

The First Law of Thermodynamics

Lectures in Physical Chemistry 2



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Thermodynamics

„Thermodynamics is a funny subject.

The first time you go through it, you don't understand it at all.

The second time you go through it, you think you understand it,
except for one or two small points.

The third time you go through it, you know you don't understand it,
but by that time you are so used to it, so it doesn't bother you any more.”

Arnold Sommerfeld

http://en.wikiquote.org/wiki/Arnold_Sommerfeld

Consequences:

If you read your notes only once before the exam,
you will fail.

You should read your notes exactly twice.
to get a good mark.



Arnold Johannes Wilhelm
Sommerfeld (1868–1951)
German physicist

Thermodynamics 2

Notes before starting the subject:

Ancient Egypt: collection of methods for marking the borders of lands having rectangular or circular shape
 well working in practice, but could not be developed further

Euclid: Euclidean geometry looks strange: unrealistic definitions, like infinitely small point, infinitely thin line
BUT: this is a consistent logical system, allows the creation of complicated geometrical structures, which can be built (buildings, machines)

thermodynamics:

- most of the definitions are not realistic (e.g. 'perfect heat insulation') these are needed to make thermodynamics logically consistent
- subject is related to work, heat and energy
- time is not present in the equations: could be called 'thermostatics'
- provides the change between the initial and the final states
- usually defines only lower and upper limiting values

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System and surroundings

<u>system</u>	part of the world we interest in
<u>surroundings</u>	rest of the world around the system
<u>boundary</u>	separates the system and the surroundings

Possible relations between the system and the surroundings

open system matter AND energy can be transferred through the boundary

closed system energy (but not matter) can be transferred through the boundary

isolated system no transfer is possible across the boundary

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Thermodynamic functions

DEF thermodynamic function:

physical quantity that is a function of the state variables
it can be either a state function OR a path function

DEF state function

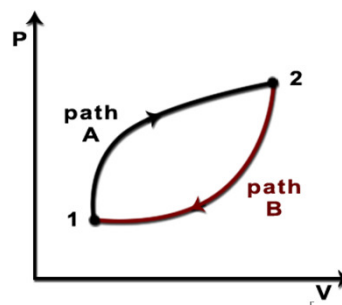
Its change depends on the initial and final values of the state properties and it is independent of intermediate values (independent of the path).

The change can be calculated
by an exact differential

DEF path function

Its change depends on the path between the initial and final values of the state properties.

The change cannot be calculated
by an exact differential



Extensive and intensive properties

DEF extensive property: depends on the amount ("extent") of the matter.
Summed up when identical systems are merged.
e.g. amount of substance, volume, mass

DEF intensive property: independent of the amount of the matter.
Levelled when systems are merged.
e.g. temperature, pressure, density

extensive/extensive = intensive
(e.g. mass/volume=density)

molar quantities

extensive property of one mole of matter: X/n
always intensive

e.g. molar volume: V_m
molar mass: M

Reversible and irreversible processes

re·vers·ible *adjective* \ri-'vər-sə-bəl\

capable of going through a series of actions (as changes) either backward or forward
<a reversible chemical reaction> (Merriam-Webster Online Dictionary)

„Reversible” has a different meaning in thermodynamics!

DEF reversible process or reversible cycle:

After a reversible cycle, the state properties in the system and its surroundings will be exactly the same.

reversible process: by means of infinitesimal changes;
the system is always in thermodynamic equilibrium
throughout the entire process

- no such a thing in the real life
- can be approximated in laboratory experiments

irreversible processes: all real life processes

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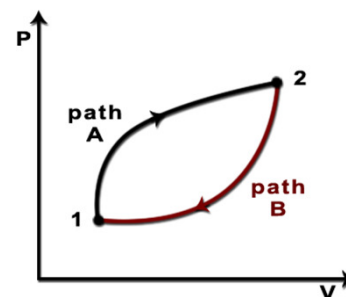
Internal energy, work and heat

DEF internal energy: interaction and kinetic energy of particles
denoted by U , unit Joule [J]

- only the change of internal energy has physical meaning
- its absolute value has no meaning
- state function and extensive property

internal energy
work, heat

state function
path functions



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First Law of thermodynamics

First Law of thermodynamics:

The internal energy of a system is constant unless it is changed by doing work or by heating.

- law of energy conservation
- work and heat are equivalent forms of energy

$$\Delta U = w + q$$

$$dU = \delta w + \delta q$$

U	internal energy [J]
w	work [J]
q	heat [J]
ΔU	finite change of internal energy
dU	infinitely small change of internal energy
δw	infinitely small amount of work
δq	infinitely small heat exchange

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Sign convention of energy change

egocentric sign convention

work done by the system and heat emitted by the system has **negative sign** (in this case the energy of the system decreases),

work done on the system and heat supplied to the system has **positive sign** (in this case the energy of the system increases)

consequence:

the **exothermic** (heat producing) physical and chemical processes are associated with negative energy change!

