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ABBREVIATIONS AND SYMBOLS

A.	Ångström unit(s)
A	anion; as, H*A*
abs.	absolute
a.c.	alternating current
ac-	alicyclic; as, *ac*-derivatives of tetrahydronaphthalene
A.C.S.	American Chemical Society
addn.	addition
A.G.A.	American Gas Association
A.I.Ch.E.	American Institute of Chemical Engineers
A.I.M.E.	American Institute of Mining and Metallurgical Engineers
alc.	alcohol, alcoholic
alk.	alkaline (not alkali)
Alk	alkyl
amp.	ampere(s)
amp.-hr.	ampere-hour(s)
amt.	amount (noun)
anhyd.	anhydrous
A.P.I.	American Petroleum Institute
app.	apparatus
approx.	approximate (adj.), approximately
aq.	aqueous
Ar	aryl
ar-	aromatic; as, *ar*-derivatives of tetrahydronaphthalene
as-	asymmetric; as, *as-m*-xylidine
ASA	American Standards Association
A.S.M.	American Society for Metals
A.S.M.E.	American Society of Mechanical Engineers
A.S.T.M.	American Society for Testing Materials
atm.	atmosphere(s), atmospheric
at. no.	atomic number
at. wt.	atomic weight
av.	average
b. (as, b_{11})	boiling (at 11 mm.)
B	base; as, *B*.2HCl
bbl.	barrel(s)
Bé.	Baumé
b.p.	boiling point
B.t.u.	British thermal unit(s)
bu.	bushel(s)
C.	centigrade
C-	denoting attachment to carbon; as, *C*-alkyl derivatives of aniline
cal.	calorie(s)
calcd.	calculated
c.f.m.	cubic foot (feet) per minute
cg.	centigram(s)
c.g.s.	centimeter-gram-second
chem.	chemical
C.I.	*Colour Index* no.
cks.	centistokes
c.l.	car lots
cm.	centimeter(s)
coeff.	coefficient
com.	commercial
compd.	compound (noun)
compn.	composition
concd.	concentrated
concn.	concentration
cond.	conductivity
const.	constant
cor.	corrected

c.p.	chemically pure
cps.	centipoise
crit.	critical
cryst.	crystalline
crystd.	crystallized
crystn.	crystallization
cu.	cubic
d (as, d_4^{20})	density (conveniently, specific gravity)
d	differential operator
d-	*dextro*-, dextrorotatory
D-	denoting configurational relationship, as to *dextro*-glyceraldehyde
d.c.	direct current
dec., decomp.	decompose(s)
decompn.	decomposition
deriv.	derivative
detd.	determined
detn.	determination
diam.	diameter
dielec.	dielectric (adj.)
dil.	dilute
dist.	distilled
distn.	distillation
DL-, *dl*-	racemic
dm.	decimeter
e	electron
ed.	edition, editor
elec.	electric, electrical
elev.	elevated
e.m.f.	electromotive force
eng.	engineering
eq.	equation
equil.	equilibrium
equiv.	equivalent
esp.	especially
estd.	estimated
estn.	estimation
e.s.u.	electrostatic unit(s)
e.u.	entropy unit(s)
e.v.	electron volt(s)
expt.	experiment
exptl.	experimental
ext.	extract
extd.	extracted
extn.	extraction
F.	Fahrenheit
Fedl.	Federal
ff.	following (pages)
fl.oz.	fluid ounce(s)
f.o.b.	free on board
f.p.	freezing point
ft.	foot (feet)
ft.-lb.	foot-pound(s)
g.	gram(s)
gal.	gallon(s)
g.p.d.	grams per denier
g.p.m.	gallons per minute
hp.	horsepower
hr.	hour(s)
hyd.	hydrated, hydrous
i.	insoluble
i-	inactive; as, *i*-methionine
i.b.p.	initial boiling point
I.C.C.	Interstate Commerce Commission
I.D.	inner diameter
in.	inch(es)
insol.	insoluble
I.P.T.	Institute of Petroleum Technologists
I.U.	International Unit(s)
I.U.C., I.U.P.A.C.	International Union of Chemistry, International Union of Pure and Applied Chemistry
j.	joule
K.	Kelvin
K	dissociation constant
Kev	kilo electron volt
kg.	kilogram(s)
kg.-cal.	kilogram-calorie(s)
kv.	kilovolt(s)
kv.-amp.	kilovolt-ampere(s)
kw.	kilowatt(s)
kw.-hr.	kilowatt-hour(s)
l.	liter(s)
l-	*levo*-, levorotatory
L-	denoting configurational relationship, as to *levo*-glyceraldehyde
lb.	pound(s)
LC_{50}	concentration lethal to 50% of animals tested

