Chemistry BC2001x: General Chemistry I

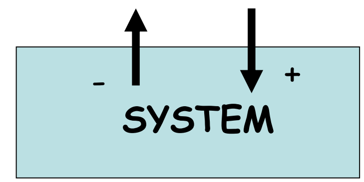
Lecture 21: Tuesday December 1, 2009

Topic: Thermodynamics I: Thermochemistry.
Energy and Enthalpy. Calorimetry.

Hand in Problem set 10

Pick up:

- "Thermodynamics in a nutshell"
  summary of key concepts and equations
  + Thermodynamic data table (on back)
- Problem Set 11



heat (q) and work (w) can be exchanged between system and surroundings

$\Delta E = q + w$ The First Law of Thermodynamics

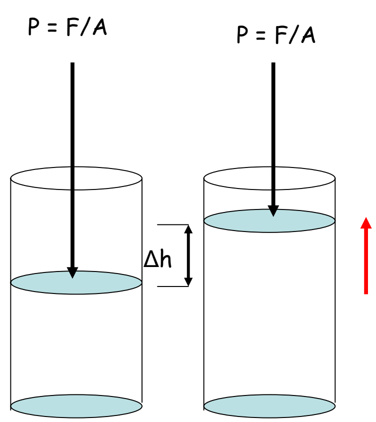
E is a state variable: the system has energy E

(the same is not true of q or w)

In going from state 1 to state 2, $\Delta E = E_2 - E_1$

In any cyclic process, $\Delta E = 0$

Work: expansion and compression



work = force x distance

If pressure P is constant,

$w = F\ \Delta h$

$= (PA)\ \Delta h$

$= P\ \Delta V$

By convention, w is positive when work goes into the system (the contents of the cylinder).

So $w = -P\Delta V$

Even without pistons and cylinders, expansion-compression (PV) work occurs!

When reactions occur, volume usually changes.

Since the atmosphere exerts (constant) pressure, this means work is involved.

$\Delta E = q + w = q - P\ \Delta V$ (some books use U for E)

$q = \Delta E + P\ \Delta V$ at constant V, $q = \Delta E$

Define a new state variable $H \equiv E + PV$

Then $\Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$

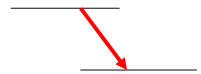
at constant P, $\Delta H = (E_2 - E_1) + P(V_2 - V_1) = \Delta E + P\Delta V$

Therefore, at constant P, $q = \Delta H$

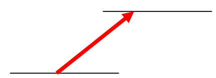
H is called enthalpy.

ΔH is called the enthalpy (or heat) of reaction.

The sign of ΔH



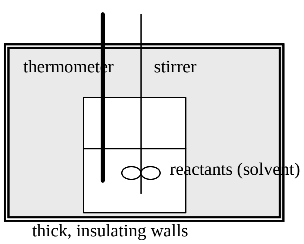
- **Exothermic: $\Delta H = H_{final} - H_{initial} < 0$**
  when an exothermic reaction occurs, the system gets hot: the heat released from the reaction shows up as thermal energy: heat (increased T).
- **Endothermic: $\Delta H = H_{final} - H_{initial} > 0$**
  when an endothermic reaction occurs, the system gets cold: thermal energy (heat) is removed from the system as the reaction proceeds.

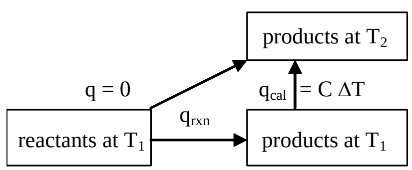


Heat capacity and specific heat

The **heat capacity** C of a system:
$C \equiv q/\Delta T$
C depends on what the system is and how much.
C per gram for liquid water is 1 calorie/gram-degree (4.184 Joules = one calorie)
The calorie was once defined as the heat required to raise the temperature of one gram of water by one degree.
C per gram called "specific heat". Chang calls this s.
then $C = w\,s$, where w is the mass in grams.
If you know q and measure ΔT, you can determine C
If you know C and measure ΔT, you can find q
Calorimeters are devices to do such measurements.

