## KMU220
## CHEMICAL ENGINEERING THERMODYNAMICS I

# INTRODUCTION
# A GENERAL REVIEW OF THERMODYNAMIC CONCEPTS

Selis Önel, Ph.D.
Hacettepe University, Department of Chemical Engineering

# Outline

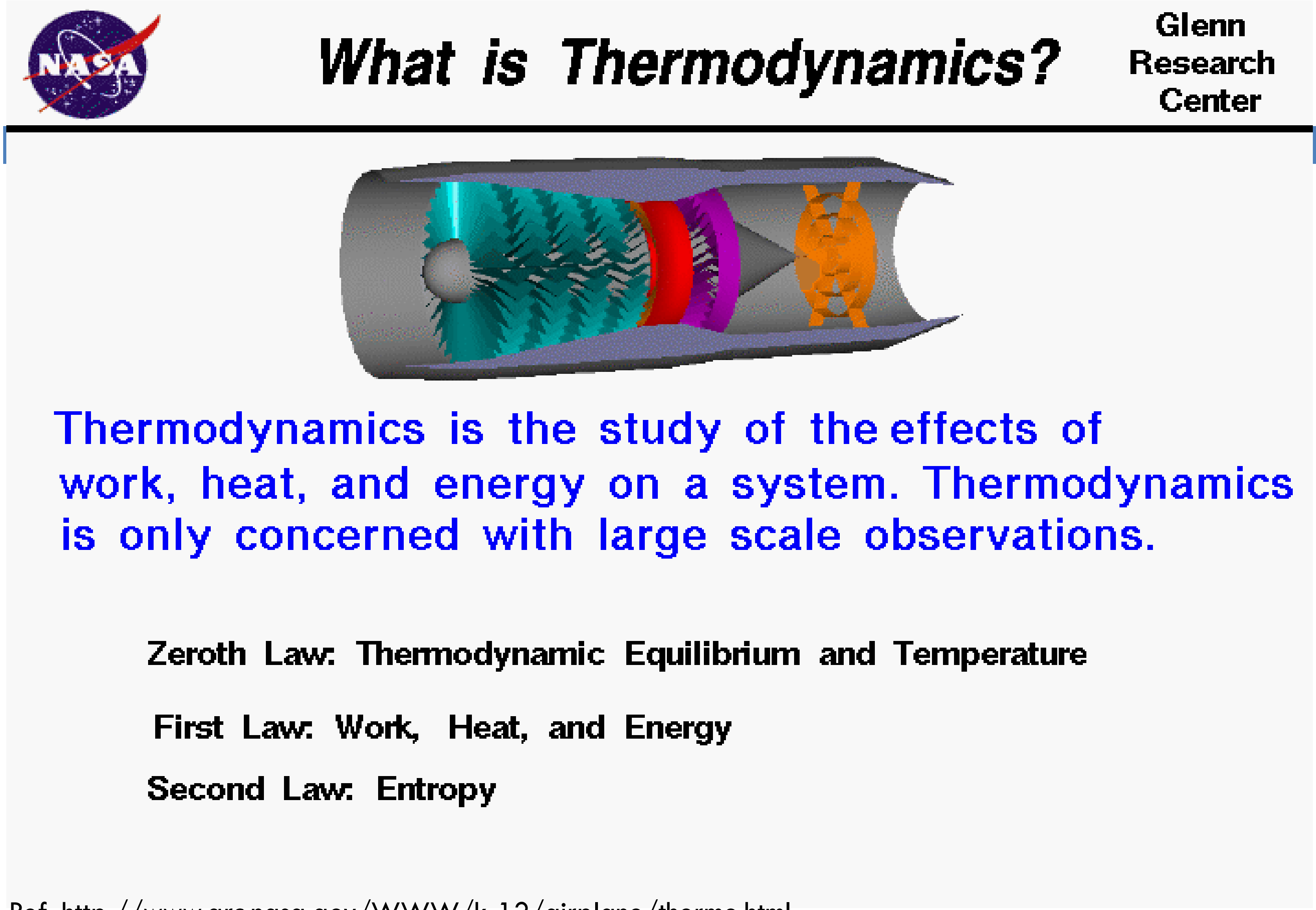
- Definition of thermodynamics
- Dimensions and units
- Force
- Temperature
- Pressure
- Work
- Energy
- Heat

# ID Card

| **Name** | **Therme Dynamis** |
|---|---|
| Date of birth | 19th century |
| Occupation | Describes operation of steam engines |
| Mother’s name | First law of thermodynamics |
| Father’s name | Second law of Thermodynamics |

Greek words: *therme (heat)* + *dynamis (power)*

*Thermodynamics* → *Power developed from heat*



# What is Thermodynamics?

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Thermodynamics is the study of the effects of work, heat, and energy on a system. Thermodynamics is only concerned with large scale observations.

