2015-2016 Spring Semester Material and Energy Balance

Energy & 1st Law of Thermodynamic

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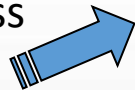
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8th Weeks

Definitions

- Every process route for a material involves at some point a physical or chemical treatment, with a corresponding exchange of energy from one type to another, or between the system and its surroundings.

- An engineer working on process improvement or design needs to account for the energy that flows into or out of each step of the process and to determine an overall energy balance for the process.

- This is done by writing energy balance equations in much the same way as material balance equations.

Definitions

- A reversible process occurs when the restoring force differs from the deforming force by an infinitesimal amount, such that after completion of the process, both the system and the surroundings can be restored to their original conditions.

- No degradation of energy occurs during a reversible process, and the availability of energy in the combined system plus surroundings remains constant.

- No real process is strictly reversible.

Reversible process: can be defined as one whose "direction" can be reversed by an infinitesimal small change in some property of the system.

① Make a video recording of a process   →   Observable process   →   reversible

② Run the recording backwards   →   Process impossible to observe   →   irreversible
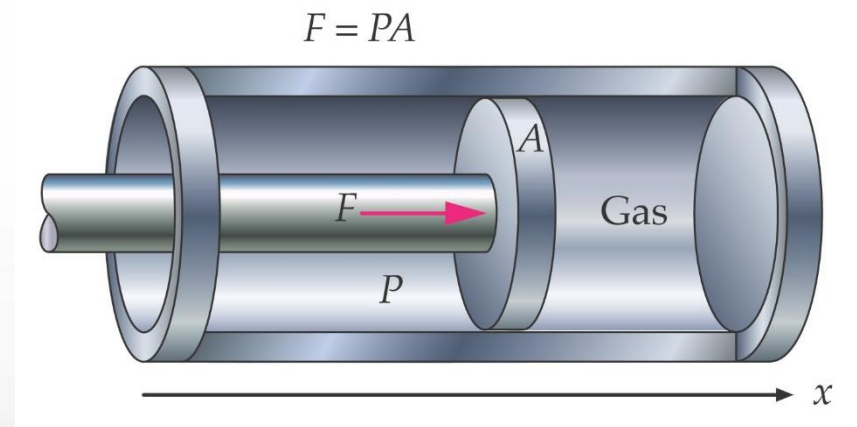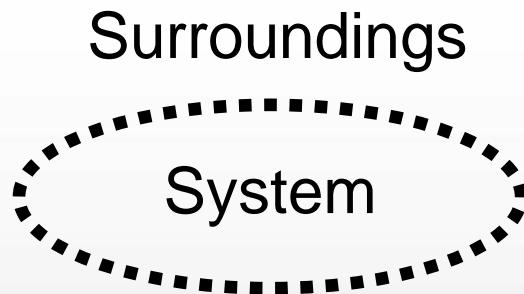
Definitions

- Various restrictions may be placed on the operation of a process. A process operating

  - at constant-temperature is **isothermal**, at constant-pressure is **isobaric**, and at constant volume is **isochoric**. A thermally isolated process is **adiabatic**.

- A non-isolated system undergoing a process interacts with its surroundings and exchanges energy.

  - **Heat** is energy crossing the system boundary under the influence of a temperature gradient. The amount of heat Q has a positive sign when heat is added to the system.

  - **Work** is energy in transit between a system and its surroundings caused (among other things) by the displacement of an external force acting on the system. The amount of work W has a positive sign when work is done by the system.

Energy

- Energy exists in many forms, such as mechanical energy, heat, light, chemical energy, and electrical energy. Energy is the ability to bring about change or to do work.

- Thermodynamics is the study of energy.

- The system can exchange mass and energy through the boundary with the environment.

- An example of "closed system" - no mass flow- is the gas confined in a cylinder. The boundary –in this case real wall- is made by the cylinder and the piston walls.

Surroundings

System

$F = PA$

A

F

Gas

P

x

Energy

- Although the word energy is used frequently, there is no generally acceptable definition of the term in a thermodynamic sense. Various forms of energy exist, each of which can be defined rigorously. Different processes may have associated with them quite different amounts of energy, in quite different forms.

