evropský sociální fond v ČR

EVROPSKÁ UNIE

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

OP Vzdělávání pro konkurenceschopnost

INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

Inovace bakalářského studijního oboru Aplikovaná chemie

Reg. č.: CZ.1.07/2.2.00/15.0247

Introduction to Physical Chemistry

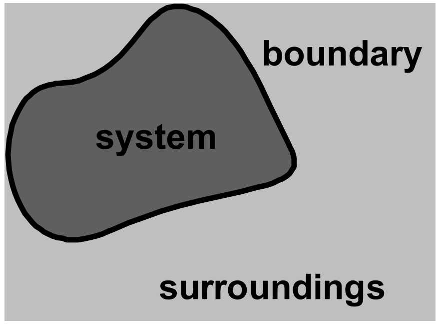
Lecture 5

- Thermodynamics
  - thermodynamic systems, processes and states
  - state variables
  - mechanical work of gas
  - adiabatic process

Lecture vocabulary:

mechanical work of gas	mechanická práce plynu
certain	určitý
region	oblast
universe	vesmír
notional	hypotetický , teoretický
delimiting	vymezující
surroundings	okolí
environment	okolí, prostředí
reservoir	rezervoár, tepelná lázeň
experimentally accessible	experimentálně dostupný
internal energy	vnitřní energie
displace	zaujmout místo
force field	silové pole
solely	výhradně, jedině
mass flow	tok hmoty
reversible x irreversible	vratný x nevratný
sign	znaménko
sign convention	znaménková konvence
expansion	expanze, rozpínání
compression	komprese, stlačení
external	vnější
at the expense	na účet, na úkor (čeho)
work obtained	získaná práce
shaft work	shaft=hřídel, jiné označení pro mechanickou práci plynu
cylinder	válec
diminish	snížit se
net	celkový
thermally insulated	tepelně izolovaný
heat exchange	výměna tepla
steeper	strmější
denoted as	označován jako
stoichiometric	stechiometrický
equilibrium	rovnováha
intake	sání
combustion	spalování, hoření
exhaust	výfuk

Thermodynamic systems, states and processes



- ***Thermodynamic system*** **is a certain macroscopic region of universe**
- **Thermodynamic system is separated by real or notional *boundary* delimiting the system volume**
- **The space outside the thermodynamic system is known as the *surroundings*, the *environment*, or a *reservoir*.**

The *state of the system* is characterised by a *set of thermodynamic parameters* the values of which are experimentally accessible macroscopic properties, such as volume, pressure, temperature, electric field etc.

System type	**Mass flow**	**Work**	**Heat**
Open	YES	YES	YES
Closed	NO	YES	YES
Isolated	NO	NO	NO

Processes:
Isobaric · Isochoric · Isothermal
Adiabatic · Isoentropic · Isoenthalpic
Quasistatic · Polytropic

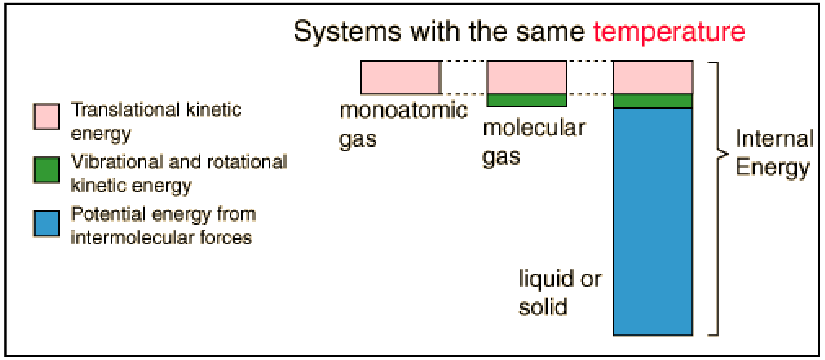
Reversible vs. irreversible

State variables

State variables – those which are independent from pathway. In a thermodynamic system, temperature, pressure, volume, internal energy, enthalpy, and entropy are state variables.

For this lecture, *internal energy* of the gas is the most important state variable

It is the energy needed to create the system, but excludes the energy to displace the system's surroundings, any energy associated with a move as a whole, or due to external force fields. Internal energy has two major components, kinetic energy and potential energy.



