

"Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by then you are so used to it, it doesn't bother you any more."

Arnold Sommerfield

Principles of Thermodynamics

Thermodynamics (energetics) \equiv the study of energy utilization and interconversion

A. Definitions

1. *System*: the region of space under consideration.

A system is in a definite *state* when each of its properties has a definite value.

State variable: one having a definite value when the state of a system is specified.

A *change in state* is completely defined when the initial and final states are specified.

The *path* of a change in state is specified by the initial state, the sequence of intermediate states, and the final state.

2. *Surroundings*: everything outside the system.

3. The interface between the system and surroundings is defined by a *boundary*.

Open system: boundary permeable to heat and matter.

Closed system: boundary impermeable to matter, permeable to heat.

Isolated (adiabatic) system: boundary impermeable to both matter and heat.

C. Heat and work

1. A system can absorb *heat* (Q) from the surroundings.

$Q > 0$, if heat is *absorbed* by the system.

$Q < 0$, if heat is *evolved* from the system to the surroundings.

Heat appears only at the system boundary.

Heat appears only during a change of state.

Strictly speaking, it is incorrect to say that a system "has heat." Rather, it has thermal energy.

2. A system can perform work (W) on the surroundings.

$W > 0$, if work is done *by* the system (work input).

$W < 0$, if work is done *on* the system (work input).

Work appears only at the system boundary.

Work appears only during a change of state.

3. Q and W can be thought of as "energy in flux."

D. The Zeroth Law of Thermodynamics

Defines the concept of temperature. If two systems are each in thermal equilibrium with a third system, they must be in thermal equilibrium with each other. (The temperature scale is universal and independent of the composition of the system).

E. The First Law of Thermodynamics

First proposed by a German physician, Julius Robert Mayer.

James Prescott Joule - careful experimental work demonstrating the conversion of electrical and mechanical energy into heat.

Hermann von Helmholtz - landmark treatise on the conservation of energy (1847) provided a systematic formulation of the concept that led to its general acceptance.

Various statements:

"Energy can neither be created nor destroyed."

"The energy of an isolated system (e.g., the universe) is constant."

"Energy is conserved during any change in state."

$$\Delta E = E_f - E_i = \Delta U + \Delta PE + \Delta KE = \sum Q - \sum W$$

Closed:

$$\frac{dE}{dt} = \sum \dot{Q} - \sum \dot{W}$$

$$\Delta E = \sum Q - \sum W + \sum m_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) - \sum m_e \left(h_e + \frac{V_e^2}{2} + gz_e \right)$$

Open:

$$\frac{dE}{dt} = \sum \dot{Q} - \sum \dot{W} + \sum \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) - \sum \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right)$$

It is readily shown that the total energy is conserved during any change in state:
 Consider two systems (A and B) - - in contact, but closed.

$$E_{Af} = E_{Ai} + Q - W$$

$$E_{Bf} = E_{Bi} + (-Q) - (-W)$$

$$E_{Af} + E_{Bf} = E_{Ai} + E_{Bi}$$

$$E_{Af} - E_{Ai} = -(E_{Bf} - E_{Bi})$$

$$\Delta E_A = -\Delta E_B$$

F. Enthalpy

In many applications we study processes conducted at constant pressure ($dP=0$).

$$dE = dQ - dW$$

$$dE = dQ - pdV \text{ considering only P - V work}$$

$$\int_1^2 dE = \int_1^2 dQ - p \int_1^2 dV$$

$$E_2 - E_1 = Q_p - p(V_2 - V_1)$$

$$(E_2 + PV_2) - (E_1 + PV_1) = Q_p$$

Since E, P , and V are state variables, $(E + PV)$ must also be a state variable.

Define *Enthalpy* (H): $H \equiv U + PV$

Assuming negligible change in potential and kinetic energy we can write

$$H_2 - H_1 = Q_p$$

$\Delta H = Q_p$ The enthalpy change of the system is equal to the heat absorbed at constant pressure. Thus, ΔH is often referred to as the "heat of reaction."