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Perpetuum mobile

Perpetuum mobile = perpetual motion machine

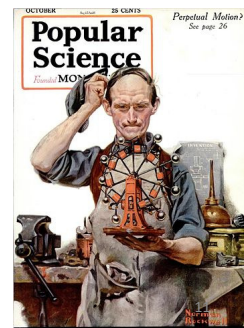
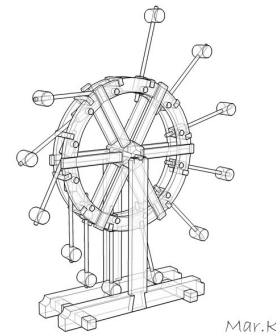
Types:

perpetuum mobile of the first kind:
producing work indefinitely with no input of energy

perpetuum mobile of the second kind:
100% conversion of heat to work

First Law \Rightarrow perpetuum mobile of the first kind does not exist, because internal energy cannot be converted to work in an unlimited way.

Second Law \Rightarrow perpetuum mobile of the second kind does not exist



Expansion work

expansion \Rightarrow expansion work

DEF infinitesimal expansion work: $\delta w = -p_{\text{ex}} dV$

dV small change of the volume of the system
 p_{ex} external pressure on the system
(not always equal to the pressure of the system)

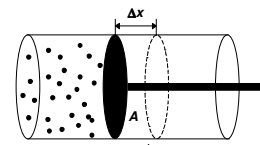
if the pressure of the system and the external pressure are only infinitesimally different (in this case $p_{\text{ex}} = p$)
 \Rightarrow quasistatic expansion
(this is the mechanical equivalent of „reversible change“).

expansion work, $\delta w = -F dx = -F/A A dx = -p_{\text{ex}} A dx = -p_{\text{ex}} dV$

unit: $[\text{Pa m}^3] = [\text{N/m}^2 \text{ m}^3] = [\text{N m}] = [\text{J}]$

expression of the First Law

with expansion work: $dU = -p_{\text{ex}} dV + \delta w_{\text{other}} + \delta q$



Enthalpy

DEF enthalpy: $H = U + pV$

denoted by H , unit: Joule [J]

meaning: internal energy corrected by expansion work

enthalpy is a state function and extensive property

dH is the change of enthalpy (cf. rule: $(uv)' = u'v + v'u$)

$$dH = dU + p dV + V dp$$

the First Law with expansion work $dU = -p_{\text{ex}} dV + \delta w_{\text{other}} + \delta q$

if $p_{\text{ex}} = p$, then

$$dU = -p dV + \delta w_{\text{other}} + \delta q$$

joining the two equations:

$$dH = V dp + \delta w_{\text{other}} + \delta q$$

If the pressure is constant ($dp = 0 \rightarrow Vdp = 0$) and there is no other work ($\delta w_{\text{other}} = 0$), then the change of the enthalpy is equal to the heat exchange:

$$dH = \delta q$$

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Exact differentials of H and U

Consider internal energy U as a function of temperature T at constant volume V

$\Rightarrow U(T)$ function

dU (i.e. a small change of U) due to a small change of temperature dT :

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT = \frac{dU}{dT} dT$$

Consider internal energy U as a function of both temperature T and volume V

$\Rightarrow U(T, V)$ function

dU due to a simultaneous small change of temperature dT and volume dV

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Consider enthalpy H as a function of both temperature T and pressure p

$\Rightarrow H(T, p)$ function

dH due to a simultaneous small change of temperature dT and pressure dp

$$dH = \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp$$

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The meaning of a partial derivative

$$\left(\frac{\partial U}{\partial T} \right)_V$$

change of this quantity is investigated

this quantity is changed

this is kept constant

In the next slides, the physical meaning of the partial derivatives will be discussed:

$$\left(\frac{\partial U}{\partial T} \right)_V = C_V \quad \text{heat capacity at constant volume}$$

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \quad (\text{for an ideal gas})$$

$$\left(\frac{\partial H}{\partial T} \right)_p = C_p \quad \text{heat capacity at constant pressure}$$

$$\left(\frac{\partial H}{\partial p} \right)_T = \mu_T \quad \text{isothermal Joule-Thompson coefficient}$$

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Internal energy of ideal gases do not depend on the volume

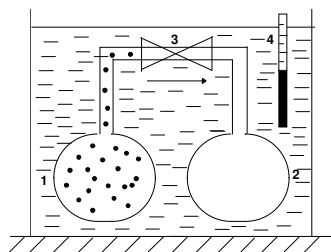
Ideal gas

U does not depend on volume: $(\partial U / \partial V)_T = 0$.