1. Nuclear fission of uranium: -1.6 x 10^{10} kJ.

2. Ionization of a hydrogen atom: +2 x 10^3 kJ.

3. Oxidation of a hydrogen molecule to water vapor: -240 kJ.

4. Vaporization of water: +40 kJ.

5. Heating water vapor from room temperature to 1000 K: +20 kJ.

6. Lifting nickel an elevation of 300 meters: +160 J.

7. Raising the velocity of nickel by 100 km/h: +20 J.

Energy

- The total energy of a system has three components:

1. Kinetic energy (E_K): Energy associated with the translational motion of a system relative to some frame of reference, which is usually the surface of the earth.

2. Potential energy (E_P): Energy associated with the position of a system in an electrical, gravitational, or magnetic field.

3. Internal energy (U): All energy possessed by the system other than kinetic and potential, such as energy stored within a system due to the relative motion and position of atoms within the system. This includes the so-called P-V energy of a gas, which is a measure of its ability to do work by reversible expansion.

Energy

- In a closed system, energy may be transferred across the boundary in two ways:

1. As *heat* (Q), or energy that flows as a result of a temperature difference across the system boundary. Heat always flows from a higher temperature to a lower one. Heat is defined as *positive* when transferred to the system from the surroundings.

2. As *work* (W), or energy that flows due to a driving force other than temperature difference. Examples are mechanical force or electric voltage. Work is defined as *positive* when done by the system on the surroundings.

The First Law of Thermodynamics

- In its most general form, the first law of thermodynamics states that the rate of energy carried into a system by streams, plus the rate of heat transferred to the system across the boundary, equals the rate at which energy is carried out by streams plus the rate at which the system does work, plus the rate of accumulation of energy in the system. This is often stated as the *law of conservation of energy*.

- The First Law of Thermodynamics (Conservation) states that energy is always conserved, it cannot be created or destroyed. In essence, energy can be converted from one form into another.

The first law in equation form is:

Input of energy to system = output of energy from system

+ accumulation

The First Law of Thermodynamics

$$E_K = \frac{1}{2} \cdot m \cdot v^2 \qquad E_P = m \cdot g \cdot z$$

$$\Delta U + \Delta E_K + \Delta E_P = Q - W$$

where ΔU = change in total internal energy of the system, ΔE_K and ΔE_P are the change in kinetic and potential energy of the system, Q = heat; positive for energy entering the system, and W = work; positive for energy leaving the system. The term Δ refers to the final - initial state.

In most cases, the system is stationary (or nearly so), so that ΔE_K and ΔE_P are zero. This simplifies the first law to:

$$\Delta U = U_f + U_i = Q - W$$

The First Law of Thermodynamics

- An **adiabatic process** transfers no heat. therefore Q = 0

$$\Delta U = Q - W$$

  - When a system expands adiabatically, W is positive (the system does work) so ΔU is negative.

  - When a system compresses adiabatically, W is negative (work is done on the system) so ΔU is positive.

- An **isothermal process** is a constant temperature process. Any heat flow into or out of the system must be slow enough to maintain thermal equilibrium. For ideal gases, if ΔT is zero, ΔU = 0. Therefore,

$$Q = W = \int_{i}^{f} P \cdot dV$$

- Any energy entering the system (Q) must leave as work (W)

The First Law of Thermodynamics

- An **isobaric process** is a constant pressure process. ΔU, W, and Q are generally non-zero, but calculating the work done by an ideal gas is straightforward

$$W = P \cdot \Delta V$$

- Water boiling in a saucepan is an example of an isobar process

$$\Delta U = Q_P - P \cdot \Delta V \qquad \rightarrow \qquad Q_P = \Delta U + P \cdot \Delta V = \Delta H$$

- An **isochoric process** is a constant volume process. When the volume of a system doesn't change, it will do no work on its surroundings. W = 0

$$\Delta U = Q_V$$

- Heating gas in a closed container is an isochoric process

Example: Work and Heat During the Compression of an Ideal Gas.

- Oxygen is placed into a closed system fitted with a piston capable of compressing the gas.