Calorimeters: measure q for reactions





Constant V (bomb): $\Delta V = 0$, so $w = 0$, so $q = \Delta E$
Constant P: $q = \Delta H$ (see slide #4)
Both: no heat is added or removed from system,
so $q_{total} = 0 = q_{rxn} + q_{cal} \rightarrow q_{rxn} = -q_{cal}$
$q_{cal} = C\,\Delta T$, so $q_{rxn} = (\Delta H \text{ or } \Delta E) = -C\,\Delta T$

Calorimeters: measure q for reactions

Two kinds of calorimeters:
Constant V: $q = \Delta E$
Constant P: $q = \Delta H$
In both, measure ΔT caused by reaction:
if exothermic, $\Delta T > 0$, if endothermic $\Delta T < 0$.
No heat is added or removed from system,
so $q_{total} = 0 = q_{rxn} + q_{cal} \rightarrow q_{rxn} = -q_{cal}$
$q_{cal} = +C\,\Delta T$, so $q_{rxn} = (\Delta H \text{ or } \Delta E) = -C\,\Delta T$
C is the total heat capacity of the system: calorimeter plus contents (products + solvent):
$C = C_{cal} + C_{contents}$ C of calorimeter includes the container, walls, thermometer, stirrer, etc.

Calorimeters: the heat capacity C

In some designs, $C_{cal} >> C_{contents}$

so (approximately) $C = C_{cal}$

determine C_{cal} by calibration:

measure ΔT for reaction with known q

then use this C_{cal} for other reactions.

In other designs, $C_{cal} << C_{contents}$

so (approximately) $C = C_{contents}$

$C_{contents}$ must account for amounts present:

C = (grams of solution)(specific heat of solution) or

C = (moles of solution)(molar heat capacity of sol'n)

Calorimeters: finding ΔH or ΔE per mole

Calorimeter insulated from the surroundings: $q_{tot} = 0$

$$q_{tot} = 0 = q_{rxn} + q_{cal}$$

q_{rxn} is the heat of the reaction at T_1

q_{cal} is the heat associated with going from T_1 to T_2

$q_{cal} = C\Delta T$

$$q_{rxn} = (\Delta H \text{ or } \Delta E) = -C\,\Delta T$$

q_{rxn} depends on how much reaction occurred.

To obtain ΔH or ΔE per mole you must divide by the number of moles of reaction that occurred.

To find moles of reaction, divide the actual number of moles of the limiting reagent by its coefficient in the balanced chemical equation.

Calorimeter Problems Example 1

$\Delta E = -5646.7$ kJ/mole for the combustion of sucrose:

$C_{12}H_{22}O_{11}(s) + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O(\ell)$

2.00257 g of sucrose, initially at 25°C, was burned in a bomb calorimeter, and the temperature rose 2.9660°C. When 0.7928 g of benzene, initially at 25°C, was burned in the same bomb calorimeter, the temperature rose 2.974°C. Calculate ΔE in kJ/mole for the combustion of benzene. Assume that the heat capacity of the contents of the calorimeter is negligible.

(molar masses: sucrose 342.30 g/mol, benzene 78.1136 g/mole)

Calorimeter Problems Example 2

When 8.005 grams of $NH_4NO_3(s)$ is dissolved in 100 mL of water at 25.00°C in a styrofoam cup calorimeter, the temperature falls to 18.05°C.

What is ΔH for dissolving ammonium nitrate in units of kJ/mole?

The molar mass of NH_4NO_3 is 80.043 g/mole. Water at 25°C has density 1.000 g/mL and specific heat 4.184 J/K-g. Assume that the heat capacity of the calorimeter is negligible, and that the heat capacity of the solution in the same as that at of water.