Real gases

$(\partial U / \partial V)_T$ is not zero, but very small.

Experimental justification: the Joule experiment



(1) high pressure gas in a container, (2) vacuum in another container. Valve (3) is opened, the volume of the gas is doubled, but the reading in thermometer (4) remains unchanged.



James Prescott Joule
(1818-1889)
Scottish brewer

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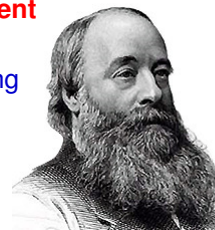
Joule-Thomson effect

determination of the isothermal Joule-Thomson coefficient

Gas is pressed through a throttle (porous plug), then the original temperature is restored by electric heating/cooling

Relation of pressure change Δp and enthalpy change ΔH is investigated.

$$\mu_T = \left(\frac{\partial H}{\partial p} \right)_T \approx \frac{\Delta H}{\Delta p}$$



James Prescott Joule
(1818-1889)

determination of the adiabatic Joule-Thomson coefficient

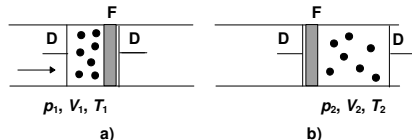
The pistons are moved in such a way that the pressure is

p_2 in the right section and it is

$p_1 > p_2$ in the left section.

The cylinder and the piston are adiabatic.

a) initial state; b) final state. F: throttle (porous plug); D: piston.



$$\mu = \left(\frac{\partial T}{\partial p} \right)_H \approx \frac{\Delta T}{\Delta p}$$



Lord Kelvin
né William Thomson
(1824-1907)

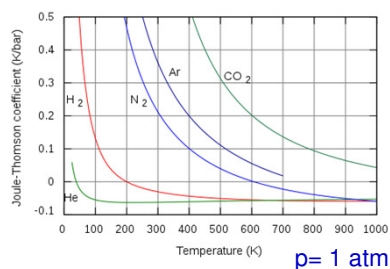
Compression of gases

adiabatic Joule-Thomson coefficient:

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H$$

expansion = decrease of pressure \Rightarrow

warming $\Leftrightarrow \mu$ negative above $T_{\text{inversion}}$
cooling $\Leftrightarrow \mu$ positive below $T_{\text{inversion}}$



DEF inversion temperature

starting from a temperature above $T_{\text{inversion}}$ the gases get warmer at expansion

starting from a temperature below $T_{\text{inversion}}$ the gases get colder at expansion

Practical applications of the Joule-Thomson effect:

- fridge
- liquification of gases

Heat capacity

Simplified definition of heat capacity:

amount of heat that increases the temperature of the system
by 1 centigrade

Exact definition:

DEF heat capacity $C = \delta q / dT$

δq infinitesimal heat exchange
 dT consequent temperature change

Heat capacity depends on the circumstances.

Heat capacity of special processes:

constant volume heat capacity C_V

constant pressure heat capacity C_p

Constant volume process, without work:

$$dU = \delta q; \quad dU = (\partial U / \partial T)_V dT = C_V dT$$

DEF constant volume heat capacity: $C_V = (\partial U / \partial T)_V$

Constant pressure process, without work:

$$dH = \delta q; \quad dH = (\partial H / \partial T)_p dT = C_p dT$$

DEF constant pressure heat capacity: $C_p = (\partial H / \partial T)_p$

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Relation of c_p and c_v

C_p and C_V extensive heat capacities (refer to the whole system)
unit: J K⁻¹ (capital letters)

c_p and c_v intensive heat capacities (refer to 1 mole of the system)
unit: J K⁻¹ mol⁻¹ (small letters)

$$H = U + p V \quad \text{definition of } H$$

$$p V = n R T \quad \text{definition of perfect gases:}$$

$$H = U + n R T$$

$$H - U = n R T \quad \text{differentiation with respect temperature } T$$

$$C_p - C_V = n R \quad \text{dividing by } n$$

$$c_p - c_v = R \quad \text{the difference of molar heat capacities is } R !$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

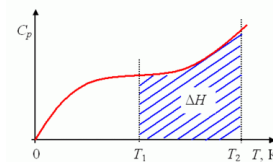
	c_p	c_v	$c_p - c_v$ (J K ⁻¹ mol ⁻¹)
He (25 °C)	20.786	12.472	8.314
N ₂ (25 °C)	29.12	20.80	8.34
CO ₂ (25 °C)	36.94	28.46	8.48
H ₂ O (100 °C)	37.47	28.03	9.44