- The initial state is 100 L of O_2 at 1.5 atm pressure and 400 K.

- The gas is compressed reversibly and isothermally until the pressure reaches 6.5 atm.

- Calculate the work done on the system.
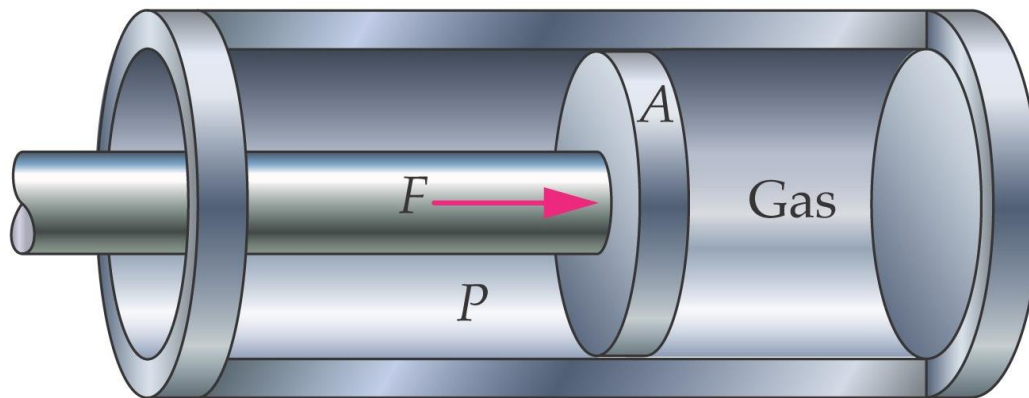
Example: Work and Heat During the Compression of an Ideal Gas.

- The amount of gas in the system is calculated first. For the initial conditions:

$$n = \# \, of \, moles \, of \, O_2 = \frac{P_i V_i}{RT} = \frac{(1.5 \, atm)(100 \, L)}{\left(0.08206 \, \frac{L.\,atm}{mol.\,K}\right)(400K)} = 4.57$$

- For a reversible isothermal process, ΔU = 0. Therefore,

$$Q = W = \int_i^f P \cdot dV = \int_i^f \mathrm{R}T \cdot \frac{dV}{V} = RT \ln\left(\frac{V_f}{V_i}\right) = RT \ln\left(\frac{P_i}{P_f}\right)$$

$$Q = W = (4.57 \, moles \, O_2)(8.3144 \, \frac{J}{mol.\,K})(400 \, K) \ln\left(\frac{1.5 \, atm}{6.5 \, atm}\right)$$

$$Q = W = -22{,}290 \, J$$

The First Law of Thermodynamics

- For an open system the first law takes the form:

$$Q - W_{me} = \Sigma[(H'_{ex} + gz_{ex} + \tfrac{1}{2}V_{ex}^2)m_{ex}] - \Sigma[H'_{in} + gz_{in} + \tfrac{1}{2}V_{in}^2)m_{in}]$$

where

W_{me} = mechanical work,

H' = specific enthalpy, $U' + P \times V'$,

P = pressure,

U' = specific energy,

V' = specific volume,

ex = subscript indicating an exit stream,

in = subscript indicating an entering stream.

- The first law expression may be simplified if the terms for kinetic and potential energy are zero or negligible. The first law expression for a steady-state system becomes:

$$Q - W_{me} = \Delta(mH') = H$$

where H is the total enthalpy.

Enthalpy, Heat Capacity, and Heat Content

- Since a system does not have an intrinsic quantity of *H* or *U*, it is the *changes* in these functions that are of interest. For example, heat balances use the enthalpy H.

- The *high temperature heat content* (also called the sensible heat) refers to the change in H of a substance when heated above a defined *reference temperature*, usually 298.15 K, or 25 °C. The change in H above the reference temperature is designated as: H_T-H_{298}. The heat content of an ideal gas is independent of pressure (or volume), but the heat content of real gases varies with pressure.

