Fire Dynamics
Thermochemistry

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Objectives

- Equating chemical reaction formula
- Understanding the concept of heat of combustion (ΔH_c)
- Calculating heat of combustion using heat of formation

Basic chemistry

- Order of balancing a chemical equation
- C -> H -> O
- Air composition
  - In reality: O_2(20.95 vol%) + N_2(78.08 vol%) + Ar(0.93 vol%) + CO_2(0.04 vol%)
  - In fire dynamics: 21 vol% O_2 + 79 vol% N_2

    Expressions:

    (0.21 O_2 + 0.79 N_2) for 1 mole of air

    (O2 + ____ N_2) for ______ moles of air

Basic chemistry (stoichiometric)

- Stoichiometric combustion: no fuel or oxidizer left after combustion.
- Methane combustion in air

$CH_4 + c(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + c(3.76N_2)$

a = ?

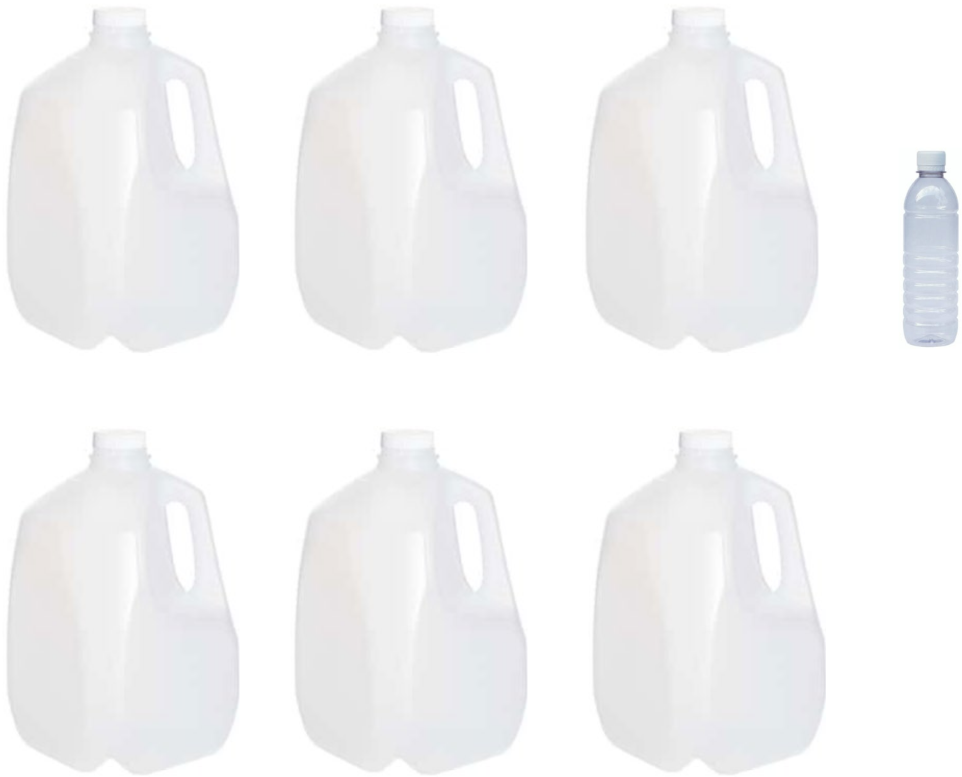
b = ?

c = ?

Mole?

- The fundamental chemical amount indicating 6.022×10^{23} atoms/molecules/particles.
- At STP (standard temperature and pressure, or 273K (0 ^{o}C) and 1 atm), 1 mole of gas takes the volume of 22.4 L.
- At NTP (normal temperature and pressure, or 293K (20 ^{o}C) and 1 atm), 24.05 L = ______gal.
- 1 gal = 3.7854 Litter

Volume of 1 mole for gases at 20 ^oC ?



Mole conservation?

- For propane,

$$C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 5(3.76N_2)$$

- # of moles of the reactants =?
- # of moles of the products =?
- Total number of moles of the reactants = total number of moles of the products?

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 2(3.76N_2)$$

- The mass of the reactants = the mass of the products?
- Atomic weight
  - **C: 12 g, H: 1 g, O: 16 g, N: 14 g**
- Molar mass of:
  - Methane:
  - Propane :
  - $O_{2:}$
  - 1 mole of Air
  - Products?

Enthalpy (H)

- **The total heat content of a system**
  - Internal energy (U) + Pressure*Volume (PV)
  - Internal energy: molecule's kinetic and potential energy
- Enthalpy at temperature, T.

$$\boxed{H^T = \Delta H_f^{298} + \int_{298}^{T} c_p dT = \Delta H_f^{298} + c_p (T - 298)}$$

  - If T = 298 K=25 °C,

$$\boxed{H^{298} = \Delta H_f^{298}}$$

Heat of formation

- Heat of formation for CH_4
- $C + 2H_2 \rightarrow CH_4 + \text{heat } (=74.9\text{kJ})$
- How much heat was used to create one mole of methane?

  Ans: -74.9 kJ/mole

$$\boxed{\text{Cold C, } 2H_2} \longrightarrow \boxed{\text{Hot } CH_4}$$

- Other values in the handout, figure 1.