For ideal gas, it depends solely on temperature (but not on the volume of the gas):

$$dU = nC_V dT$$

Believe it for now, will be explained in the next lecture

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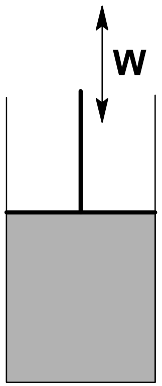
Mechanical work of gas

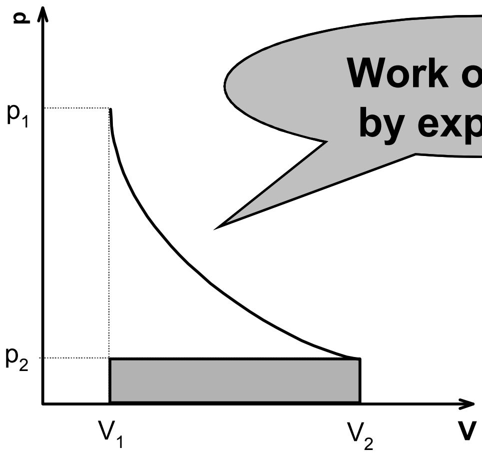


$$dW = -pdV$$

External pressure !!!

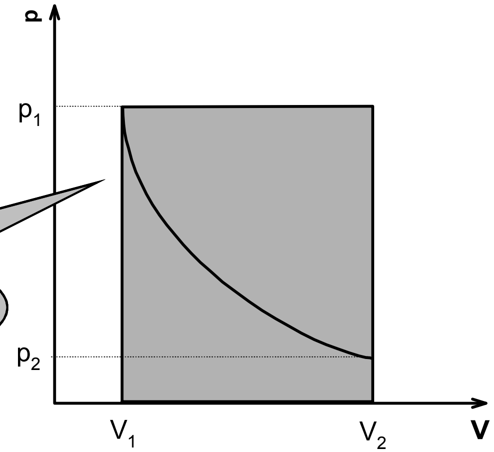
Sign convention: **work supplied to the environment is negative (expansion) or positive in the case of compression**

Work is done at the expense of the thermal energy of the environment or the internal energy of the gas (or both)