Zeroth Law: Thermodynamic Equilibrium and Temperature

First Law: Work, Heat, and Energy

Second Law: Entropy

Ref: http://www.grc.nasa.gov/WWW/k-12/airplane/thermo.html

# Thermodynamics Definition

*Thermodynamics* is *a* science of energy where temperature is related to the average molecular motion → statistical mechanics

**Guggenheim's definition:** "Thermodynamics is a part of physics concerned with any equilibrium property's dependence on temperature"

Thermodynamics also formulates the average changes taking place among large numbers of molecules; therefore, it is a macroscopic science

# History

- First emergence as a science: After construction and operation of steam engines
  - in 1697 by Thomas Savery and
  - in 1712 by Thomas Newcomen in England.
- Formulations of thermodynamic principles for describing the conservation and conversion of energy
  - Carnot: @1824 →heat-fluid theory

    2nd law of thermodynamics=limitations in transferring heat into work
  - R.J. Mayer: @1842→equivalence of heat and mechanical work

    1st law of thermodynamics=Conservation of energy
  - Rankine
  - Clausius
  - Kelvin
  - Statistical mechanics: Maxwell, Boltzmann, Gibbs
  - Nernst: 3rd law

# Chemical engineer & thermodynamics

- Calculation of heat and work requirements for physical and chemical processes
- Determination of equilibrium conditions for
  - Chemical reactions
  - Transfer of chemical species between phases (mass transport)
- Thermodynamics
  - deals with driving force
  - does not deal with RATEs of physical or chemical phenomena
- Rate=f(driving force, resistance)

# Basic Thermodynamic definitions

- A ***system*** contains a substance with a large amount of molecules or atoms, and is formed by a geometrical volume of macroscopic dimensions subjected to controlled experimental conditions
- A *simple system* is a single state system with no internal boundaries, and is not subject to external force fields or inertial forces
- A *composite system* has at least two simple systems separated by a barrier restrictive to one form of energy or matter
- The *boundary* of the volume separates the system from its *surroundings*
- A system may be taken through a complete cycle of states, in which its final state is the same as its original state