- It is now appropriate to define *heat capacity C*, which is the ratio of heat added to the temperature increase. For an incremental addition of heat: $C = \delta Q/\delta T$

Enthalpy, Heat Capacity, and Heat Content

- However, the addition of heat Q does not define the final state, since the path has not been specified. Since processes are often either isobaric or isochoric, we define Cp and Cv as:

$$C_p = \delta Q_p / \delta T = (H_{T_2} - H_{T_1})/dT$$

$$C_v = \delta Q_v / \delta T = (H_{T_2} - H_{T_1})/dT$$

- For the addition of heat to a closed isobaric system,

$$H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} C_p \, dT$$

Enthalpy, Heat Capacity, and Heat Content

C_p and C_v are important in calculating work and heat effects in adiabatic processes caused by reversible expansion or compression of a gas. For an adiabatic process, $Q = 0$, so $dU = -\delta W = -PdV = C_v dT$. From various relationships involving the ideal gas law, and for one mole of gas, integration of the $C_v dT$ expression (assuming C_v does not vary with temperature) gives:

$$C_v \ln\left(\frac{T_2}{T_1}\right) = R\ln\left(\frac{V_1}{V_2}\right)$$
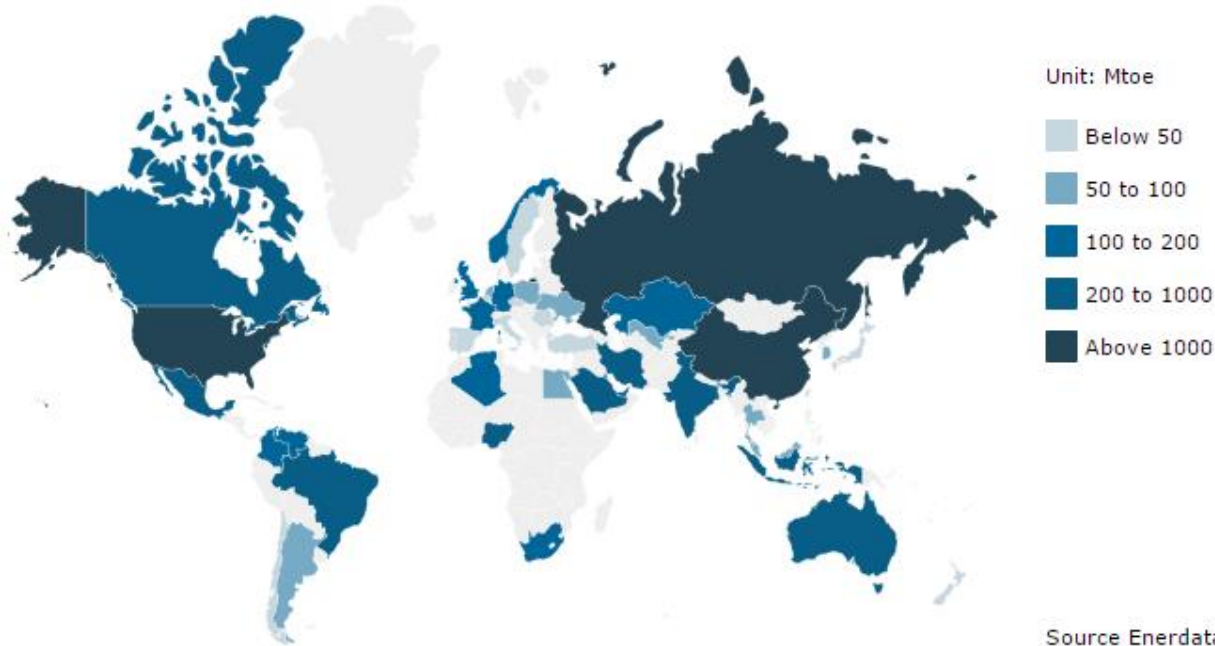
The relationship between pressure and volume during reversible adiabatic expansion is:

$$PV^{C_p/C_v} = \text{constant}$$

Global Energy Statistics

Total primary production

(2014 – increased by 1.1%)

million of tonnes of oil equivalent

Unit: Mtoe

Below 50
50 to 100
100 to 200
200 to 1000
Above 1000

Source Enerdata

Year: 2014	Unit: Mtoe	Highest ten ▾
China		2,555
United States		1,989
Russia		1,334
Saudi Arabia		630
India		571
Indonesia		457
Canada		452
Australia		357
Iran		308
Brazil		269