Work obtained by expansion

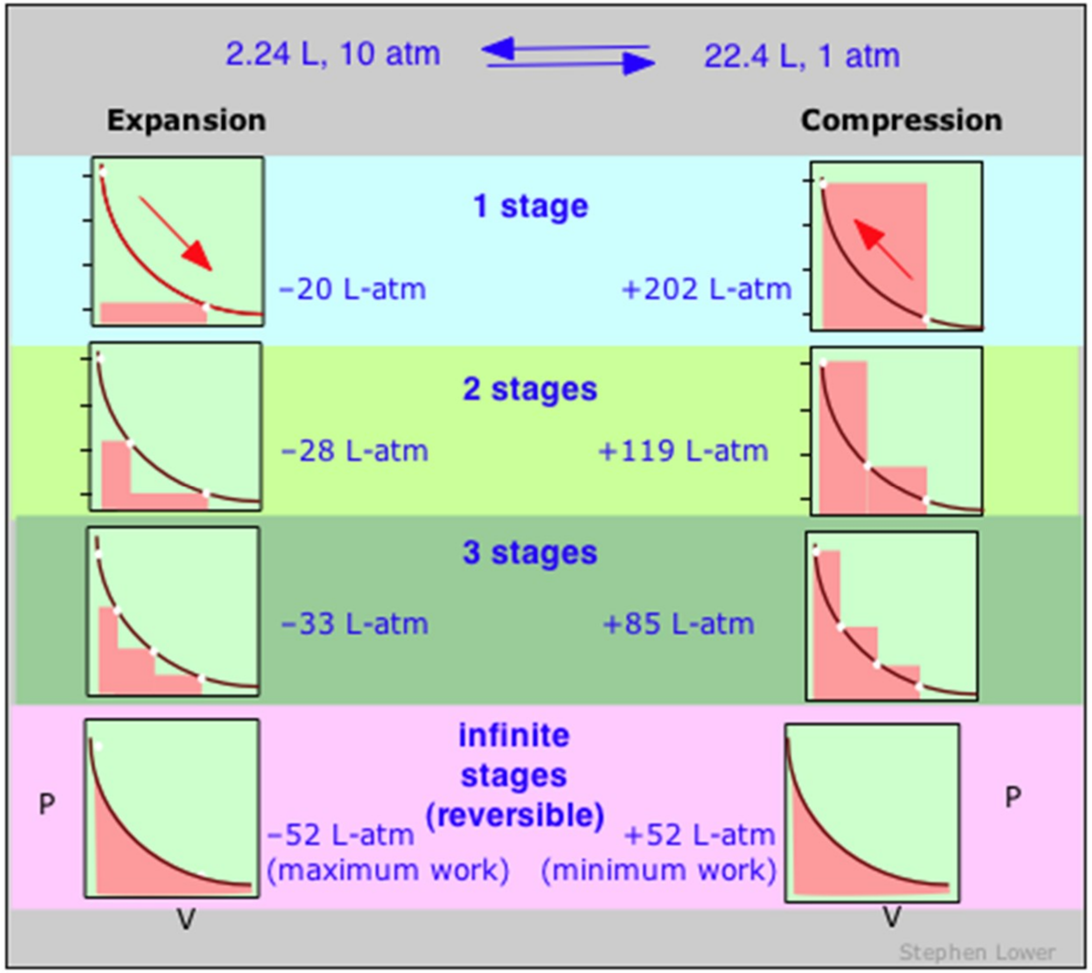
Work required for compression



Processes during which shaft work is done can be divided into:

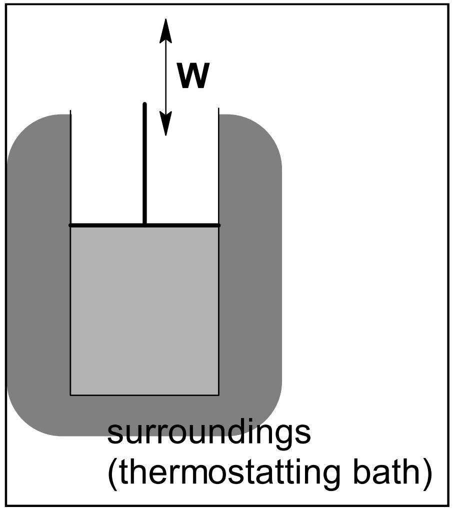
- **irreversible** ← constant external pressure
- **reversible** ← external pressure is always slightly lower than is the pressure inside the cylinder

Mechanical work of gas – reversibility



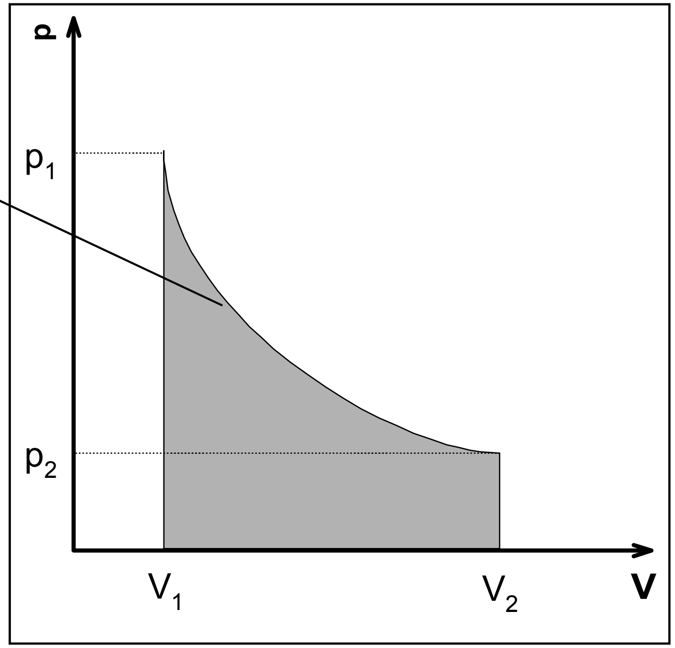
As the number of steps increases, the overal process becomes less irreversible; that is, the difference between the work done in expansion and that required to re-compress the gas diminishes.