Thermochemistry

- Methane combustion

  $CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 2(3.76N_2)$ **+ Heat**

  Heat = enthalpy change of reactants and products

- Heat of combustion (ΔH_c)
  - Enthalpy change of reactants and products both at **1 atm and 298 K**
  - $$\Delta H_c = \sum_i n_i H^{298}_{react,i} - \sum_j n_j H^{298}_{prod,j}$$

Methane combustion in air at 298K

- $CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 2(3.76N_2)$
  - **Enthalpy of reactants at 298K**

$$H_{CH_4}^{298} + 2(H_{O_2}^{298} + 3.76H_{N_2}^{298})$$

$$= H_{CH_4}^{298} + 2H_{O_2}^{298} + 7.52H_{N_2}^{298}$$

$$= \Delta H_f(CH_4) + 2\Delta H_f(O_2) + 7.52\Delta H_f(N_2) = -74.9 + 0 + 0 = -74.9 \text{ kJ}$$

  - **Enthalpy of products at 298K**

$$\Delta H_f(CO_2) + 2\Delta H_f(H_2O) + 7.52\Delta H_f(N_2) = -393.5 - 2(241.8) = -877.1 \text{ kJ}$$

  - **Heat of combustion of methane**

$$\Delta H_c = -74.9 - (-877.1) = 802.2 \text{ kJ}$$

Methane combustion in air at 298K

- $CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 2(3.76N_2)$
  - **Amount of heat generated per g of methane consumed ?**

    _______ [kJ/g of CH4]
  - **Amount of heat generated per g of Oxygen consumed ?**

    _______[kJ/g of O2]
  - **Amount of heat generated per g of air consumed ?**

    _______[kJ/g of air]

Thermochemistry

Table 2.2 Heat of formation $\Delta \tilde{h}_f^\circ$ in kJ/mole (at 25 °C and 1 atm)[a] (abstracted from Reference [2])

Substance	Formula	State	$\Delta \tilde{h}_f^\circ$ (kJ/mole)
Oxygen	O_2	g	0
Nitrogen	N_2	g	0
Graphite	C	s	0
Diamond	C	s	1.88
Carbon dioxide	CO_2	g	−393.5
Carbon monoxide	CO	g	−110.5
Hydrogen	H_2	g	0
Water	H_2O	g	−241.8
Water	H_2O	l	−285.9
Chlorine	Cl_2	g	0
Hydrogen chloride	HCl	g	−92.3
Hydrogen cyanide	HCN	g	+135.1
Methane	CH_4	g	−74.9
Propane	C_3H_8	g	−103.8
n-Butane	C_4H_{10}	g	−124.7
n-Heptane	C_7H_{16}	g	−187.8
Benzene	C_6H_6	g	+82.9
Formaldehyde	CH_2O	g	−115.9
Methanol	CH_4O	g	−201.2
Methanol	CH_4O	l	−238.6
Ethanol	C_2H_6O	l	−277.7
Ethylene	C_2H_4	g	52.5

[a] Values for gaseous substances not in equilibrum at the standard state have been determined from the liquid and the heat of vaporization.

Table 1-5.3 ***Heats of Combustion of Selected Fuels at 25°C (298 K)[a]***

Fuel	ΔH_c (kJ/mol)	ΔH_c (kJ/g)	$\Delta H_c{}^c$ [kJ/g(O_2)]	ΔH_c [kJ/g(air)]
Carbon monoxide (CO)	283	10.10	17.69	4.10
Methane (CH_4)	800	50.00	12.54	2.91
Ethane (C_2H_6)	1423	47.45	11.21	2.96
Ethene (C_2H_4)	1411	50.53	14.74	3.42
Ethyne (C_2H_2)	1253	48.20	15.73	3.65
Propane (C_3H_8)	2044	46.45	12.80	2.97
n-Butane (n-C_4H_{10})	2650	45.69	12.80	2.97
n-Pentane (n-C_5H_{12})	3259	45.27	12.80	2.97
n-Octane (n-C_8H_{18})	5104	44.77	12.80	2.97
c-Hexane (c-C_6H_{12})	3680	43.81	12.80	2.97
Benzene (C_6H_6)	3120	40.00	13.06	3.03
Methanol (CH_3OH)	635	19.83	13.22	3.07
Ethanol (C_2H_5OH)	1232	26.78	12.88	2.99
Acetone (CH_3COCH_3)	1786	30.79	14.00	3.25
D-glucose ($C_6H_{12}O_6$)	2772	15.40	13.27	3.08
Cellulose[b]	—	16.09	13.59	3.15
Polyethylene	—	43.28	12.65	2.93
Polypropylene	—	43.31	12.66	2.94
Polystyrene	—	39.85	12.97	3.01
Polyvinylchloride	—	16.43	12.84	2.98
Polymethylmethacrylate	—	24.89	12.98	3.01
Polyacrylonitrile	—	30.80	13.61	3.16
Polyoxymethylene	—	15.46	14.50	3.36
Polyethyleneterephthalate	—	22.00	13.21	3.06
Polycarbonate	—	29.72	13.12	3.04
Nylon 6,6	—	29.58	12.67	2.94

Extracted from “fundamentals of fire dynamics,” by Prof. Quintiere

Table extracted SFPE HB 3rd Ed.

Heat released from air consumption

- For most fuels, about __3.0 kJ__ is generated from 1 g of **air** consumed in combustion reactions.
- For most fuels, about __13.1 kJ__ is generated from 1 g of **Oxygen** consumed in combustion reactions.