

Materials Engineering Science  
MESC. 5025

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Chapter 1.  
Thermodynamics

# Introduction and Nomenclature

- **Thermodynamics:** Study of Transformation of Energy
- **The Four Laws of Thermodynamics:**
  - **Zeroth Law:** Concept of Temperature
  - **First Law:** Conservation of Energy in Isolated Systems
  - **Second Law:** Evolution of the Entropy During a Process
  - **Third Law:** Entropy is a State Function of well defined magnitude.
- **Zeroth Law:** If A is in thermal equilibrium with B and B is in thermal equilibrium with C, then A is in thermal equilibrium with C ( $T_A = T_B = T_C$ ). Thermometer and the Absolute Temperature (Kelvin) Scale (ideal gas law).

## Definitions:

- **System:** Part of the Universe you wish to study and model.
- **Surroundings:** Part of the Universe outside the System that interacts with the System.
- **Process:** Evolution of a System from one State to another State (i.e. change in Physical State (Solid, Liquid, Vapor, Composition, Number of Phases) or change in Chemical State (reaction)).
- **Work:** A Process that Does Work is one that could be used to bring about a change in the height of a weight in the surroundings.

Work = opposing force x distance

Volumetric Expansion/Compression:  $w = -P_{\text{ext}} dV$

Surface Creation/Shrinkage:  $w = \gamma dA$

Uniaxial Tension/Compression:  $w = f dl$

Electrical:  $w = q d\phi$

- **State Function:** Function well defined for any equilibrium state of a system (homogeneous, time invariance, continuity, differentiability)

- **Energy:** Energy of a system is its capacity to do work.
- **Heat:** Experience has shown that the energy of a system can be changed by means other than work. When the energy of a system changes as a result of a temperature difference between system and surroundings, energy has been transferred as heat. Note that during isothermal expansion of an ideal gas heat is exchanged with surroundings.
- **Closed System:** No matter is exchanged between system and surroundings.
- **Isolated System:** No energy and no matter can be exchanged between system and surroundings.
- **Open System:** Energy and matter can be exchanged with surroundings
- **Adiabatic Process:** No heat is exchanged between system and surroundings. (**Diathermic Process:** Not adiabatic).
- **Isothermal, Isochoric, Isobaric:** resp. cst T, V, P

- Note that Work is a transfer of energy that makes use of an organized motion of its constituents (atoms, electrons, etc..) whereas Heat makes use of chaotic motion.
- The Energy of the System is called the **Internal Energy (U, E)**. The work is denoted by **w** and the heat by **q**.  
For elementary processes, we define **dU, w, q**. Note that whereas U is a state function (dU is an exact differential), w and q are not state functions ( w and q are not exact differentials).
- **First Law of Thermodynamics:**

$$\Delta U = U_{\text{fin}} - U_{\text{init}} = w + q \qquad dU = w + q$$

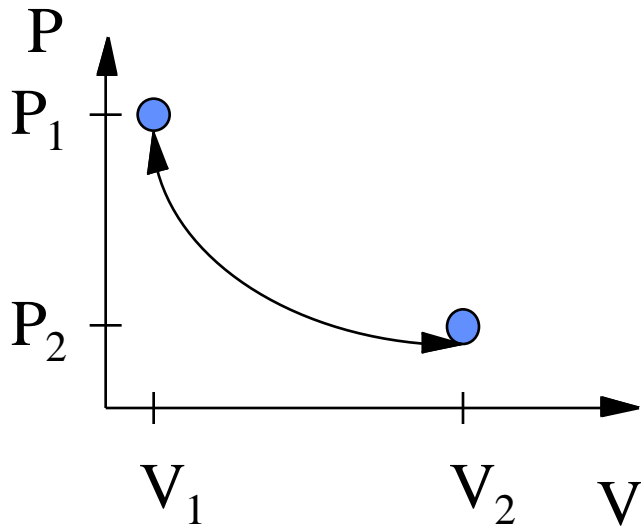
U is the **CHANGE** in internal energy of the system during the process for which q and w are the heat and the work exchanged between system and surroundings.