Year: 2014	Unit: Mtoe	Lowest ten ▴
Portugal		6
Belgium		13
Taiwan		14
Chile		15
New Zealand		17
Japan		26
Romania		27
Czech Rep.		28
Spain		32
Turkey		33

Global Energy Statistics

Total balance of trade

(2014)

Unit: Mtoe

- Below -100
- -100 to 0
- 0 to 100
- 100 to 200
- Above 200

Source Enerdata
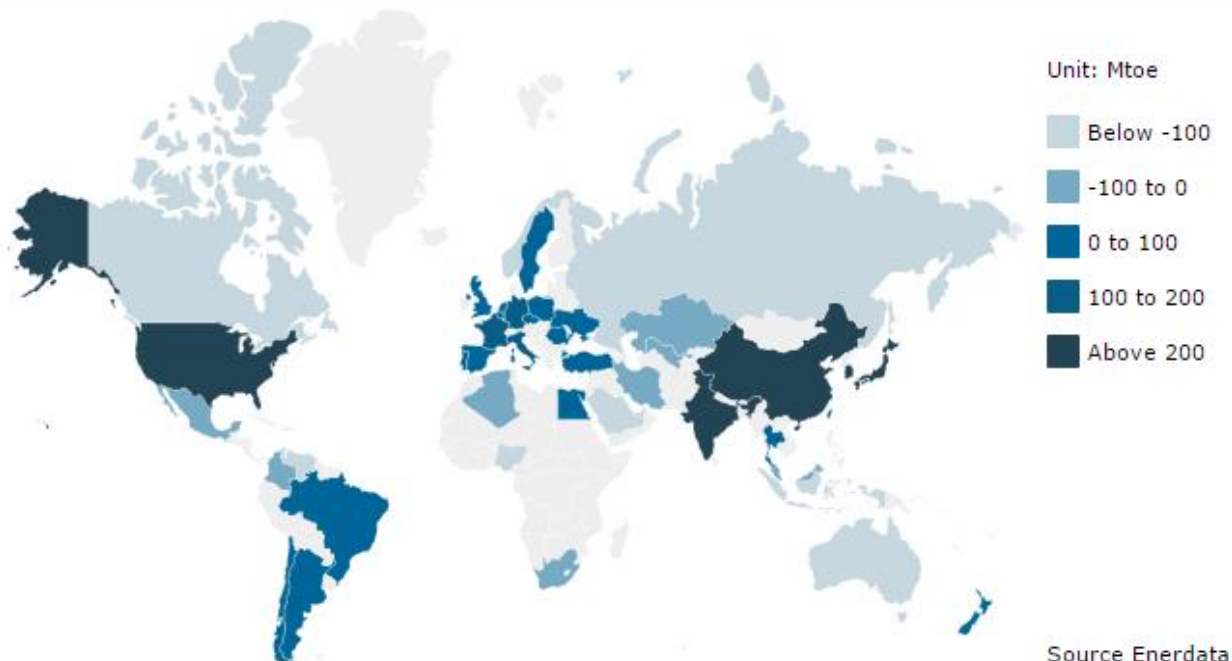
Year: 2014	Unit: Mtoe	Highest ten ▾
China		511
Japan		424
India		300
United States		278
South Korea		231
Germany		195
Italy		116
France		112
Taiwan		99
Spain		90

Year: 2014	Unit: Mtoe	Lowest ten ▴
Russia		-568
Saudi Arabia		-413
Indonesia		-230
Australia		-227
Canada		-199
Norway		-159
Kuwait		-145
Nigeria		-133
Venezuela		-115
United Arab Emirates		-112

Global Energy Statistics

Total energy consumption

(2014)

Unit: Mtoe

- Below 50
- 50 to 100
- 100 to 200
- 200 to 2000
- Above 2000

Source Enerdata

Year: 2014 Unit: Mtoe	Highest ten ▼
China	3,034
United States	2,224
India	872
Russia	751
Japan	437
Germany	307
Brazil	306
South Korea	277
Canada	251
France	243