G. Heat capacity $\equiv C_p \equiv$ energy required to raise the temperature of a system by one degree (at constant pressure).

$$C_p = \frac{dQ_p}{dT} = \frac{dH}{dT}$$
$$dH = C_p dT$$

$$\int_{T_1}^{T_2} dH = C_p \int_{T_1}^{T_2} dT$$

$$\Delta H = H_2 - H_1 = C_p (T_2 - T_1) \text{ Assume } C_p \text{ is independent of } T$$

$$H_2 = H_1 + C_p (T_2 - T_1)$$

$$\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)$$

Parenthetically, $C_p \approx C_v$ for solids, liquids

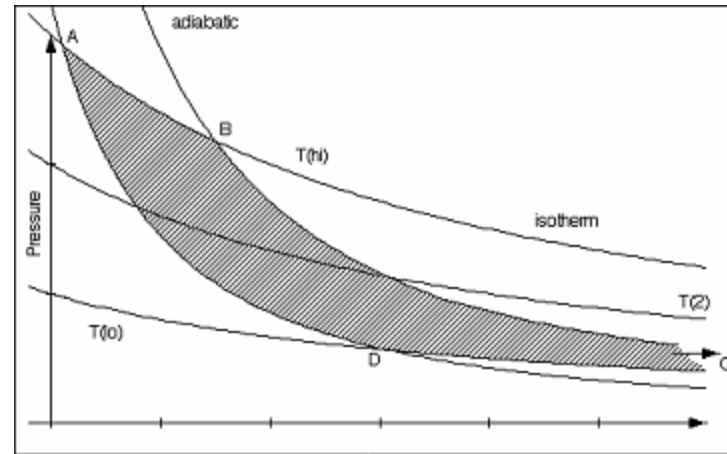
$$C_p = C_v + R \text{ for ideal gases}$$

H. Entropy and the Second Law of Thermodynamics

Although we customarily associate entropy with disorder or randomness, the first recognition of this fundamental quantity emerged from Sadi Carnot's work on "heat engines" in the early 1800's.

Consider a system consisting of a cylinder and piston subjected to the following cyclic transformation (Carnot cycle):

1. Isothermal expansion
 $T_H; Q_1$
2. Adiabatic expansion
 $T_H \rightarrow T_L; Q_2 = 0$
3. Isothermal compression
 $T_L; Q_3$
4. Adiabatic compression
 $T_L \rightarrow T_H; Q_4 = 0$



$W_{\text{cyc}} = W_1 + W_2 + W_3 + W_4; Q_{\text{cyc}} = Q_1 + Q_3$; From the First Law, $W_{\text{cyc}} = Q_{\text{cyc}} = Q_1 + Q_3$
Efficiency (ϵ) \equiv the ratio of the work produced to the quantity of heat extracted from the high temperature heat reservoir.

$$\epsilon = \frac{Q_1 + Q_3}{Q_1} = 1 + \frac{Q_3}{Q_1}; \epsilon \leq 1, \text{ since } Q_1 \text{ and } Q_3 \text{ have opposite sign.}$$

$$Q_1 = a \cdot T_H \text{ and } Q_3 = -a \cdot T_L$$

$$W_{\text{cyc}} = a(T_H - T_L)$$

$$\epsilon = \frac{W_{\text{cyc}}}{Q_1} = \frac{a(T_H - T_L)}{a \cdot T_H} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H}$$

Subtracting the two expressions for ϵ yields:

$$\frac{Q_1}{T_H} + \frac{Q_3}{T_L} = 0; \text{ generalizing, we obtain } \oint \frac{\delta Q}{T} = 0$$

Thus, $\delta Q/T$ must be a state function, which Rudolf Clausius named *entropy* (from the Greek word *entropē*, meaning “change” or “transformation”). Credit for recognizing $\delta Q/T$ as a state function is given to William Thomson (Lord Kelvin) and Clausius. It was Kelvin who formulated the first statement of the Second Law of Thermodynamics, based on a consideration of the limiting behavior of the efficiency of a process.

$$\text{Recalling that } \varepsilon = \frac{T_H - T_L}{T_H},$$

it is apparent that $\varepsilon \rightarrow 1$ as $T_H \rightarrow \infty$ or as $T_L \rightarrow 0$.

It is also apparent that, as $T_L \rightarrow T_H$, $\varepsilon \rightarrow 0$.

Thus, it is impossible for a system operating in a cycle and connected to a single heat reservoir to produce a positive amount of work in the surroundings.

