symbol  $\epsilon$

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## Average Bond Energies



$$\begin{aligned} \Delta_{\text{r}}\text{H}^{\circ} &= \Delta_{\text{f}}\text{H}^{\circ}(\text{C}) + 4 \Delta_{\text{f}}\text{H}^{\circ}(\text{H}) - \Delta_{\text{f}}\text{H}^{\circ}(\text{CH}_4) \\ &= 716.68 + 4(217.965) - (-74.81) = 1663.35 \end{aligned}$$

$$\epsilon(\text{CH}) = 415.8 \text{ kJ/mole}$$

What is  $\Delta_{\text{r}}\text{H}^{\circ}$  for  $\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g})$ ?

CH<sub>3</sub>(g) radical is not found in typical tables, but this  $\Delta_{\text{r}}\text{H}^{\circ}$  has been measured: **512 kJ/mol**.

Average bond energies are approximate (and can be quite far from the exact value)!

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## Determining Bond Energies

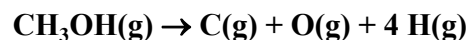
Use water to define  $\epsilon(\text{O-H})$ :



$$\begin{aligned} \Delta_{\text{r}}\text{H}^{\circ} &= \Delta_{\text{f}}\text{H}^{\circ}(\text{O}) + 2\Delta_{\text{f}}\text{H}^{\circ}(\text{H}) - \Delta_{\text{f}}\text{H}^{\circ}[\text{H}_2\text{O}(\text{g})] \\ &= 925.2 \text{ kJ/mol} \end{aligned}$$

$$\epsilon(\text{O-H}) = 463 \text{ kJ/mole}$$

Use these, with methanol, to determine  $\epsilon(\text{C-O})$ :



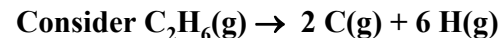
$$\Delta_{\text{r}}\text{H}^{\circ} = \epsilon(\text{C-O}) + \epsilon(\text{O-H}) + 3 \epsilon(\text{C-H})$$

$$\epsilon(\text{C-O}) = 351 \text{ kJ/mole}$$

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## Determining Bond Energies

Use ethane to determine  $\epsilon(\text{C-C})$ :



$$\Delta_{\text{r}}\text{H}^{\circ} = \epsilon(\text{C-C}) + 6 \epsilon(\text{C-H})$$

$$\text{Using } \Delta_{\text{r}}\text{H}^{\circ}\text{'s} \rightarrow \epsilon(\text{C-C}) = 331 \text{ kJ/mol}$$

Continuing in this way, using smallest molecules, could generate a large table of  $\epsilon$  values.

Average data from a *larger set of molecules* has been combined to determine a set of **average bond energies**.

If we assume that bond energies are similar among molecules, we can use them to **estimate** thermochemical data when none is available.

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## Using Average Bond Energies

Common tabulated values are averages for a range of molecules. See Atkins 7/e, table 14.3b.

Atkins calls these “notoriously unreliable”, but chemists do use them (with caution).

**Example:** estimate the enthalpy of formation of acetone.

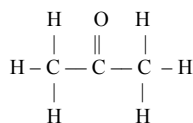
Consider the **atomization** reaction:



break 6 C-H, 1 C=O, and two C-C bonds

Reaction involves **all gases!**

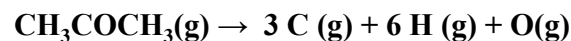
(For liquid acetone, must also include  $\Delta_{\text{vap}}H^\circ$ )



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## Estimate the enthalpy of formation of acetone

Consider **atomization** of gaseous acetone:



$$\Delta_r H^\circ(\text{atomization}) = 2 \epsilon(\text{C-C}) + 6 \epsilon(\text{C-H}) + \epsilon(\text{C=O})$$

$$= 2(331) + 6(412) + 743 = 3911 \text{ kJ/mole}$$

$$\Delta_r H^\circ = 3 \Delta_f H^\circ(\text{C}) + 6 \Delta_f H^\circ(\text{H}) + \Delta_f H^\circ(\text{O}) - \Delta_r H^\circ[\text{A}]$$

$$\text{where A} = \text{CH}_3\text{COCH}_3(\text{g})$$

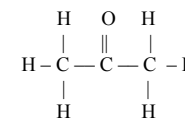
$$\Delta_r H^\circ[\text{A}] = 3 \Delta_f H^\circ(\text{C}) + 6 \Delta_f H^\circ(\text{H}) + \Delta_f H^\circ(\text{O}) - \Delta_r H^\circ(\text{atomization})$$

$$= 3(716.8) + 6(217.97) + 249.17 - 3911$$

$$= -204 \text{ kJ/mole} \leftarrow \text{our prediction}$$

**NIST Webbook:**  $\Delta_f H^\circ[\text{CH}_3\text{COCH}_3(\text{g})] = -218.5 \pm 0.6 \text{ kJ/mole}$ .

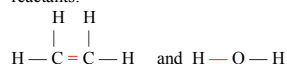
The answer is pretty good.



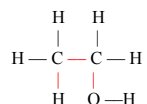
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## Using bond energies: Estimating $\Delta_r H$ for adding water to ethylene $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g})$

reactants:



products



Break a C=C double bond and turn it into a C-C single bond; break an O-H bond; make a C-H and a C-O bond. So

$$\begin{aligned} \Delta_r H^\circ &= \epsilon(\text{C=C}) + \epsilon(\text{O-H}) - \epsilon(\text{C-C}) - \epsilon(\text{C-H}) - \epsilon(\text{C-O}) \\ &= 615 + 463 - 348 - 413 - 351 = -34 \text{ kJ/mole} \end{aligned}$$

$$\begin{aligned} \text{Using } \Delta_f H^\circ \text{ 's: } \Delta H^\circ &= -235.1 - (52.56) - (-241.82) \\ &= -45.54 \text{ kJ/mole.} \end{aligned}$$

Estimate is not too bad.

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