Note  $U = 0$  for isolated system and  $U_{\text{univ}} = \text{cst}$

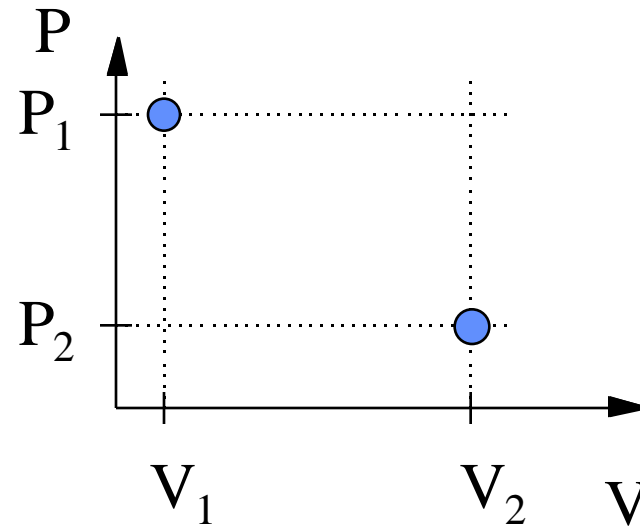
sign Convention: w and q are positive when they flow into the system (work done on system is positive, by system is negative).

# Concept of Mechanical and Thermal Equilibrium

- A system is in equilibrium if infinitesimal changes in its state in opposite directions result in opposite changes in its state.
- **Mechanical Equilibrium:** Example Ideal Gas Comp./Exp.



Reversible, “Slow”, Quasistatic Process: System remains near equilibrium at all times.  $P_{\text{ext}}$  is equal to  $P$  throughout.



Irreversible, “Fast”, Process: System is out of equilibrium at all times except initial and final states.  $P_{\text{ext}}$  differs from  $P$ .

- **Thermal Equilibrium:** Temperature of the system is equal to that of the surroundings at all times during the process, the system is in thermal equilibrium with the surroundings.
- **Isochoric Processes (constant Volume Processes):**

$$dU = w_{\text{exp}} + w_{\text{oth}} + q$$

If  $V$  is constant and no other work, then:  $dU = q_V$

$C_V =$  Heat Capacity at constant Volume ( $C_{V_m}, C_V$ )

$$C_V = \lim_{dT \rightarrow 0} \frac{\partial q}{\partial T}_V = \frac{\partial U}{\partial T}_V$$

$$U = C_V T \quad \longrightarrow$$

if  $C_V$  can be assumed independent of  $T$  between  $T_i$  and  $T_f$ .

$$U = \int_{T_i}^{T_f} C_V(T) dT \quad \longrightarrow$$

general expression

- **Isobaric Processes (Constant Pressure Processes):**

- Many physical processes occur at constant P ( $dP = 0$ )

- Define an equivalent relationship at cst P using the enthalpy state function  $H = U + PV$

$$dH = d(U+PV) = dU + PdV + VdP$$

$$dH = w_{\text{exp}} + w_{\text{oth}} + q + PdV$$

$$dH = -P_{\text{ext}} dV + w_{\text{oth}} + q + PdV$$

assume the system is under mechanical equilibrium

( $P_{\text{ext}} = P$ ) and there is no other work.  $dH = q_P$

$C_P$  = Heat Capacity at constant Pressure ( $C_{Pm}$ ,  $C_P$ )

$$C_P = \lim_{dT \rightarrow 0} \frac{\partial q}{\partial T}_P = \frac{\partial H}{\partial T}_P$$

$H = C_P T$   $\longrightarrow$  if  $C_P$  can be assumed independent of

$T$  between  $T_i$  and  $T_f$ .

$H = \int_{T_i}^{T_f} C_P(T) dT$   $\longrightarrow$  general expression

$$C_{P,m} = a + bT + \frac{c}{T^2}$$

# General Expressions for U, H for Closed Systems of Constant Composition

- For a closed system with a single component, only two intensive variables are sufficient to describe any other intensive property of the system (**Gibbs Rule of Phase**).
- **Intensive Property**: independent of the number of moles or mass of system. **Extensive Property** increases linearly with the number of moles or mass of the system.
- Internal Energy:  $U = U(V, T)$  or  $U_m = U_m(V_m, T)$ :

$$dU = \frac{\partial U}{\partial T}_V dT + \frac{\partial U}{\partial V}_T dV = C_V dT + \pi_T dV$$

$$\frac{\partial U}{\partial T}_P = C_V + \pi_T \frac{\partial V}{\partial T}_P = C_V + \alpha \pi_T V$$

Internal Pressure

$$\alpha = \frac{1}{V} \frac{\partial V}{\partial T}_P \longrightarrow \text{Isobaric Coefficient of Thermal Expansion}$$

