

# Thermodynamics

## Thermodynamic terms

**Intensive:** These do not depend upon quantity of matter. e.g.,  $T, P$ .

**Extensive:** These depend upon quantity of matter. e.g., mass, volume, energy.

## Thermodynamic laws

**Properties of system:** Physical quantities which are used to define the system.

**Thermodynamic processes**

- If  $dq = 0$ , process is adiabatic.
- If  $dT = 0$  and  $dE = 0$ , the process is isothermal.
- If  $dV = 0$ , process is isochoric.
- If  $dP = 0$ , process is isobaric.

**Heat ( $q$ ) and heat capacity ( $C$ )**

- Heat capacity,  $C = dq/dT$
- $C_v = \left(\frac{\partial U}{\partial T}\right)_V$ ;  $C_p = \left(\frac{\partial H}{\partial T}\right)_P$
- When  $n_1$  moles of gas A and  $n_2$  moles of gas B are mixed.

$$(C_v)_{\text{mix}} = \frac{n_1 C_{v1} + n_2 C_{v2}}{n_1 + n_2}$$

- $C_p - C_v = nR$

**Work ( $W$ )**

- $W = -P_{\text{ext}} \Delta V$   
[irreversible isothermal expansion]
- $W = -2.303nRT \log(P_1/P_2)$
- $W = -2.303nRT \log(V_2/V_1)$   
[reversible isothermal expansion]
- $W = nC_v dT = \frac{nR}{\gamma - 1}(T_2 - T_1)$   
[reversible adiabatic expansion]  
where,  $\gamma = C_p/C_v$
- $W = -P_{\text{ext}} R \left( \frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right)$   
[irreversible adiabatic expansion]

**Bond enthalpy**  
It is the enthalpy change accompanying the breaking of one mole of covalent bonds.  
Bond enthalpy =  
 $\sum$  Bond enthalpies of reactants  
 $- \sum$  Bond enthalpies of products

**Enthalpy ( $H$ )**  
Total heat of the system

- $H = U + PV$
- $\Delta H = \Delta U + P\Delta V = C_p \Delta T = \Delta U + \Delta n_p RT$  (at constant pressure)
- $\Delta H = \sum H_{\text{product}} - \sum H_{\text{reactant}}$   
= -ve (exothermic)  
= +ve (endothermic)

**Gibbs Free Energy ( $G$ )**  
Useful work done by the system

- $G = H - TS$
- $\Delta G = \Delta H - T\Delta S$   
(Gibbs - Helmholtz equation)
- $\Delta G^\circ = \sum G_f^\circ(\text{product}) - \sum G_f^\circ(\text{reactant})$
- $\Delta G^\circ = -2.303 RT \log K_{\text{eq}}$
- If  $\Delta G = +ve$  (Non-spontaneous)
- If  $\Delta G = -ve$  (Spontaneous)

**Enthalpy of combustion,  $\Delta_c H$**   
It is the enthalpy change when 1 mole of a substance burnt completely in air.

**Hess's law of constant heat summation**  
 $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

**Enthalpy change of a reaction**  
It is the enthalpy change when a given reactant reacts completely.

**Enthalpy of formation**  
It is the enthalpy change occurring during the formation of 1 mole of a substance from its elements.

**Enthalpy of solution**  
 $\Delta_{\text{sol}} H = \Delta_{\text{ionise}} H + \Delta H_{\text{hyd}}$   
where,  $\Delta_{\text{ionise}} H = S + I + \frac{1}{2} D - \Delta_f H + E.A.$

**Zeroth law:** System in thermal equilibrium with each other have same temperature.

**First law:** The total energy of the universe remains constant although it may undergo transformation from one form to the other.  
 $\Delta U = q + w$  ( $\Delta U =$  internal energy)

**Second law:** In a spontaneous process total energy of the universe increases.  
 $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