l.c.l.	less than car lots
LD_{50}	dose lethal to 50% of animals tested
ln	logarithm (natural)
log	logarithm (common)
m.	meter(s)
m-	meta: as *m*-xylene
M	metal
M	molar (as applied to concn.; not molal, which is written out)
ma.	milliampere(s)
manuf.	manufacture
manufd.	manufactured
manufg.	manufacturing
max.	maximum
M.C.A.	Manufacturing Chemists' Association
m.c.f.	million cubic feet
m.e., meq.	milliequivalent(s)
mech.	mechanical
M.e.v.	million electron volts
mg.	milligram(s)
m.g.d.	million gallons per day
min.	minimum; minute(s)
misc.	miscellaneous
mixt.	mixture
ml.	milliliter(s)
M.L.D.	minimum lethal dose
mm.	millimeter(s)
mM	millimole(s)
mol.	molecule, molecular
m.p.	melting point
m.p.h.	miles per hour
M.R.	molar refraction
mv.	millivolt(s)
$m\mu$	millimicron(s)
n (as, n_D^{20})	index of refraction (for 20°C., and sodium light)
n-	normal; as, *n*-butyl
N	normal (as applied to concn.)
N-	denoting attachment to nitrogen; as, *N*-methylaniline
neg.	negative (adj.)
no.	number
N.O.I.B.N.	not otherwise indexed by name
o-	ortho; as, *o*-xylene
O-	denoting attachment to oxygen; as, *O*-acetylhydroxylamine
O.D.	outer diameter
oz.	ounce(s)
p., pp.	page, pages
p-	para; as, *p*-xylene
pos.	positive (adj.)
powd.	powdered
p.p.m.	parts per million
ppt.	precipitate
pptd.	precipitated
pptn.	precipitation
prepd.	prepared
prepn.	preparation
Pr. no.	Foreign Prototype no. (for dyes)
p.s.i.(g.),(a.)	pound(s) per square inch (gage), (absolute)
pt.	point
pts.	parts
quad. pt.	quadruple point
qual.	qualitative
quant.	quantitative
q.v.	"which see"
R	univalent hydrocarbon radical (or hydrogen)
R.	Rankine
ref.	reference
resp.	respectively
r.h.	relative humidity
R.I.	*Ring Index* no.
r.p.m.	revolutions per minute
r.p.s.	revolutions per second
s.	soluble
s-	symmetric(al); as, *s*-*m*-xylidine
S-	denoting attachment to sulfur; as, *S*-methylcysteine
S.A.E.	Society of Automotive Engineers
satd.	saturated
satn.	saturation

S.C.F.	standard cubic foot (feet)
Sch.	Schultz no. (for dyes)
sec.	second(s)
sec-	secondary; as, *sec*-butyl
S.F.s.	Saybolt Furol second(s)
sl.s.	slightly soluble
sol.	soluble
soln.	solution
soly.	solubility
sp.	specific
sp., spp.	species
spec.	specification
sp.gr.	specific gravity
sq.	square
S.T.P.	standard temperature and pressure
subl.	sublime(s), subliming
S.U.s.	Saybolt Universal second(s)
sym-	symmetric(al); as, *sym-m*-xylidine
T.A.P.P.I.	Technical Association of the Pulp and Paper Industry
tech.	technical
temp.	temperature
tert-	tertiary; as, *tert*-butyl
theoret.	theoretical
t.p.h.	tons per hour
t.s.i.	tons per square inch
Twad.	Twaddell
u.v.	ultraviolet
v.	volt(s)
var.	variety
vic-	vicinal; as, *vic-m*-xylidine
vol.	volume(s) (not volatile)
v.s.	very soluble
w.	watt(s)
wt.	weight
X.U. (10^{-10} mm.)	X-unit
yd.	yard(s)
yr.	year(s)
$[\alpha]_D^{20}$	optical rotation (for 20°C. and sodium light)
γ	microgram(s)
∂	differential operator (partial)
Δ	finite difference
η	viscosity
λ	wave length
μ	micron(s)
Ω	ohm(s)
$<$	less than
$>$	more than
$\sim$	cycle(s)
$\backsimeq$	approximately equal to