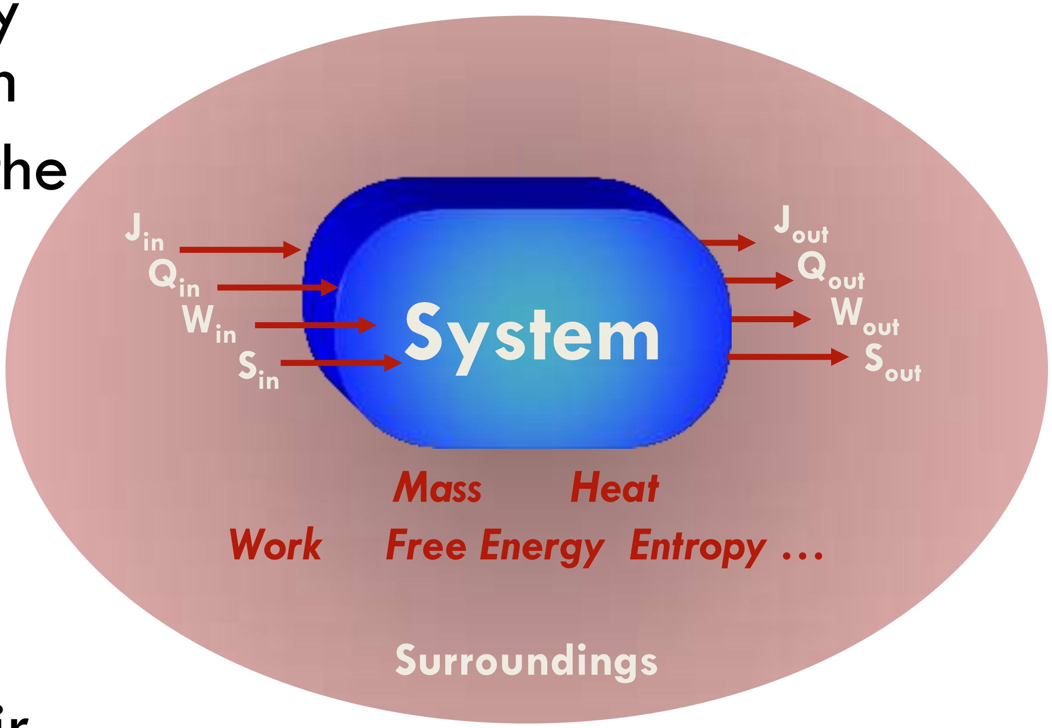
# Closed and Open systems

## Closed system:

- ☐ Material content is fixed
- ☐ Internal mass changes only due to a chemical reaction
- ☐ Exchange energy only in the form of heat or work with the surroundings

## Open system:

- ☐ Material and energy content are variable
- ☐ Systems freely exchange mass and energy with their surroundings



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# Other systems

**Isolated system:**

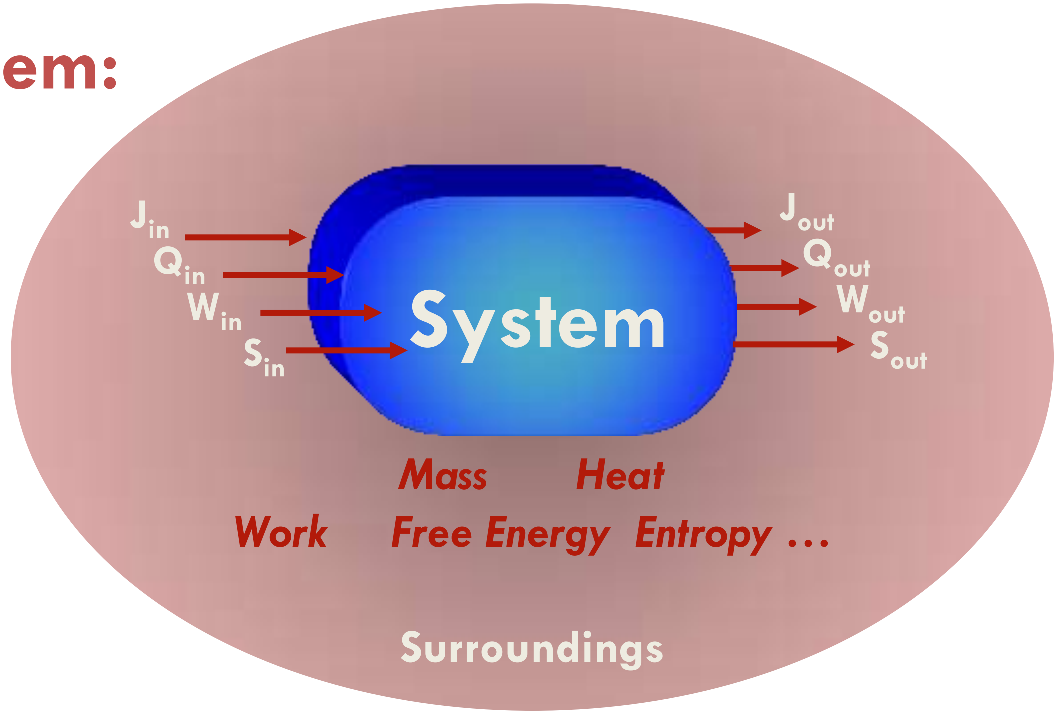
- ☐ Cannot exchange energy and matter

**Thermally insulated system:**

- ☐ System surrounded by an insulating boundary

**Universe:**

- ☐ A system and its surroundings



# Classical vs. Statistical Thermodynamics

*Classical thermodynamics* formulate the macroscopic state

- Studies the average behavior of large groups of molecules
- Defines macroscopic properties such as temperature and pressure

*Statistical thermodynamics* formulate the microscopic state

- Defines the properties of a system based on the behavior of molecules/atoms

# Processes

Energy conversion and degradation → physical and chemical processes

**A process takes place in a system!**

Adiabatic process:

- Any process within an adiabatic system (no heat transfer through the system boundaries)

Steady state process:

- Variables in the system remain constant with time
- System exchanges energy or matter at a constant rate

Unsteady state process (transient process):

- Variables in the system change with time

Infinitesimal process:

- A process that takes place with only an infinitesimal change in the macroscopic properties of a system

# Processes

Planck's classification considering three independent infinitesimal processes:

- Natural processes actually occur and always proceed in a direction toward equilibrium
- Unnatural processes are those that proceed in a direction away from equilibrium that never occurs
- Reversible process is a case between natural and unnatural processes and proceeds in either direction through a continuous series of equilibrium states

# Ex: Processes

Consider the evaporation of a liquid at an equilibrium pressure $P_{eq}$:

- If $P<P_{eq}$ → a natural evaporation takes place
- When $P>P_{eq}$ → evaporation is unnatural
- If $P=P_{eq}-\delta$, where $\delta>0$, evaporation takes place and in the limit $\delta \to 0$ process becomes reversible

Source: E.A. Guggenheim, Thermodynamics. An Advanced Treatment for Chemists and Physicists, North Holland, Amsterdam (1967)

# Thermodynamic properties

are derived from the statistical averaging of the observable microscopic coordinates of motion

- If a thermodynamic property is a *state function*
  - → its change is independent of the path between the initial and final states
  - → depends on only the properties of the initial and final states of the system
- The infinitesimal change of a state function is an exact differential

# What do we mean by the State of a System?

- The state of a system is fixed by knowing a minimum number of the system properties

  - **EXTENSIVE**
    - are additive and depend upon the mass of the system, e.g. m, n, V, H, U, etc.
  - **INTENSIVE**
    - are not additive and do not depend upon the mass of the system,e.g. P, T, refractive index,density,thermal conductivity,etc.

# Extensive properties

Properties like mass *m* and volume *V* are:

- ☐ Defined by the system as a whole (total amounts)
- ☐ Additive

All extensive properties are homogeneous functions of the first order in the mass of the system

Ex: Doubling the mass of a system at constant composition doubles the internal energy

