Bomb Calorimetry: Heat of Combustion of Naphthalene

Most tabulated ΔH values of highly exothermic reactions come from "bomb" calorimeter experiments.

Heats of combustion are most common, in which the combustible material is explosively burned in a strong, steel container (the "bomb").

From the temperature increase of the system and the heat capacity of the system, ΔH of the reaction may be calculated.

H = U + pV (by **definition**)

where H = enthalpy,

U = energy,

p=pressure,

V= volume

all for the **system**.

During an explosive reaction, p and p_{ext} are uncontrollable, so one resorts to finding

$\Delta H_{reaction} = \Delta U_{reaction} + \Delta(pV)_{reaction}$

using the **First Law**.

Why $H = U + pV$ (by **definition**)**???**

H was defined this way because when *three* common conditions are met:

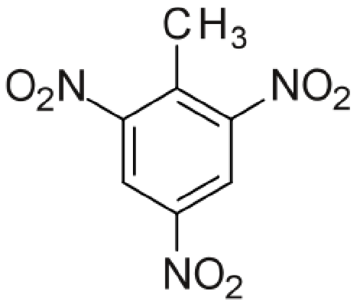
$p = p_{ext}$ = constant, and

only pV work on or by the ***atmosphere*** due to expansion or contraction of the system is done,

then—*and only then*: $\Delta H = q$

$$\Delta H_{\text{reaction}} = \Delta U_{\text{reaction}} + \Delta(pV)_{\text{reaction}}$$

$\Delta(pV)_{\text{reaction}}$ is kind of **pain**. It adds a lot of messiness, but it is ***always small*** if external p is near 1 atm. Consider the explosion of TNT:



(solid) → 11 moles of very hot gas

Upon detonation, TNT decomposes as follows:

$$2\ C_7H_5N_3O_6 \rightarrow 3\ N_2 + 5\ H_2O + 7\ CO + 7\ C$$
$$2\ C_7H_5N_3O_6 \rightarrow 3\ N_2 + 5\ H_2 + 12\ CO + 2\ C$$

V of TNT	0.137576	L/mol
V of gas	903.1	L/ 11 mol
ΔH reaction	**950**	**kJ/mol**
Δ(pV)	**90**	**kJ/mol at 1000 K**

pV= nRT

$\Delta U_{\text{reaction}}$ = 860 kJ/mol always at least 90% of $\Delta H_{\text{reaction}}$

Always think of $\Delta H_{\text{reaction}}$ as nearly $\Delta U_{\text{reaction}}$

First Law: $\Delta U = q + w$,

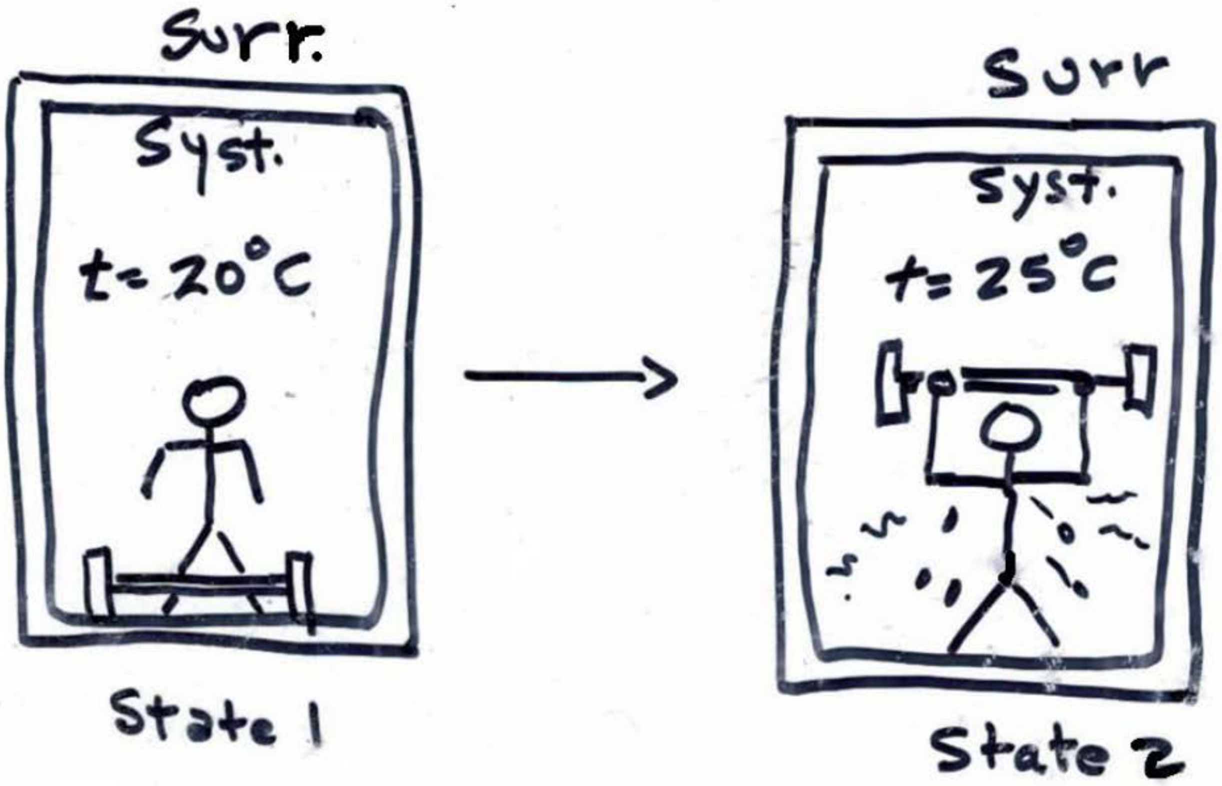
where **q = energy transferred from the surroundings as heat**