Other letter symbols may be found in "Standard System of Nomenclature for Chemical Engineering Unit Operations" adopted by the American Institute of Chemical Engineers.

SHIPPING REGULATIONS

Complete information for the U.S. is given in "Tariff No. 9 Publishing Interstate Commerce Commission Regulations for Transportation of Explosives and Other Dangerous Articles by Land and Water in Rail Freight Service and by Motor Vehicle (Highway) and Water Including Specifications for Shipping Containers," with supplements, issued by H. A. Campbell, Agent, 30 Vesey Street, New York 7, N.Y. (1954). The following terms for labeling explosives and other dangerous articles have been used in the Encyclopedia:

Red label (for inflammable liquids)
Yellow label (for inflammable solids and oxidizing materials)
White label (for acids and corrosive liquids)
Red label (for inflammable compressed gases)
Green label (for noninflammable compressed gases)
N.O.I.B.N. (not otherwise indexed by name)

In the text of the Encyclopedia the preferred terms "flammable" and "nonflammable" are used in place of "inflammable" and "noninflammable," respectively.

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PERIODICAL ABBREVIATIONS

The abbreviations used are, for the most part, those given in the "List of Periodicals Abstracted by Chemical Abstracts" (Vol. **45**, No. 24, Pt. 2 (1951), also published separately). See also *Literature (survey)*, especially the sections on "Reviews, yearbooks, and monographs" and "Periodicals," Vol. **8**, pp. 437–40.

Am. Soc. Testing Materials, Proc.	American Society for Testing Materials, Proceedings
Anal. Chem. (superseding *Ind. Eng. Chem., Anal. Ed.*)	Analytical Chemistry
Angew. Chem. (superseding *Die Chemie*; *Z. angew. Chem.*)	Angewandte Chemie
Ann. Chem., Justus Liebigs	Annalen der Chemie, Justus Liebigs
Arch. Biochem. and Biophys. (superseding *Arch. Biochem.*)	Archives of Biochemistry and Biophysics
Arch. Ind. Hyg. and Occupational Med. (superseding *J. Ind. Hyg. Toxicol.*)	Archives of Industrial Hygiene and Occupational Medicine
Biochem. J. (London)	Biochemical Journal, The
Biochem. Z.	Biochemische Zeitschrift
Biochim. et Biophys. Acta	Biochimica et Biophysica Acta
BIOS Repts.	British Intelligence Objectives Subcommittee Reports
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan
Bull. soc. chim. or *Bull. soc. chim. France*	Bulletin de la société chimique de France
C.A.	Chemical Abstracts
Can. J. Research	Canadian Journal of Research
Chem. Ber. (superseding *Ber.*)	Chemische Berichte
Chem. Eng. (superseding *Chem. & Met. Eng.*)	Chemical Engineering with Chemical & Metallurgical Engineering
Chem. Eng. News (superseding *News Ed. (Am. Chem. Soc.)*; *Ind. Eng. Chem., News Ed.*)	Chemical and Engineering News
Chem. Eng. Progress (superseding *Trans. Am. Inst. Chem. Engrs.*)	Chemical Engineering Progress with Transactions of American Institute of Chemical Engineers
Chem. Eng. Science	Chemical Engineering Science
Chemische Industrie	Chemische Industrie
Chemistry & Industry (formerly part of *J. Soc. Chem. Ind.*)	Chemistry & Industry
Chem. Revs.	Chemical Reviews
Chem. Tech. (Berlin) (superseding *Chem. Fabrik*)	Chemische Technik, Die (Berlin)
Chem. Week (superseding *Chem. Inds. Week*)	Chemical Week
Chem. Zentr.	Chemisches Zentralblatt
Chem.-Ztg.	Chemiker-Zeitung mit dem Sonderteil, Die Chemische Praxis und der Beilage, Chemisch-technische Übersicht
Chimica e industria (Italy) or *Chimica e industria (Milan)*	Chimica, La, e l'industria (Italy) or (Milan)
Chimie & industrie	Chimie & industrie
CIOS Repts.	Combined Intelligence Objectives Subcommittee Reports
Compt. rend.	Comptes rendus hebdomadaires des séances de l'académie des sciences
FIAT Repts.	Field Information Agency Technical Reports
Fortschr. chem. Forsch.	Fortschritte der chemischen Forschung
Gazz. chim. ital.	Gazzetta chimica italiana
Helv. Chim. Acta	Helvetica Chimica Acta
Ind. Chemist	Industrial Chemist and Chemical Manufacturer, The