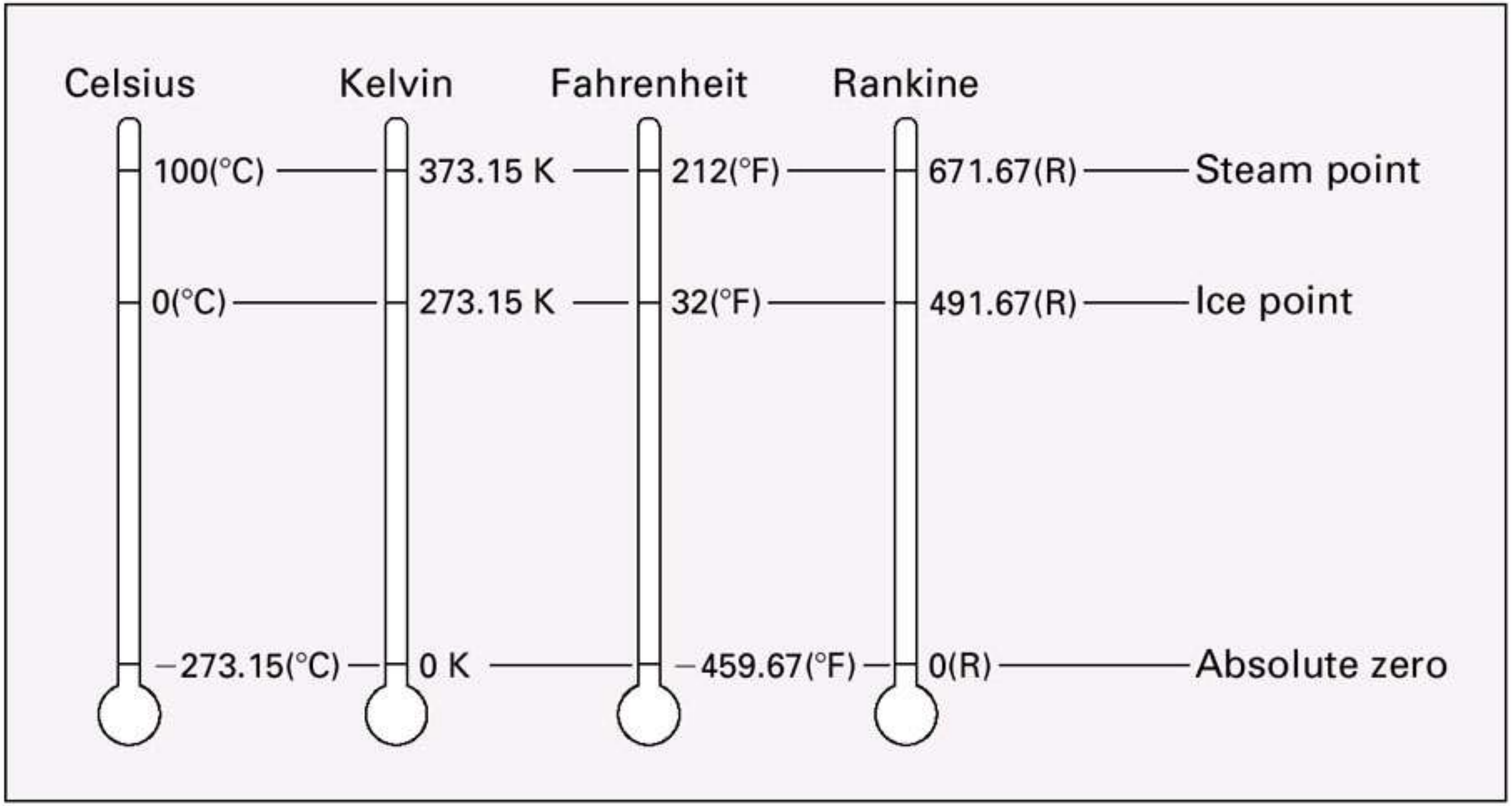
# Intensive properties

Pressure *P* and temperature *T* define the values at each point of the system and are therefore called intensive properties

- Intensive properties can be expressed as derivatives of extensive properties

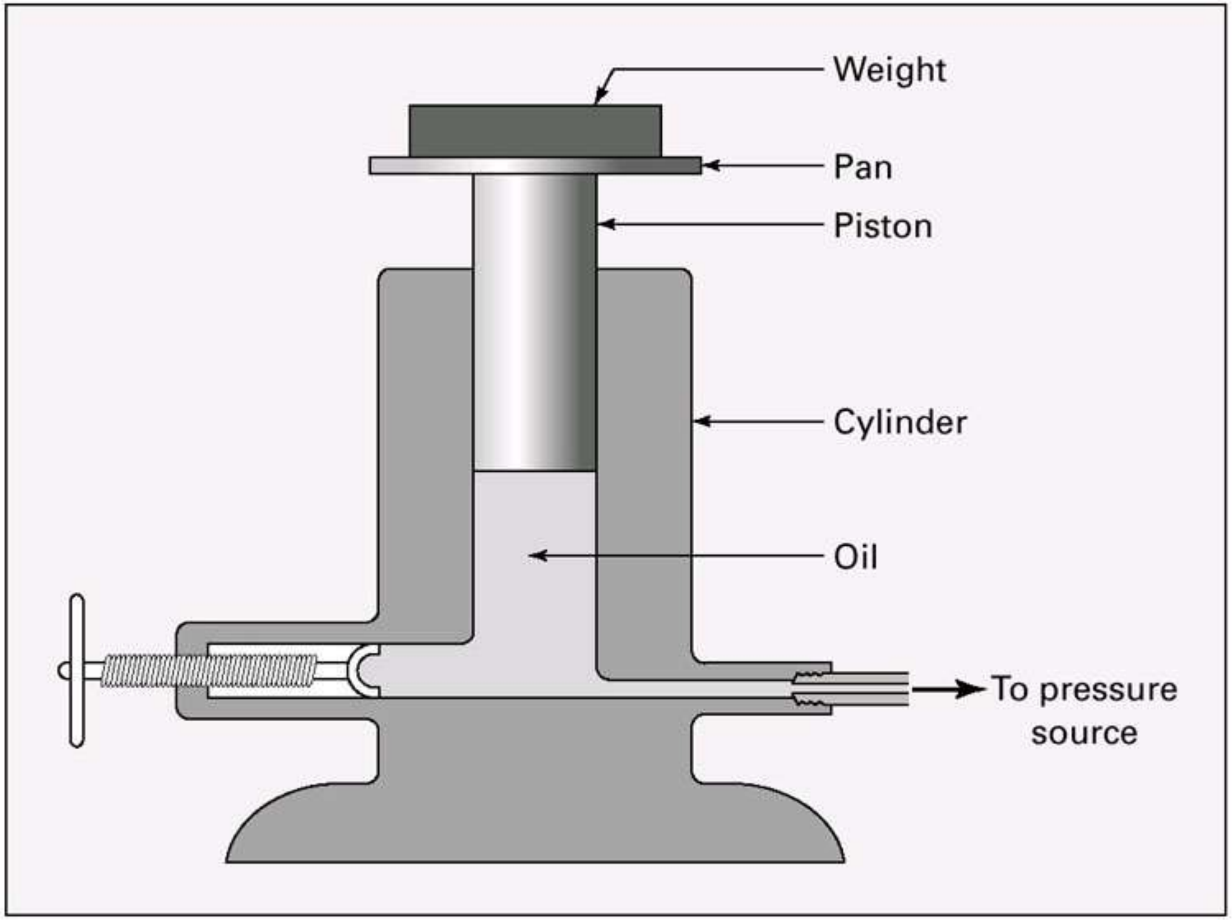
  Ex: $T = (\partial U/\partial S)_{V,Ni}$