(energy transferred by ***thermal contact measured by a temperature change in the surroundings***

w = work done on the system by the surroundings,

as measured by a ***mechanical change in the surroundings*** (including *electric current*).

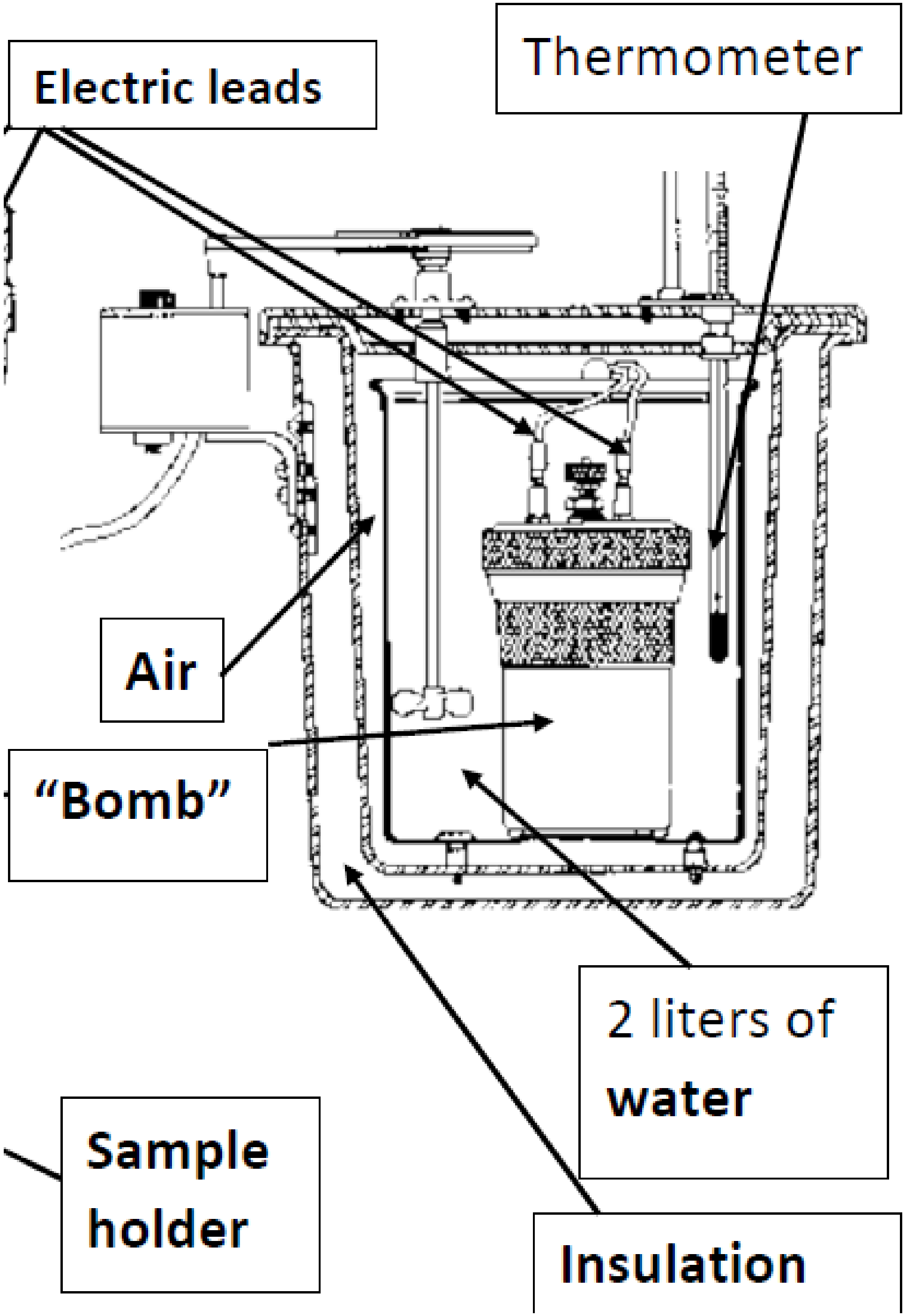
Isolated System = Thermally **insulated** & No mechanical connection to surroundings