Isothermal process



$$p = \frac{nRT}{V}$$

T is constant here



$$-dW = pdV$$

$$-W = \int_{V_1}^{V_2} pdV = nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$-W = nRT \left[\ln V\right]_{V_1}^{V_2} = nRT \ln\left(\frac{V_2}{V_1}\right) \equiv nRT \ln\left(\frac{p_1}{p_2}\right)$$

Adiabatic process

Is a thermodynamic process in which there is no net heat transfer to or from the working gas. Adiabatic process is said to occur when:

- **the container of the system has thermally-insulated walls**

or

- **there is no opportunity for significant heat exchange (the process occurs in a short time)**
- **can be reversible or irreversible**

Reversible adiabatic process

$$dU = -p_{external}\,dV$$

$$nc_V\,dT = -p_{ext}\,dV$$

$$nRT = pV \Rightarrow$$

$$\Rightarrow nRdT = d(pV) = Vdp + pdV$$

$$nc_V \frac{pdV + Vdp}{nR} = -p_{ext}\,dV$$

For reversible process p_{ext}=p and we can rearrange:

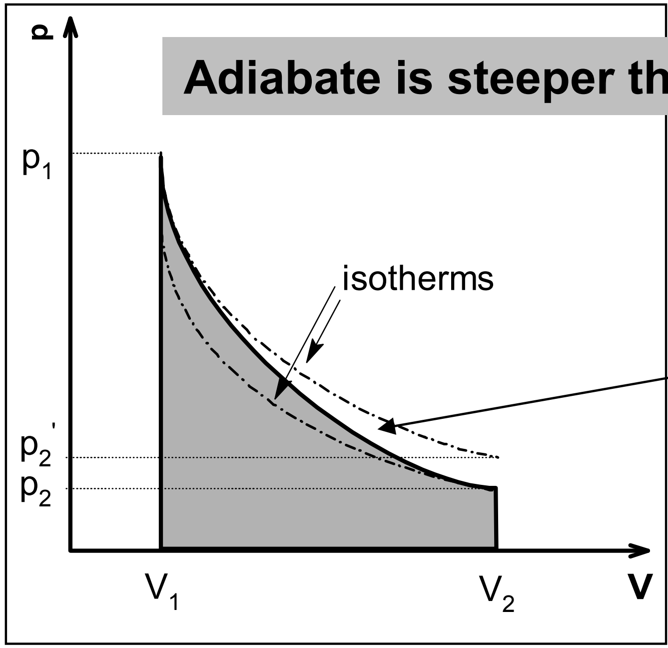
$$\frac{dp}{p} = -\frac{(c_V + R)}{c_V}\frac{dV}{V} = -\frac{c_p}{c_V}\frac{p}{V}$$

After integration we get Poisson eq.

$$\ln\frac{p}{p_1} = \frac{c_p}{c_V}\ln\frac{V_1}{V} \Rightarrow pV^{\kappa} = p_1V_1^{\kappa}$$

$$\left(\kappa = \frac{c_p}{c_V}\right)$$

Adiabatic process

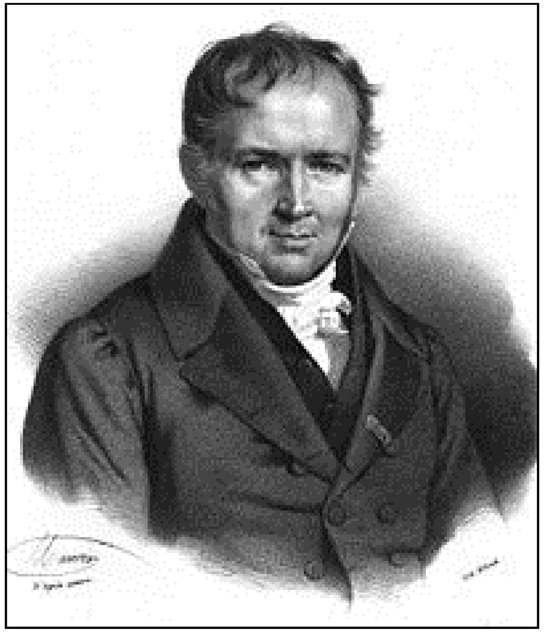


…valid as well, but T is changing

$$p = \frac{p_1 V_1^{\kappa}}{V^{\kappa}} \qquad p = \frac{nRT}{V}$$

$$TV^{\kappa-1} = T_1 V_1^{\kappa-1}$$

$$\frac{T^{\kappa}}{p^{\kappa-1}} = \frac{T_1^{\kappa}}{p_1^{\kappa-1}}$$



Siméon Denis Poisson (1781-1840)