Ind. Eng. Chem. (superseding *J. Ind. Eng. Chem.*)	Industrial and Engineering Chemistry
J. Agr. Food Chem.	Journal of Agricultural and Food Chemistry
J. Am. Chem. Soc.	Journal of the American Chemical Society, The
J. Am. Med. Assoc.	Journal of the American Medical Association, The
J. Am. Pharm. Assoc.	Journal of the American Pharmaceutical Association
J. Appl. Chem. (*U.S.S.R.*) (see also *Zhur. Priklad. Khim.*)	Journal of Applied Chemistry (U.S.S.R.)
J. Appl. Phys. (superseding *Physics*)	Journal of Applied Physics
J. Assoc. Offic. Agr. Chemists	Journal of the Association of Official Agricultural Chemists
J. Biol. Chem.	Journal of Biological Chemistry, The
J. Chem. Phys.	Journal of Chemical Physics, The
J. Chem. Soc.	Journal of the Chemical Society (London)
J. Colloid Sci.	Journal of Colloid Science
J. Electrochem. Soc. (superseding *Trans. Electrochem. Soc*; *Trans. Am. Electrochem. Soc.*)	Journal of the Electrochemical Society
J. Gen. Chem. (*U.S.S.R.*) (see also *Zhur. Obshcheĭ Khim.*)	Journal of General Chemistry (U.S.S.R.)
J. Indian Chem. Soc.	Journal of the Indian Chemical Society
J. Inst. Metals	Journal of the Institute of Metals and Metallurgical Abstracts
J. makromol. Chem. (superseding *J. prakt. Chem.*)	Journal für makromolekulare Chemie
J. Org. Chem.	Journal of Organic Chemistry, The
J. Phys. Chem. (superseding *J. Phys. & Colloid Chem.*)	Journal of Physical Chemistry, The
J. Polymer Sci. (superseding *J. Polymer Research*)	Journal of Polymer Science
J. Research Natl. Bur. Standards (superseding *Bur. Standards J. Research*)	Journal of Research of the National Bureau of Standards
J. Sci. Food Agr.	Journal of the Science of Food and Agriculture
J. Soc. Chem. Ind. or *J. Soc. Chem. Ind.* (*London*) (formerly containing *Chemistry & Industry*)	Journal of the Society of Chemical Industry (London)
J. Soc. Chem. Ind., Japan	Journal of the Society of Chemical Industry, Japan
Kolloid-Z.	Kolloid-Zeitschrift
Mfg. Chemist	Manufacturing Chemist and Pharmaceutical and Fine Chemical Trade Journal Incorporating Manufacturing Perfumer
Monatsh. Chem.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften
Nature	Nature
Nucleonics	Nucleonics
Office Tech. Services (*OTS*) *Repts.* (superseding *Office Publication Board Repts.*)	Office of Technical Services Reports
Oil, Paint Drug Reptr.	Oil, Paint and Drug Reporter
Phys. Rev.	Physical Review, The
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas
Research (*London*)	Research, A Journal of Science and Its Applications
Revs. Mod. Phys.	Reviews of Modern Physics
Science	Science
Trans. Am. Inst. Mining Met. Engrs.	Transactions of the American Institute of Mining and Metallurgical Engineers
Trans. Am. Soc. Metals (superseding *Trans. Am. Soc. Steel Treating*)	Transactions of the American Society for Metals
Trans. Inst. Chem. Engrs. (*London*)	Transactions of the Institution of Chemical Engineers (London)
Z. anorg. u. allgem. Chem. (superseding *Z. anorg. Chem.*)	Zeitschrift für anorganische und allgemeine Chemie
Z. Elektrochem.	Zeitschrift für Elektrochemie und angewandte physikalische Chemie
Zhur. Obshcheĭ Khim.	Zhurnal Obshcheĭ Khimii (Journal of General Chemistry (U.S.S.R.))
Zhur. Priklad. Khim.	Zhurnal Prikladnoĭ Khimii (Journal of Applied Chemistry (U.S.S.R.)
Z. physik. Chem.	Zeitschrift für physikalische Chemie