Weight lifter works out and the room heats up from 20° C to 25° C

Are ΔU, q, w positive, zero, or negative?

Bomb Calorimeter.htm



Electric leads

Thermometer

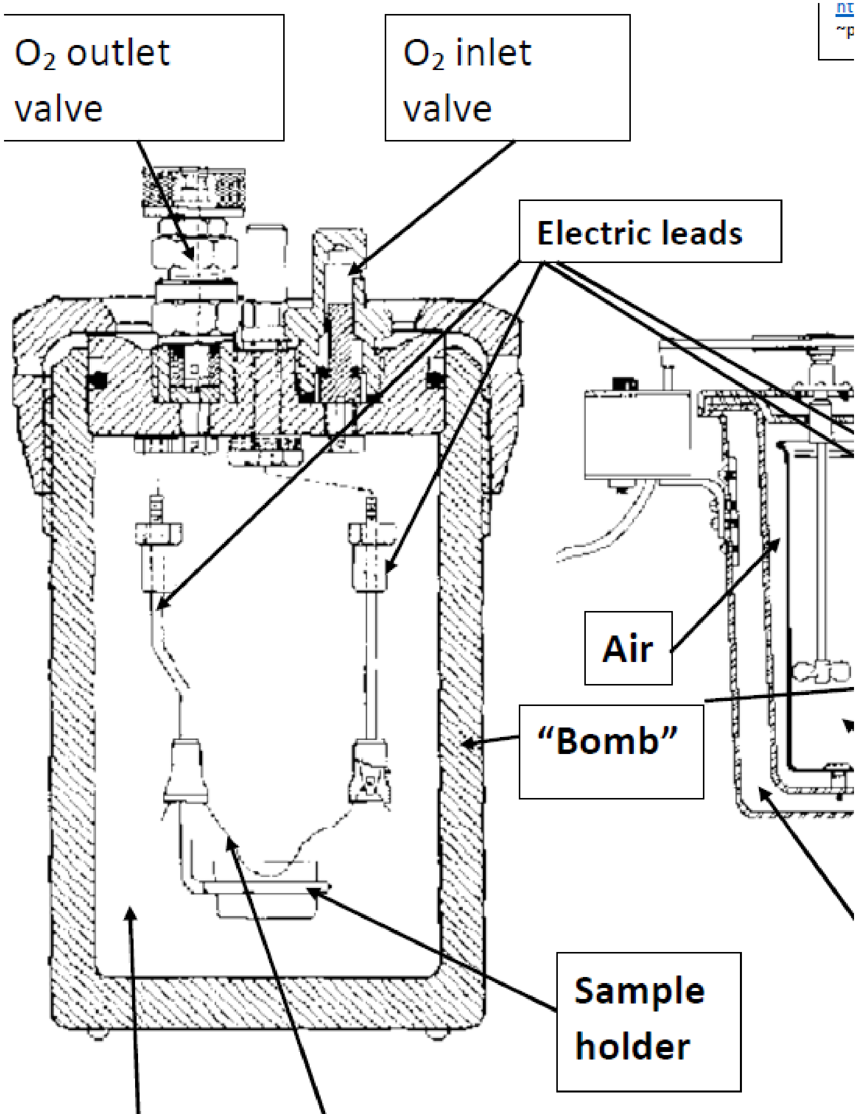
Air

“Bomb”