Standard Enthalpies of formation $\Delta H_f°$

We can never measure H (or E),
only changes ΔH (or ΔH).

Define the enthalpy of formation $\Delta H_f°$ of any substance as *ΔH for the reaction in which one mole of the substance is formed from elements in their standard state.*

Units are typically kJ/mole

$\Delta H_f°$ of any element in standard state is zero.

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

Examples: $H_2(g)$, Cu(s), Hg(ℓ), C(s, graphite)

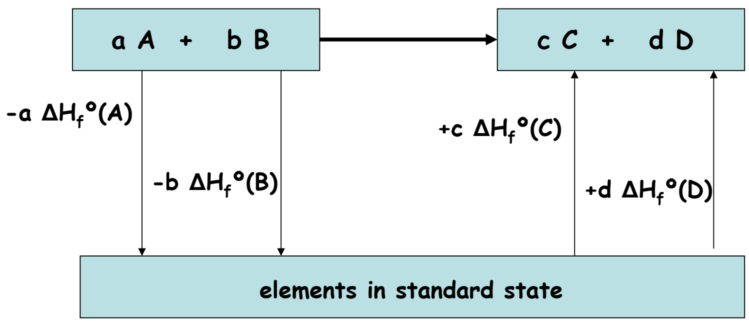
Using Standard enthalpies of formation

For any reaction, imagine

1) converting reactants to elements in standard state

2) converting these elements into products.

ΔH for the direct reaction is the sum of these ΔH's



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SUBSTANCE	$\Delta H_f°$ (kJ / mole)	$\Delta G_f°$(kJ / mole)	S° (J / K-mole)
$Br_2(g)$	30.907	3.144	245.35
Br(g)	111.88	82.43	174.91
HBr(g)	–36.40	–53.43	198.59
CaO(s)	–635.09	–604.05	39.75
$CaCO_3(s)$	–1206.92	–1128.84	92.9
CO(g)	–110.525	–137.15	197.56
$CO_2(g)$	–393.51	–394.36	213.64
$CH_4(g)$	–74.81	–50.75	186.15
$C_2H_2(g)$	226.73	209.20	200.83
$C_2H_4(g)$	52.26	68.12	219.45
$C_2H_6(g)$	–84.68	–32.89	229.49
$C_6H_6(g)$	82.927	129.66	269.2
$CH_3OH(\ell)$	–238.66	–166.35	126.8
$CH_3CH_2OH(\ell)$	–277.69	–174.89	160.7
HCl(g)	–92.307	–95.299	186.80
HF(g)	–271.1	–273.2	173.67
H(g)	217.965	203.263	114.60
$Fe_2O_3(s)$	–824.2	–742.2	87.40
$PbO_2(s)$	–277.4	–217.4	68.6
PbS(s)	–100.4	–98.7	91.2
Hg(g)	61.317	31.853	174.85
NO(g)	90.25	86.55	210.652
$NO_2(g)$	33.8	51.29	239.95
$NH_3(g)$	–46.11	–16.48	192.34
$N_2H_4(g)$	95.40	159.35	238.47
$NH_4NO_3(s)$	–365.56	–184.02	151.08
$O_3(g)$	142.7	163.2	238.82
$H_2O(g)$	–241.82	–228.59	188.72
$H_2O(\ell)$	–285.83	–237.18	69.91
$SO_2(g)$	–296.830	–300.194	248.11
$SO_3(g)$	–395.72	–371.08	256.65

ELEMENT	S° (J / K-mole)	ELEMENT	S° (J / K-mole)	ELEMENT	S° (J / K-mole)
Al(s)	28.33	$Cl_2(g)$	222.96	Fe(s)	27.28
$Br_2(\ell)$	152.23	$F_2(g)$	202.67	Hg(ℓ)	76.02
Ca(s)	41.42	$H_2(g)$	130.57	$N_2(g)$	191.50
C(graphite)	5.740	$I_2(s)$	116.14	$O_2(g)$	205.03