- Enthalpy:  $H = H(P, T)$  or  $H_m = H_m(P, T)$ :

$$dH = \left. \frac{\partial H}{\partial T} \right|_P dT + \left. \frac{\partial H}{\partial P} \right|_T dP = C_P dT + \left. \frac{\partial H}{\partial P} \right|_T dP$$

$$\left. \frac{\partial H}{\partial T} \right|_V = C_P + \left. \frac{\partial H}{\partial P} \right|_T \left. \frac{\partial P}{\partial T} \right|_V = C_P - \left. \frac{\partial T}{\partial P} \right|_H \left. \frac{\partial H}{\partial T} \right|_P \left. \frac{\partial P}{\partial T} \right|_V$$

$$\mu = \left. \frac{\partial T}{\partial P} \right|_H \quad \text{and} \quad \kappa_T = \frac{-1}{V} \left. \frac{\partial V}{\partial P} \right|_T \quad \begin{array}{l} \mu: \text{Joule-Thomson Coefficient} \\ \kappa_T: \text{Isothermal Compressibility} \end{array}$$

$$\left. \frac{\partial H}{\partial T} \right|_V = 1 - \frac{\alpha \mu}{\kappa_T} C_P$$

- Universal Relationship Between  $C_P$  and  $C_V$

$$C_P - C_V = \frac{\alpha^2 V T}{\kappa_T} \quad (\text{demonstrate yourself !!!})$$

# Thermodynamic Definition of Entropy

- The entropy is an extensive state function defined by:  
 $dS_{\text{Total}} = dS_{\text{Surr}} + dS$  and  $dS_{\text{Surr}} = -q / T$   
where  $q$  is the heat increment exchanged between system and surroundings (note  $q > 0$  if heat flows into the system).
- Therefore:  $dS = dS_{\text{Total}} + q / T$
- **The Second Law of Thermodynamics** states (without proof) that for a spontaneous (irreversible) process  $dS_{\text{Total}} > 0$  (or  $dS > q / T$ ) and for a reversible process (under mechanical, thermal and chemical equilibrium)  $dS_{\text{Total}} = 0$  (or  $dS = q / T$ ).
- Entropy is a state function:  $dS_{\text{rev}} = \frac{\delta q}{T} = 0$
- Entropy change for adiabatic reversible processes:  $S = 0$

- Entropy Change associated with a Phase Transition:

If a phase transformation occurs under reversible conditions (i.e. at equilibrium T, P states along the phase coexistence curve),

$dS = q / T = dH / T$  therefore:

$$S_{\text{trans}} = H_{\text{trans}} / T_{\text{trans}} \text{ (increase in order implies decrease in } S)$$

- Entropy Change resulting from a Reversible Expansion or Compression of an Ideal Gas under Isothermal Conditions:

$$S = nR \ln (V_f / V_i) \text{ Note: Equation of State } f(P, V, T) \text{ is needed}$$

- Entropy Change resulting from a Reversible Temperature Change at Constant Pressure (any material):

$$S = C_P \ln (T_f / T_i) \text{ assuming } T_f - T_i \text{ small}$$

- Entropy Change resulting from a Reversible Temperature Change at Constant Volume (any material):

$$S = C_V \ln (T_f / T_i) \text{ assuming } T_f - T_i \text{ small}$$

## Measurement of Entropies:

- Defining  $T_m$  and  $T_b$ , respectively as the melting temperature and the boiling point of a pure substance at a pressure  $P$ , we can calculate the entropy change between zero Kelvin and some temperature  $T$  above the boiling point starting with:

$$dS = \frac{\delta q}{T} = \frac{dH}{T} = C_P(T) \frac{dT}{T} \quad \text{for heating reversibly at constant } P$$

$$dS = \frac{\delta q}{T} = \frac{dH}{T} \quad \text{for a phase transformation occurring reversibly at constant } P, T$$

$$S(T) - S(0) = \int_0^{T_m} C_P^S(T) \frac{dT}{T} + \frac{H_m}{T_m} + \int_{T_m}^{T_b} C_P^L(T) \frac{dT}{T} + \frac{H_b}{T_b} + \int_{T_b}^T C_P^V(T) \frac{dT}{T}$$

All quantities on the R.H.S. of the above equation can be measured readily by calorimetry. Data at very low  $T$  is obtained from the Debye eqn. ( $C_p = a T^3$ ) through fitting of data at slightly higher  $T$ . Only  $S(0)$  cannot be obtained experimentally.

# The Third Law of Thermodynamics: Entropy and Disorder

- At  $T = 0$  Kelvin, all thermal motion has been quenched and in a perfect crystal all particles are in a regular uniform array. The absence of both spatial disorder and thermal motion “suggests” that such materials also have zero entropy as zero Kelvin.
- **Boltzmann Formula:**  $S = k \ln \Omega$  with  $\Omega = 1$  and  $S = 0$
- **Nernst Theorem:**  
The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero.
- **Third Law:**  
If the entropy of every element in its most stable state at  $T = 0$  K is taken as zero, then every substance has a positive entropy which at  $T = 0$  K may become zero, and which does become zero for all perfect crystalline substance, including compounds.