I. Entropy and irreversible processes.

For real (i.e., irreversible) processes:

$$dS > \frac{\delta Q_{irrev}}{T} \text{ ("Clausius inequality")};$$

For an isolated system, $\delta Q_{irrev} = 0$. Hence, $dS > 0$.

This result yields the most common statements of the second law :

"The entropy of an isolated system tends to a maximum."

"The entropy of the universe must increase."

J. Temperature-dependence of entropy

$$dS = \frac{\delta Q_p}{T}; \text{ but } \delta Q_p = C_p dT, \text{ because } C_p \equiv \frac{\delta Q_p}{dT}$$

$$dS = \frac{C_p}{T} dT$$

$$\int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

$$S_2 = S_1 + C_p \ln\left(\frac{T_2}{T_1}\right) \text{ Assumes that } C_p \text{ is temperature - independent .}$$

$$\Delta S_2 = \Delta S_1 + \Delta C_p \ln\left(\frac{T_2}{T_1}\right)$$

K. Fundamental Thermodynamic Equations

Every system has:

two mechanical properties: P, V

three fundamental thermodynamic properties: T, E, S

three composite properties: H, G (Gibbs Free Energy), A (Helmholtz Free Energy)

$$H = E + PV$$

$$G = H - TS$$

$$A = E - TS$$

The fundamental equations:

$$1. \quad dE = TdS - PdV$$

$$\begin{aligned} 2. \quad dH &= dE + d(PV) \\ &= dE + PdV + VdP \\ &= TdS + VdP \\ dH &= TdS + VdP \end{aligned}$$

L. Real Gas vs. Ideal Gas

- Recall ideal gas as a *simplified* (yet *powerful*) model for real gas behavior
- Its original derivation assumes *negligible mutual interaction* between gas molecules. Hence, it is expected to work well for gases under *low pressure*.
- But, the next logical question will be: “How low is low?” or “Against what standard is low pressure measured with respect to?”
- To answer this question, we need to recall the *phase diagrams* of a general substance.

M. Revisit Ideal Gas Specific Heats

- In general,

$$u = u(T, v) \longrightarrow du = \underbrace{\left(\frac{\partial u}{\partial T}\right)_v}_{c_v} dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

- For an ideal gas, the specific internal energy (u), hence, specific enthalpy (h) are functions of temperature only.
- For an ideal gas, the change in specific internal energy and specific enthalpy can be simplified as:

$$h = h(T, P) \longrightarrow dh = \underbrace{\left(\frac{\partial h}{\partial T}\right)_P}_{c_p} dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

Or

$$du = c_v dT \qquad dh = c_p dT$$

N. Entropy Variation in Ideal Gas

- Recall the Gibbs equation for a general substance:

$$Tds = du + Pdv \quad \text{or} \quad Tds = dh - vdP$$

- For an ideal gas, the Gibbs equation reduces to a simpler form.

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v} \qquad ds = c_p \frac{dT}{T} - R \frac{dP}{P}$$

O. Variation in Specific Heats

- In general, the specific heats (c_v , c_p) are NOT true constants. They vary (increase) slightly with temperature even for ideal gases.
- After all, it is the change in properties that matters (their absolute values depend on the chosen reference state.)
- For an ideal gas with finite temperature change:

$$\Delta u = \int du = \int c_v dT \qquad \Delta h = \int dh = \int c_p dT$$

$$\Delta s = \int ds = \int c_v \frac{dT}{T} + \int R \frac{dv}{v} \quad \text{or} \quad \Delta s = \underbrace{\int c_p \frac{dT}{T}} - \underbrace{\int R \frac{dP}{P}}$$

P. Reference Entropy

- For variable specific heats, due to the frequent usage of the integrals, its value (from a common reference point) is tabulated.
- For entropy, a new variable is defined:

$$s^0 = \int_0^T c_p(T) \frac{dT}{T}$$

which is the temperature dependent part in entropy change

- By making use of this newly defined variable, the entropy difference between any two states can be easily expressed as:

$$s_2(T, P) - s_1(T, P) = \underbrace{s_2^0(T_2) - s_1^0(T_1)}_{\text{due to temperature change}} - \underbrace{R \ln \left(\frac{P_2}{P_1} \right)}_{\text{due to pressure change}}$$