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THERMODYNAMICS

Thermodynamics deals with energy and its transformation, driving potential of a process, and equilibrium with reference to either physical change of state or chemical reaction. As the result of experience, three laws of thermodynamics have been developed as the backbone of thermodynamics. Based upon facts and basic principles of chemistry and physics, these laws have found wide applications to problems in various fields of engineering as well as in pure science.

In chemical technology, thermodynamics has been successfully applied in prediction of limiting conditions of unit operations or processes and the energy quantities involved. As a powerful and versatile tool in process research, development, design and operation, thermodynamics is indispensable in the solution of an ever-increasing number of process problems. During recent developments in petroleum refining, petroleum chemicals, synthetic rubber, plastics, synthetic fibers, and other synthetic organic chemicals, many new compounds and processes have been encountered. Only with the aid of thermodynamics has it been possible to get the most out of research and engineering effort. For instance, the process design can be performed by means of thermodynamic correlations of various thermochemical and phase equilibrium data without an excessive amount of pilot-plant work. The optimum operating temperature and pressure for a given chemical reaction can be predicted to save time-consuming effort in laboratories. This is especially important in making the cost estimate of a plant or preliminary proposal for an engineering service.

It must be emphasized that thermodynamics deals with equilibrium situations. It has nothing to say about the rate at which equilibrium is approached from any nonequilibrium situation. See *Equilibrium, chemical*; *Reaction kinetics*.

Basic Concepts and Definitions

System and Surroundings. The so-called system in thermodynamics designates a specific part of the material universe to be set apart for the purpose of study. It may consist of a single body, part of a body, or a number of bodies, large or small. The system can be either homogeneous or heterogeneous. The choice of a system, which depends largely upon the individual situation, may affect the analysis of a problem by thermodynamics. A wise choice of the system can provide a convenient route in solving complex problems. With an improper selection of a system, some thermodynamic problems may even become unsolvable.

Once a system is specified, the rest of the universe becomes "surroundings." The term "surroundings" in thermodynamics refers more particularly to the surroundings immediately adjacent to the system. Between a system and its surroundings lies a boundary. In locating a boundary exactly between a system and its surroundings, the system can be unmistakably identified.

Several kinds of systems are frequently encountered. During the change of state, if there is no material flowing across the boundary between a system and its surroundings, the system is defined as a *closed system.* An *open system* is one involving the exchange of material across the boundary. In a multiphase system each separate phase is usually considered an open system wherein materials are flowing freely from one phase to the other, although the system as a whole may be a closed one.

A closed system may be free to absorb from or reject heat to the environment. It is also possible for a closed system to perform or to receive work. However, when the boundary between a system and its surroundings is made impervious to the heat flow, the closed system becomes *thermally isolated.* The closed system becomes *mechanically isolated* if a rigid boundary is present to prevent any volume change. When neither heat nor work is added or removed during a change of state, the closed system involved becomes a *completely isolated system.*

Two kinds of open systems are frequently encountered in industries, steady-state and unsteady-state. If the properties of any part of the system are constant regardless of the duration of an operation or a process, the so-called open system is a *steady-state flow system.* Most large-scale plants in industries which are operated continuously with a feed of constant composition at a carefully controlled operating condition belong to this class. On the other hand, if the properties of any part of a system undergo fluctuation and variation, the open system is an *unsteady-state flow system.* The compression of gases by a compressor into a storage tank is an example of this type of open system. The quantitative evaluation of a problem dealing with an unsteady-state flow system is more involved because the duration of the process becomes an additional variable.