Year: 2014 Unit: Mtoe	Lowest ten ▲
New Zealand	21
Portugal	22
Norway	29
Romania	32
Colombia	35
Kuwait	37
Chile	38
Czech Rep.	42
Uzbekistan	48
Sweden	49

Global Energy Statistics

World[1] total primary energy supply (TPES) from 1971 to 2013 by fuel (Mtoe)

Coal[2] | Oil | Natural gas | Nuclear | Hydro | Biofuels and waste | Other[3]

1973

Biofuels and waste 10.5%
Hydro 1.8%
Nuclear 0.9%
Natural gas 16.0%
Other[3] 0.1%
Coal[2] 24.5%
Oil 46.2%

6 100 Mtoe

2013

Biofuels and waste 10.2%
Hydro 2.4%
Nuclear 4.8%
Natural gas 21.4%
Other[3] 1.2%
Coal[2] 28.9%
Oil 31.1%

13 541 Mtoe
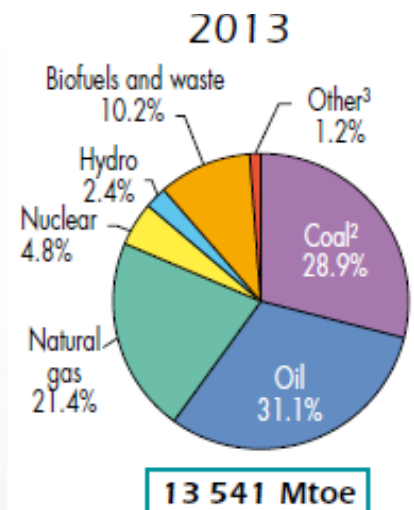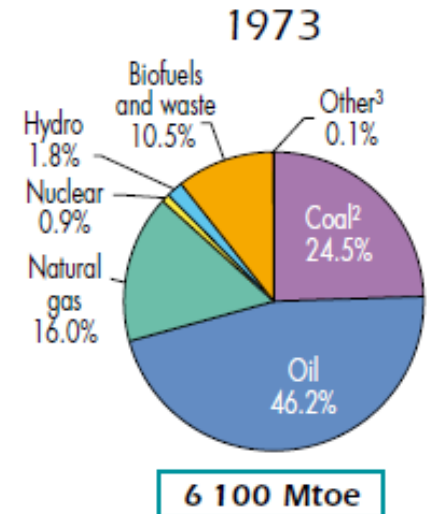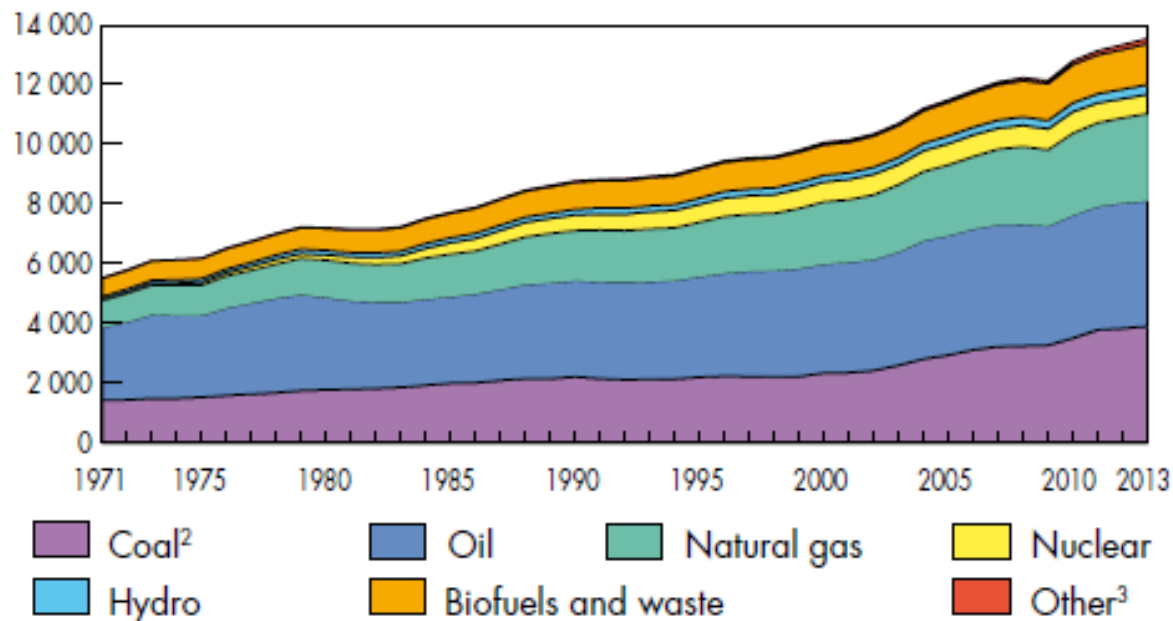
Global Energy Statistics