# Helmoltz and Gibbs Free Energies

- Entropy is the basic concept for discussing the direction of spontaneous change between two states. However it is awkward as it requires calculations both for the system and for the surroundings.
- The goal here is to define new thermodynamic functions that provide us with a simple criterion for the direction of spontaneous change under practical conditions (cst T, cst P, cst V, etc...)
- Second Law:  $dS_{\text{Total}} = - q / T + dS > 0$  (spontaneous)  
Therefore  $q - T dS < 0$  (spontaneous)
- **Processes occurring at constant Temperature and Volume**  
 $q_V = dU$  implies  $dU - T dS = d(U-TS) < 0$   
We thus define the state function A (Helmoltz Free Energy):  
 $A = U - TS$      $dA = dU - TdS$  at constant T

- Processes occurring at constant Temperature and Pressure:

$$q_p = dH \text{ implies } dH - T dS = d(H - TS) < 0$$

We thus define the state function G (Gibbs Free Energy).

$$G = H - TS \quad dG = dH - TdS \text{ at constant T}$$

- The New Criteria for Spontaneity and Equilibrium are:

$$dA_{T,V} < 0 \text{ Spontaneous Process}$$

$$dA_{T,V} = 0 \text{ Reversible Process (Equilibrium State)}$$

and

$$dG_{T,P} < 0 \text{ Spontaneous Process}$$

$$dG_{T,P} = 0 \text{ Reversible Process (Equilibrium State)}$$

- The maximum work that can be done by a system at cst T and V is  $w_{\max} = -\Delta A$  (work done under reversible conditions)
- The maximum non-expansion work that can be done by a system at cst T and P is  $w_{\text{non-exp,max}} = -\Delta G$

# The Four Maxwell Relations

- First Maxwell Relation (based on  $dU$ )

- Let us consider a reversible process

$$w = -P_{\text{ext}} dV = -P dV \quad \text{and} \quad q = T dS$$

$$dU = -P dV + T dS$$

$U$  is a state function, therefore  $dU$  is an exact differential and the value of  $dU$  is independent of the path chosen.

$$U = f(V, S) \quad dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad \text{and} \quad \left(\frac{\partial U}{\partial S}\right)_V = T$$

$dU$  is an exact differential

$$\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S = \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V$$

Therefore

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$$

- Second Maxwell Relation (based on dH)

$$dH = d(U + PV) = dU + P dV + V dP$$

$$dH = - P dV + T dS + P dV + V dP$$

$$dH = V dP + T dS$$

leads to:

$$\frac{\partial T}{\partial P} \Big|_S = \frac{\partial V}{\partial S} \Big|_P$$

- Third Maxwell Relation (based on dA)

$$dA = d(U - TS) = dU - T dS - S dT$$

$$dA = - P dV + T dS - T dS - S dT$$

$$dA = - P dV - S dT$$

leads to:

$$\frac{\partial P}{\partial T} \Big|_V = \frac{\partial S}{\partial V} \Big|_T$$

- **Fourth Maxwell Relation (based on dG):**

$$dG = d(H - TS) = dH - T dS - S dT$$

$$dG = dU + P dV + V dP - T dS - S dT$$

$$dG = -P dV + T dS + P dV + V dP - T dS - S dT$$

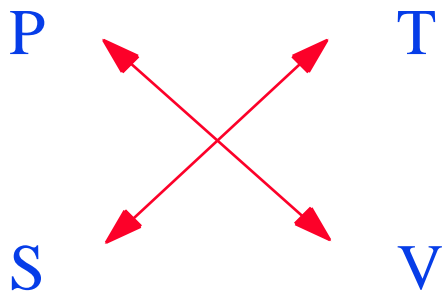
$$dG = V dP - S dT$$

Therefore:

$$\frac{\partial G}{\partial P} \Big|_T = V \quad \text{and} \quad \frac{\partial G}{\partial T} \Big|_P = -S$$

$$\frac{\partial V}{\partial T} \Big|_P = - \frac{\partial S}{\partial P} \Big|_T$$

- **Mnemotechnic and Common Sense:**



(P,V) and (S,T) are conjugate pairs

P is differentiated only w/r to S & T

S is differentiated only w/r to P & V

Use common sense for the signs...