Adiabatic process

Work is done at the expense of the internal energy of gas. We can calculate it if we know both initial and final temperatures:

$$-W = -\Delta U = \int_{T_1}^{T_2} nC_v dT = nC_v\left(T_2 - T_1\right)$$

Alternatively, to calculate reversible work, we can integrate the Poisson eq.:

$$-dW = pdV$$

$$-W = \int_{V_1}^{V_2} pdV = p_1 V_1^{\kappa} \int_{V_1}^{V_2} \frac{1}{V^{\kappa}} dV$$

$$-W = \frac{p_1 V_1^{\kappa}}{-\kappa + 1}\left(V_2^{-\kappa+1} - V_1^{-\kappa+1}\right)$$

Real processes are something in between isothermal and adiabatic, they are denoted as *polytropic*

Adiabatic flame temperature

the theoretical temperature of the combustion if no energy is lost to the outside environment

- **Constant volume**
- **Constant pressure**

$$\Delta H = \int_{T_1}^{T_2} \sum_i \nu_i C_{p_i}(prod.)dT$$

the combustion of an organic compound with n carbons involves breaking roughly

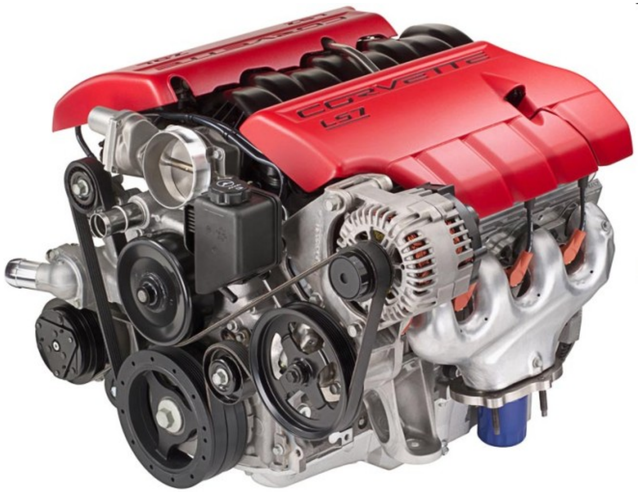
2n C–H	**bonds,**
n C–C	**bonds, and**
1.5n O_2	**bonds to form roughly**
n CO_2	**molecules and**
n H2O	**molecules.**

Fuel	Oxidizer	Tad (°C)
Acetylene (C2H2)	air	2500
Acetylene (C2H2)	Oxygen	3480
Butane (C4H10)	air	1970
Cyanogen (C2N2)	Oxygen	4525
Dicyanoacetylene (C4N2)	Oxygen	4990
Ethane (C2H6)	air	1955
Hydrogen (H2)	air	2210
Hydrogen (H2)	Oxygen	3200
Methane (CH4)	air	1950
Natural gas	air	1960
Propane (C3H8)	air	1980
Propane (C3H8)	Oxygen	2526
MAPP gas Methylacetylene (C3H4)	air	2010
MAPP gas Methylacetylene (C3H4)	Oxygen	2927
Wood	air	1980
Kerosene	air	2093
Light fuel oil	air	2100
Medium fuel oil	air	2100
Heavy fuel oil	air	2100
Bituminous Coal	air	2170
Anthracite	air	2180
Anthracite	Oxygen	2900

- **AFT is maximum for stoichiometric fuel-oxidizer mixture**
- **asssumes equilibrium – AFT can be exceeded in nonequilibrium conditions**