World[1] total final consumption from 1971 to 2013 by fuel (Mtoe)

Legend: Coal[2], Oil, Natural gas, Biofuels and waste[3], Electricity, Other[4]

1973

Electricity 9.4%
Other[4] 1.6%
Coal[2] 13.6%
Biofuels and waste[3] 13.1%
Natural gas 14.0%
Oil 48.3%

4 667 Mtoe

2013

Other[4] 3.3%
Coal[2] 11.5%
Electricity 18.0%
Biofuels and waste[3] 12.2%
Natural gas 15.1%
Oil 39.9%

9 301 Mtoe
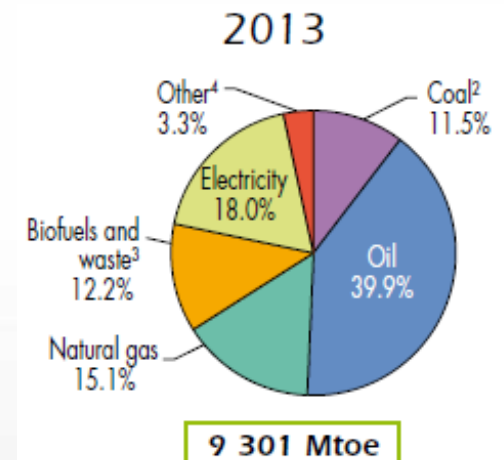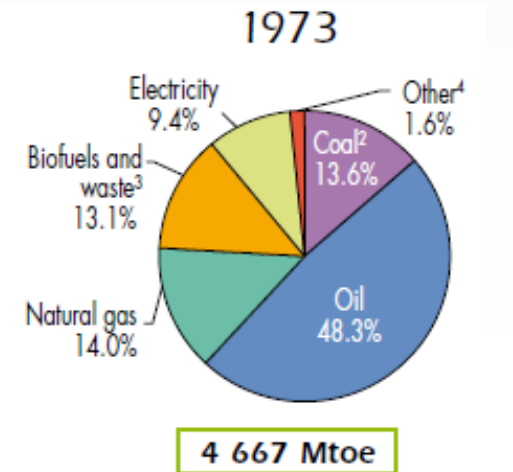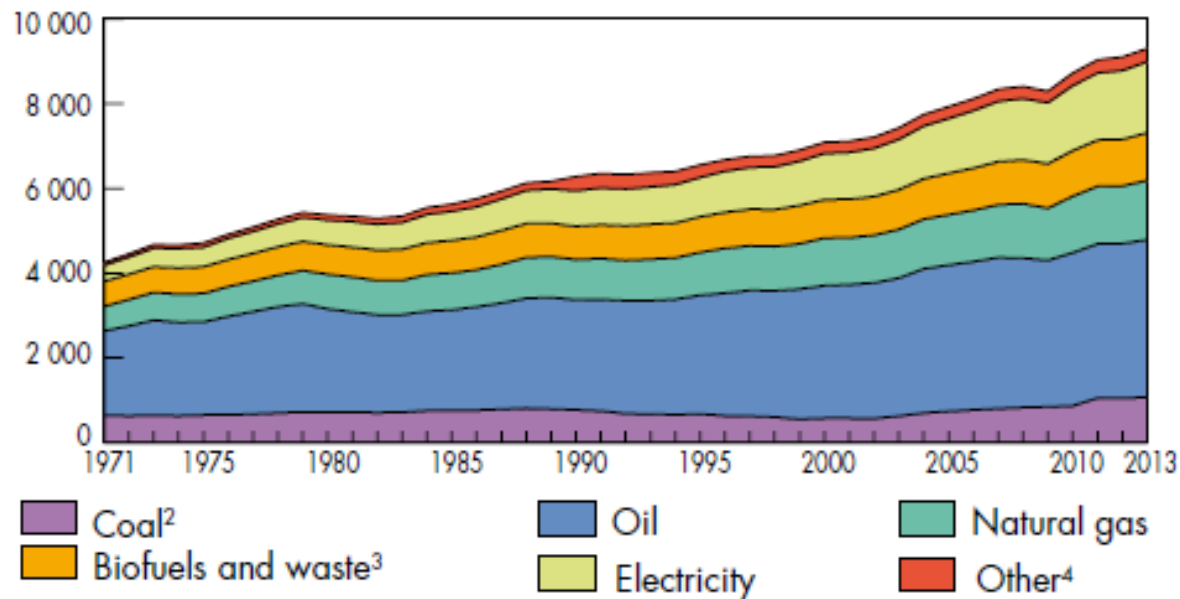
Global Energy Statistics

