

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)

Thermodynamics Mechanical Engineering Notes

Mansfield Merriman



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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* Thermodynamics and Energy Conversion Henning Struchtrup, 2014-07-02 This textbook gives a thorough treatment of engineering thermodynamics with applications to classical and modern energy conversion devices Some emphasis lies on the description of irreversible processes such as friction heat transfer and mixing and the evaluation of the related work losses Better use of resources requires high efficiencies therefore the reduction of irreversible losses should be seen as one of the main goals of a thermal engineer This book provides the necessary tools Topics include car and aircraft engines including Otto Diesel and Atkinson cycles by pass turbofan engines ramjet and scramjet steam and gas power plants including advanced regenerative systems solar tower and compressed air energy storage mixing and separation including reverse osmosis osmotic power plants and carbon sequestration phase equilibrium and chemical equilibrium distillation chemical reactors combustion processes and fuel cells the microscopic definition of entropy The book includes about 300 end of chapter problems for homework assignments and exams The material presented suffices for two or three full term courses on thermodynamics and energy conversion *Annual Catalogue of the Stevens Institute of Technology* Stevens Institute of Technology, 1921 Thermodynamics Notes J. Patterson, 1970 *Advances in Heat Transfer*, 1982-06-24 *Advances in Heat Transfer* *Report of the Proceedings*, 1911 *Locomotive Sparks* William Freeman Myrick Goss, 1907 **Analytical chemistry v.2** Frederick Pearson Treadwell, 1904 Mathematical Monographs David Raymond Curtiss, 1896 *Concrete-block Manufacture* Harmon Howard Rice, 1906 **The Economic Theory of the Location of Railways** Arthur Mellen Wellington, 1887 *A Text-book on Roofs and Bridges: Graphic statics. 1890* Mansfield Merriman, 1907 **Synthetic Projective Geometry** George Bruce Halsted, 1896 The Disposal of Municipal Refuse Harry de Berkeley Parsons, 1906 **A Text-book of Field Astronomy for Engineers** George Cary Comstock, 1905 Microscopical Physiography of the Rock-making Minerals i.e. Karl Harry Ferdinand Rosenbusch, 1905 A Text-book of physiological chemistry Olof Hammarsten, 1904 **Steam-turbines** Carl Clapp Thomas, 1906 *General chemistry* Wilhelm Ostwald, 1906 **Grassman's Space Analysis** Edward Wyllys Hyde, 1896

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