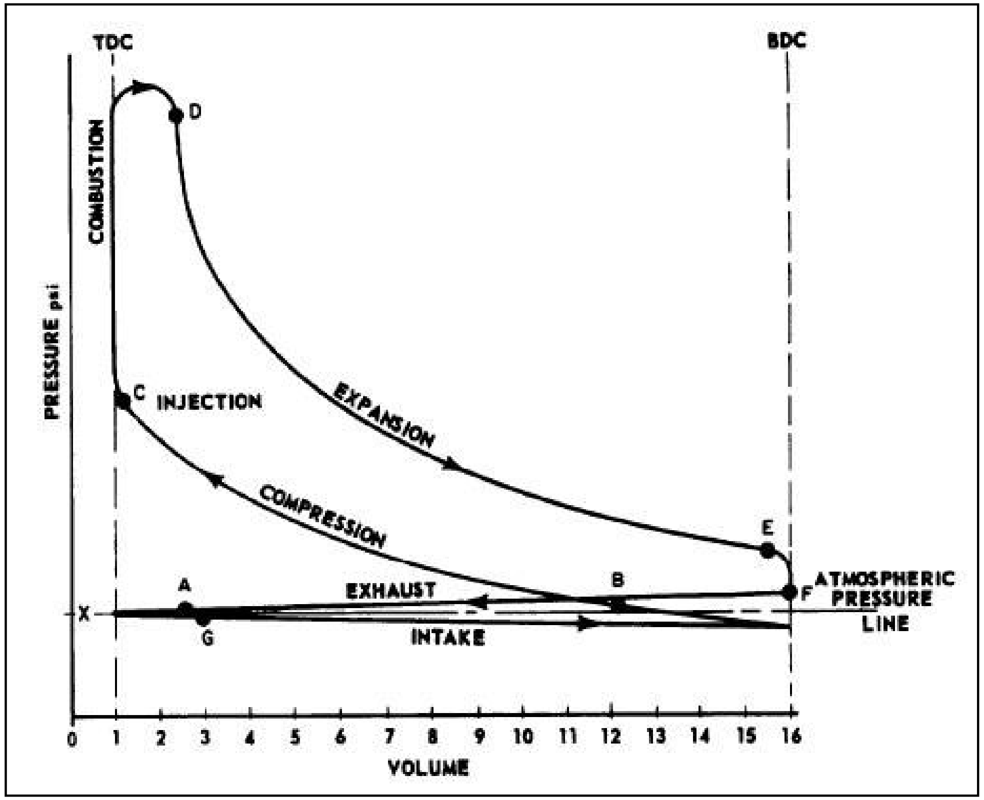
Constant pressure adiabatic flame temp.

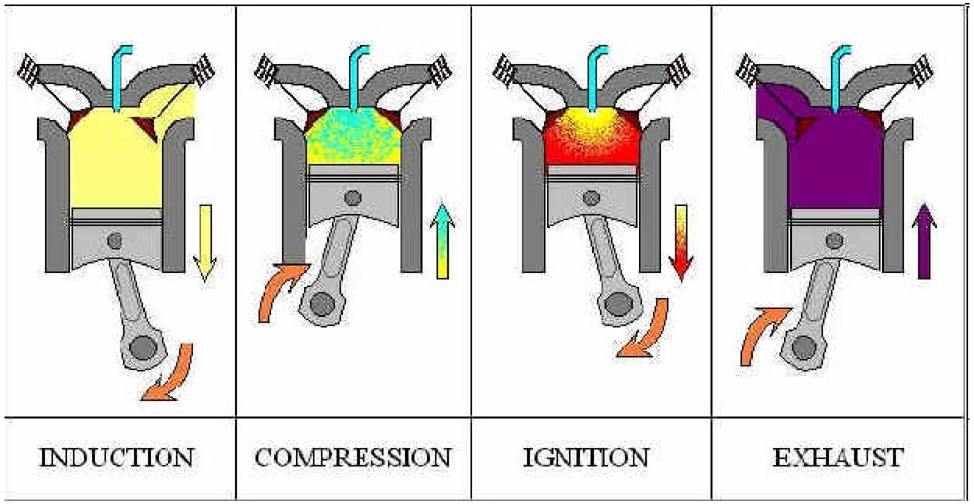
Internal combustion engine



Four-stroke cycle (Otto Cycle)

- Intake stroke
- Compression stroke.
- Combustion stroke
- Exhaust stroke






"That's all Folks!"