Region/ Country/ Economy	Popu-lation (million)	GDP (billion 2005 USD)	GDP (PPP) (billion 2005 USD)	Energy prod. (Mtoe)	Net imports (Mtoe)	TPES (Mtoe)	Elec. cons.[1] (TWh)	CO_2 emissions[2] (Mt of CO_2)	TPES/ pop. (toe/capita)	TPES/ GDP (toe/000 2005 USD)	TPES/ GDP (PPP) (toe/000 2005 USD)	Elec. cons./pop. (kWh/ capita)	CO_2/ TPES (t CO_2/ toe)	CO_2/ pop. (t CO_2/ capita)	CO_2/ GDP (kg CO_2/ 2005 USD)	CO_2/ GDP (PPP) (kg CO_2/ 2005 USD)	Region/ Country/ Economy
Turkey	75.77	654.07	1057.98	32.35	86.67	116.49	209.22	283.84	1.54	0.18	0.11	2761	2.44	3.75	0.43	0.27	Turkey
World	7118	56519	86334	13594	-	13541[3]	21538	32190[4]	1.90	0.24	0.16	3026	2.38	4.52	0.57	0.37	World
OECD	1261	40615	40316	3977	1441	5300	10179	12038	4.20	0.13	0.13	8072	2.27	9.55	0.30	0.30	OECD
Middle East	218	1490	4299	1791	-1059	689	841	1647	3.17	0.46	0.16	3863	2.39	7.57	1.11	0.38	Middle East
Non-OECD Europe and Eurasia	341	1679	4164	1861	-677	1156	1538	2573	3.39	0.69	0.28	4510	2.23	7.54	1.53	0.62	Non-OECD Europe and Eurasia
China	1367	5105	14257	2566	532	3023	5165	9023	2.21	0.59	0.21	3778	2.98	6.60	1.77	0.63	China
Asia	2348	3754	13293	1473	247	1655	2155	3607	0.71	0.44	0.12	918	2.18	1.54	0.96	0.27	Asia
Non-OECD Americas	472	2468	5546	796	-164	619	1011	1128	1.31	0.25	0.11	2142	1.82	2.39	0.46	0.20	Non-OECD Americas
Africa	1111	1408	4459	1129	-365	747	649	1075	0.67	0.53	0.17	584	1.44	0.97	0.76	0.24	Africa

1. *Gross production + imports – exports – losses.*
2. *CO_2 emissions from fuel combustion only. Emissions are calculated using the IEA's energy balances and the Revised 2006 IPCC Guidelines.*

Gross domestic product (GDP)
gross domestic product (at purchasing power parity) per capita GDP(PPP)
Total primary energy supply (TPES)

Next Week

- **Enthalpy Balances in Non-Reactive Systems**
- **Material and Energy Balance Application on Molybdenum Production (A Case Study)**