**Entropy ( $S$ )**  
Measure of randomness or disorder

- $\Delta S = \frac{q_{\text{rev}}}{T}$  (reversible process)
- $\Delta S = 2.303n C_v \log\left(\frac{T_2}{T_1}\right) + 2.303nR \log\left(\frac{V_2}{V_1}\right)$
- $\Delta S = 2.303n C_p \log\left(\frac{T_2}{T_1}\right) + 2.303nR \log\left(\frac{P_1}{P_2}\right)$
- $\Delta S = 2.303nR \log\left(\frac{V_2}{V_1}\right)$  } isothermal
- $\Delta S = 2.303nR \log\left(\frac{P_1}{P_2}\right)$  }
- $\Delta S = 2.303n C_p \log\left(\frac{T_2}{T_1}\right)$  [isobaric]

**Third law**

- Entropy of all pure crystals is zero at the absolute zero temperature.
- $\lim_{T \rightarrow 0} S = 0$
- Residual Entropy  
 $S_R = k \ln W$   
( $W =$  thermodynamic probability)

# Engineering Thermodynamics Notes

**Massachusetts Institute of  
Technology. Department of  
Mechanical  
Engineering, Massachusetts Institute  
of Technology. Special Summer  
Program on Thermodynamics for  
Engineers and Chemists, 1958**

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**Engineering Thermodynamics** David J. Timoney, 2000 *Engineering Thermodynamics (MEEN 1003)* David J. Timoney, 2001 Lecture Notes on Fundamentals of Combustion, **Advances in Heat Transfer**, 1982-06-24 *Advances in Heat Transfer* *Lecture Notes for Thermodynamics for Engineers and Chemists* Massachusetts Institute of Technology. Department of Mechanical Engineering, Massachusetts Institute of Technology. Special Summer Program on Thermodynamics for Engineers and Chemists, 1958, 1958\* Commonly Asked Questions in Thermodynamics Marc J. Assael, Geoffrey C. Maitland, Thomas Maskow, Urs von Stockar, William A. Wakeham, Stefan Will, 2022-08-05 CRC Press is pleased to introduce the new edition of *Commonly Asked Questions in Thermodynamics* an indispensable resource for those in modern science and engineering disciplines from molecular science engineering and biotechnology to astrophysics Fully updated throughout this edition features two new chapters focused on energy utilization and biological systems This edition begins by setting out the fundamentals of thermodynamics including its basic laws and overarching principles It provides explanations of those principles in an organized manner using questions that arise frequently from undergraduates in the classroom as the stimulus These early chapters explore the language of thermodynamics the first and second laws statistical mechanical theory measurement of thermodynamic quantities and their relationships phase behavior in single and multicomponent systems electrochemistry and chemical and biochemical reaction equilibria The later chapters explore applications of these fundamentals to a diverse set of subjects including power generation with and without fossil fuels for transport industrial and domestic use heating decarbonization technologies energy storage refrigeration environmental pollution and biotechnology Data sources for the properties needed to complete thermodynamic evaluations of many processes are included The text is designed for readers to dip into to find an answer to a specific question where thermodynamics can provide some if not all of the answers whether in the context of an undergraduate course or not Thus its readership extends beyond conventional technical undergraduates to practicing engineers and also to the interested lay person who seeks to understand the discourse that surrounds the choice of particular technological solutions to current and future energy and material production problems *Catalog* University of Colorado Boulder, 2009 **Engineering Magazine**, 1914 **The Engineering Index Annual for ...**, 1915 Since its creation in 1884 Engineering Index has covered virtually every major engineering innovation from around the world It serves as the historical record of virtually every major engineering innovation of the 20th century Recent content is a vital resource for current awareness new production information technological forecasting and competitive intelligence The world's most comprehensive interdisciplinary engineering database Engineering Index contains over 10.7 million records Each year over 500,000 new abstracts are added from over 5,000 scholarly journals trade magazines and conference proceedings Coverage spans over 175 engineering disciplines from over 80 countries Updated weekly *The American Catalogue*, 1908 American national trade bibliography

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