Temperature dependence of enthalpy

C_p is the derivative of enthalpy with respect T $C_p = (\partial H / \partial T)_p$, therefore integrating C_p provides the change of enthalpy with temperature

$$\Delta H = H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT$$

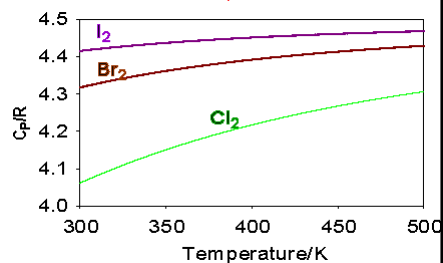
$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$



If enthalpy is known at temperature T_1 , then by integrating C_p the enthalpy can be calculated at T_2 .

if C_p is considered constant in temperature interval $T_1 - T_2$:

$$H(T_2) = H(T_1) + C_p(T_2 - T_1)$$



In general, heat capacity depends on temperature, but it can be considered constant in a small temperature interval.

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Thermochemistry

DEF thermochemistry: investigation of the heat effect of reactions

exothermic process:	produces heat
endothermic process	consumes heat

constant volume

heat = change of internal energy $q = \Delta U$

constant pressure

heat = change of enthalpy $q = \Delta H$

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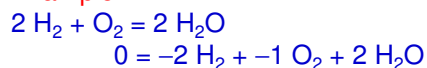
Stoichiometric coefficient

ν_j stoichiometric coefficient (it will be used also in other topics)

chemical reaction in general: $\sum_j \nu_j A_j = 0$

ν_j negative for a reactant, positive for a product
 A_j chemical formula of the species

Example:



$$\Rightarrow \quad \begin{array}{lll} \nu_1 = -2 & \nu_2 = -1 & \nu_3 = +2 \\ A_1 = \text{"H}_2\text{"} & A_2 = \text{"O}_2\text{"} & A_3 = \text{"H}_2\text{O"} \end{array}$$

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Basics of thermochemistry

DEF standard state of a substance at a specified temperature is its

- (1) chemically pure form
- (2) at $p^\ominus = 1 \text{ bar} = 10^5 \text{ Pa}$ pressure

Note: temperature is arbitrary!

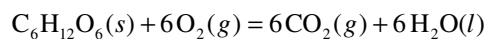
Notes:

- 1) Not to be confused with notion „standard state of gases“ !
 The thermodynamic standard state may refer to any substance (not only for gases) and the temperature is arbitrary.
- 2) The thermodynamic data are frequently published for temperature $T^\ominus = 298.15 \text{ K}$. This is called the „recommended temperature“.

DEF thermochemical equation:

usual chemical equation + the state of the compounds are also indicated.

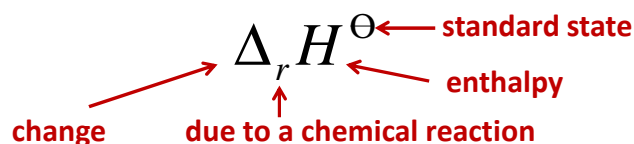
e.g. physical state (*g*: gas, *l*: liquid, *s*: solid) or solvatic state.



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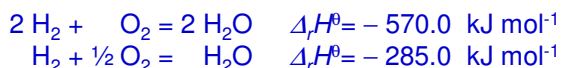
Basics of thermochemistry 2

DEF standard reaction enthalpy: enthalpy change due to a reaction that transforms standard state reactants to standard state products [J mol^{-1}]



Notes:

- this is a **molar quantity**: enthalpy change if the reaction occurs 1 mole times (= 6.022×10^{23} times)
- **Not related to the chemical process**, it is related to the actual chemical equation:

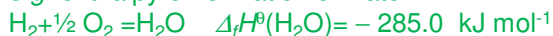


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Basics of thermochemistry 3

DEF $\Delta_f H^\ominus$ standard molar enthalpy of formation: enthalpy of a reaction in which one mole compound is formed from its reference state elements [J mol^{-1}]

Note: molar quantity, because this is the enthalpy change related to the production of 1 mole of species
e.g. enthalpy of formation of water:



DEF Reference state element: The most stable state of an element at pressure p^\ominus (1 bar) and a given temperature (the single exception is the white phosphorus P)

Notes:

- it depends on temperature what is the reference state of an element
- examples for room temperature: N_2 , O_2 , graphite (C), white tin (Sn)
- **standard molar enthalpy of formation of reference state elements is always zero** (a consequence of the definition)
- an element may have a non-zero standard molar enthalpy of formation, like at room temperature elements O_3 , diamond (C), grey tin (Sn)

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Calculation of reaction enthalpy

Calculating reaction enthalpy from the molar enthalpy of the species

$$\Delta_r H^\theta = \sum_j \nu_j H_m^\theta(j)$$

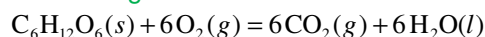
Not used, since molar enthalpy means that there is a common zero level for all species

Calculating reaction enthalpy from the molar enthalpy of formations of the species

$$\Delta_r H^\theta = \sum_j \nu_j H_f^\theta(j)$$

well applicable „the basic equation of thermochemistry”; for each species the own zero level is defined by the energy level of the reference state elements

Example: combustion of glucose



$$\Delta_r H^\theta = 6H_m^\theta(\text{CO}_2(g)) + 6H_m^\theta(\text{H}_2\text{O}(l)) - H_m^\theta(\text{C}_6\text{H}_{12}\text{O}_6(s)) - 6H_m^\theta(\text{O}_2(g)),$$

$$\Delta_r H^\theta = 6\Delta H_f^\theta(\text{CO}_2(g)) + 6\Delta H_f^\theta(\text{H}_2\text{O}(l)) - \Delta H_f^\theta(\text{C}_6\text{H}_{12}\text{O}_6(s))$$

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Hess's Law

Hess's law: Enthalpy change of a reaction is equal to the sum of the enthalpy changes of the composite reactions.

Notes:

- These composite reactions may be not real.
- Hess's Law is a simple consequence of that enthalpy is a state function, therefore the reaction enthalpy is independent of the path.

The Hess's law is very useful if the enthalpy of a reaction cannot be measured well, because

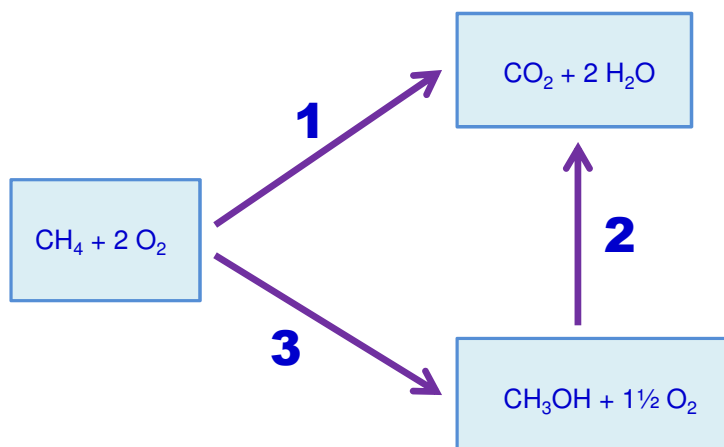
- ☐ the reaction is too slow
- ☐ it leads to an equilibrium
- ☐ side reactions occur



Герман Иванович Гесс
Germain Henri Hess
(1802-1850)
Russian chemist

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Example for Hess's Law



- 1) complete combustion of methane: $\Delta_r H^\theta = -890.0 \text{ kJ mol}^{-1}$
 2) complete combustion of methanol: $\Delta_r H^\theta = -726.0 \text{ kJ mol}^{-1}$
 3) partial combustion of methane: $\Delta_r H^\theta = -164.0 \text{ kJ mol}^{-1}$

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Temperature dependence of reaction enthalpy Kirchhoff's Law

Calculation of reaction enthalpy from the molar enthalpy of species:

$$\Delta_r H^\theta = \sum_j \nu_j H_m^\theta(j)$$

Differentiation with respect temperature T :

$$\left(\frac{\partial \Delta_r H^\theta}{\partial T} \right)_p = \sum_j \nu_j c_p(j) = \Delta c_p$$

Kirchhoff's Law (differential form)

Integrating it:

$$\Delta_r H^\theta(T_2) = \Delta_r H^\theta(T_1) + \int_{T_1}^{T_2} \Delta c_p dT$$

$$\Delta_r H^\theta(T_2) = \Delta_r H^\theta(T_1) + \Delta c_p (T_2 - T_1); \quad (\text{if } \Delta c_p \text{ constant}).$$



Gustav Robert Kirchhoff
(1824-1887)
German physicist

Kirchhoff's Law allows the calculation of reaction enthalpy at temperature T_2 , if it is known at temperature T_1 , and we know the average heat capacity of the reaction mixture (averaged according to the stoichiometric numbers).

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THE END

of topic

First Law of Thermodynamics



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