# Temperature scales



Ref: Smith, Van Ness and Abbott, Introduction to Chemical Engineering Thermodynamics, 7th Ed, McGraw-Hill

# Pressure: Dead-weight gauge



$$P = F/A = mg/A$$
$$= Ah\rho g/A$$
$$P = h\rho g$$

Ref: Smith, Van Ness and Abbott, Introduction to Chemical Engineering Thermodynamics, 7th Ed, McGraw-Hill

# Partial properties

If $X$ denotes any extensive property (not necessarily a thermodynamic property) of a phase:

- It is possible to derive intensive properties denoted by $X_i$

  Partial property →

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_j} , \quad (i \neq j)$$

- For any partial property at constant $T$ and $P$:
- $dX = \Sigma_i(\partial X/\partial n_i)dn_i = \Sigma_i X_i dn_i$
- Euler theorem gives: $X = \Sigma_i X_i n_i$
- $v = \Sigma_i v n_i$ → Specific volume

# Energy

***Energy in Transit:*** Energy may be transferred in the form of heat or work through the system boundary

Conversion of **work** to **heat** or heat to work:

Work → Heat or Heat → Work ….. Efficiency= ?

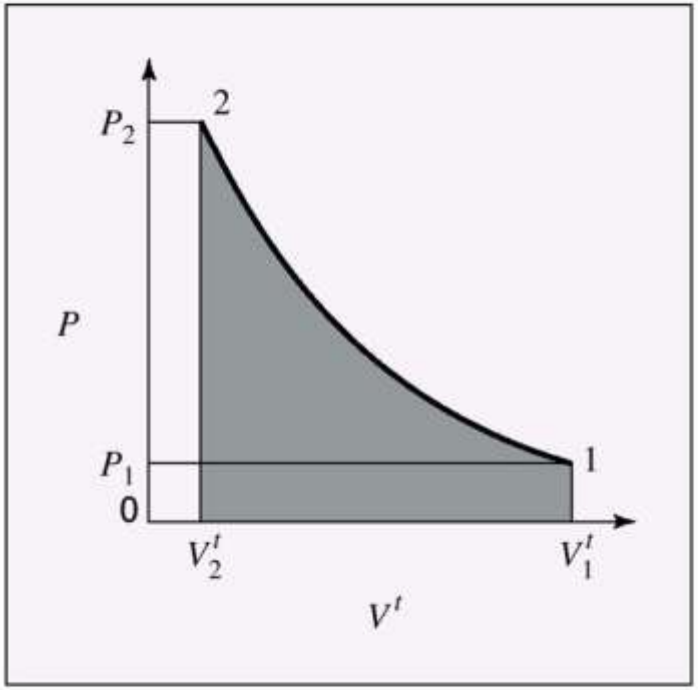
**|Work| ≠ |Heat|**

- ☐ In a complete cycle of steady-state process
  - → |work|=|heat|
  - → Internal energy change is zero ∴ work done on the system is converted to heat by the system

# Energy

- **Mechanical work** of expansion or compression proceeds with the observable motion of the coordinates of the particles of matter
- **Chemical work** proceeds with changes in internal energy due to changes in the chemical composition (mass action)
- **Potential energy** is the capacity for mechanical work related to the position of a body
- **Kinetic energy** is the capacity for mechanical work related to the motion of a body
- **Potential and kinetic energies are external energies**
- **Sensible heat and latent heat are internal energies**

# Mechanical Work: P-V



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$$dW = Fdl = -PAd\left(\frac{V^t}{A}\right) = -PdV^t$$

$$W = -\int_{V_1^t}^{V_2^t} PdV^t$$

(-) → work is done on the system, piston moves down to compress fluid,
i.e. volume change is positive
(+) → work is done on the surroundings, piston moves up to expand fluid,
i.e. volume change is negative