2 liters of **water**

Sample holder

Insulation



O$_2$ outlet valve

O$_2$ inlet valve

Electric leads

Air

“Bomb”

Sample holder

35 atm of O$_2$ gas

Fuse wire:

Heated to white hot with 4 amps of current, which ignites the sample

Choice of system and surroundings is somewhat arbitrary.

For this experiment, we ***choose*** to call ***everything*** within the ***insulated*** shell to be the system.

That is, the system consists of the **hardware (the bomb and water bucket)** + **sample** + **fuse wire** + **water.**

Thus, no heat is absorbed, **q = 0**, i.e., an **adiabatic process**.

The system is not quite isolated because a small amount of electricity (considered work) enters the system to ignite the reaction

$$\boldsymbol{\Delta U = q + w} = \Delta U_{\text{hardware}} + \Delta U_{\text{water}} + \Delta U_{\text{reaction}} + \Delta U_{\text{fuse}} = 0 + w_{\text{Electricity}}$$

The sample and the fuse both undergo combustion. The electricity from the surroundings (work) heats the wire to a high temperature, and heats the system slightly before it and the sample explode in the nearly ***40 atm*** of O_2 gas!!!

$$\boldsymbol{\Delta U_{\text{reaction}} = w_{\text{Electricity}} - [\Delta U_{\text{hardware}} + \Delta U_{\text{water}} + \Delta U_{\text{fuse}}]}$$

$$\boldsymbol{\Delta H_{\text{reaction}} = \Delta U_{\text{reaction}} + \Delta(pV)_{\text{reaction}}}$$

(Actually ΔH^0 so use p = 1 bar and 298 K if comparing to a 25 ^{0}C table)

By far the largest item is ΔU_{water} which we get from the mass, heat capacity, and temperature change,

$\mathbf{\Delta U_{water}} = C_{p,water}\Delta T$; weigh water to get C_p; measure ΔT

$\mathbf{\Delta U_{fuse}}$ comes from the measured mass of fuse burned and known ΔU per gram.

$\mathbf{\Delta U_{hardware}}$ will be determined by doing the experiment on benzoic acid, for which we know $\mathbf{\Delta H_{reaction}}$.

In addition, the manufacturer states:

"The factor (heat capacity) for the 1341 calorimeter with an 1108 Oxygen Combustion Vessel will usually fall within a range from 2410 to 2430 calories per degree Celsius, with the exact value for each installation to be determined by the user." Note: THIS INCLUDES THE WATER, which = 2000 cal/°C .

Also note: **cal/°C is the unit of HEAT CAPACITY! (the authors called it $\mathbf{\Delta U_{hardware}}$**

Thus, $\mathbf{\Delta C_{p,\ hardware}} = \mathbf{410\text{-}430\ cal/^{o}C}$

$w_{\text{Electricity}}$ and ΔU_{fuse}:

Formally, $w_{\text{Electricity}}$ is estimated from the voltage x current x time = 23 J/coulomb x 4 coulombs/second x 0.5 seconds/4.184 J/cal.

This number will be small, which is good because we don’t really know the numbers at all well.

23 volts   4 amps   0.5 seconds

23 J/coulomb x 4 coulombs/second x 0.5 seconds/4.184 J/cal.

(23 * 4 *0.5) J/4.184J/cal = 11 cal

For benzoic acid, ΔH^0 at 25^0 C = -3226.9 kJ/mol,
MW = 122 g/mol,   1 gram = 0.008 mol

Expect about .008 * 3226.9 = 26.4 kJ =26400 J = 5459 cal

5459 cal/ 2420 cal/deg = about 2.3 degs C temperature increase

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