State and State Function. To characterize any system it is necessary to find out the state in which the system exists. The term "state," in any thermodynamic discussion, is a kind of statistical average of the state assumed by all minute components of the system. This is a state in its gross sense, which is a macroscopic one. For instance, 10 cu. ft. of oxygen gas has its state completely defined if the temperature and pressure are given. The state of the oxygen so defined is a statistical average of the microscopic "states" of all individual oxygen molecules.

The variables which are used to characterize or to define completely the state of a system are called *state functions* or sometimes, simply, "properties." Once the state of a system is given, the "properties" or state functions are fixed irrespective of any changes undergone by the system. Although a system can have fixed values for different properties at a given state, the minimum number of properties required to define the state of a system at equilibrium is determined by the number of components and phases present in the system. This minimum number of properties is identified as the degrees of freedom. The quantitative relation known as the phase rule is:

$$F = C - P + 2 \tag{1}$$

See *Phase rule.*

Process. Any change of state taking place in a system is called a *process*. The process can be either a physical change of state or a chemical reaction. In other words, "process" as used in thermodynamics refers to unit operations as well as to unit processes.

Depending upon the limitation imposed upon a system during a process, special kinds of processes can be distinguished. An *adiabatic process* is one in which no heat flows across the boundary between the system and its surroundings; an *isobaric process* takes place at constant pressure. In general, it is desirable to have a chemical reaction carried out as an *isothermal process*, for this leads to a higher equilibrium conversion in either an endothermic or an exothermic reaction. In most organic reactions a large number of undesirable side reactions accompany a main reaction. The control of reaction at one uniform temperature throughout the reactor can either eliminate or reduce the extent of the side reactions.

On the other hand, it is always more economical to carry out some unit operations, such as fractional distillation, evaporation, other heat exchanges, and drying adiabatically. In gas absorption, where a large amount of heat is evolved, isothermal operation is desirable to obtain the maximum recovery.

Heat Reservoir. This is an ideal piece of equipment conceived for the convenience of theoretical thermodynamic treatment. A heat reservoir, as normally referred to in thermodynamic consideration, is one of infinite capacity. Any transfer of a finite quantity of heat in or out of the heat reservoir has a negligible effect on its temperature. The ocean and the atmosphere are practical examples that approach this type of heat reservoir.

Reversible and Irreversible Processes. The rate of a process can always be expressed as follows:

$$\text{Rate} = \frac{\text{driving force}}{\text{resistance}}$$

When all the forces acting upon a system are balanced, the driving force for a change of state is equal to zero, and the rate of a process becomes zero. Under this condition a system is said to be at equilibrium, and its state remains the same.

For a *reversible process* the driving force is made infinitesimally small. This makes the rate of a process negligibly small, so that a truly reversible process would require an infinite number of years before reaching its final state. Since the driving force in one direction is almost equal to zero, its direction can easily be reversed by an extremely small external force. On the other hand, an *irreversible process* is one proceeding under a driving force of finite order of magnitude. All actual processes are spontaneous, proceeding at a finite rate, and are therefore irreversible. However, an irreversible process can be made to approach a reversible one by some device with a suitable choice of conditions.

Consider a process involving the expansion of a gas against a piston in a vertical cylinder. To simplify the explanation, it is assumed that the piston and piston rod have no weight of their own. The gas inside the cylinder has an initial pressure of 10 atm. and is allowed to expand to 1 atmosphere pressure. If the pressure acting on the outside of the piston is 1 atm., the piston will continue to move upward, with a variable speed of finite order of magnitude, until the pressure of the gas inside the cylinder becomes identical with the outside pressure, that is, 1 atm. This actual process of expansion is irreversible because it proceeds under a driving force greater than an