

# Thermodynamics

## Fundamental Concepts

### Properties and State

**Intensive Properties:** Independent of mass (T, P,  $\rho$ ,  $v$ )

**Extensive Properties:** Depend on mass (V, m, E, H, S)

**Specific Property:**

$$\text{specific property} = \frac{\text{extensive property}}{\text{mass}}$$

Example:  $v = V/m$  (specific volume)

### Pressure

**Absolute Pressure:**

$$P_{abs} = P_{atm} + P_{gage}$$

**Vacuum Pressure:**

$$P_{vac} = P_{atm} - P_{abs}$$

Standard atmospheric pressure:  $P_{atm} = 101.325 \text{ kPa} = 1 \text{ atm} = 14.7 \text{ psi}$

### Temperature

**Conversions:**

$$T(K) = T(^{\circ}C) + 273.15$$

$$T(R) = T(^{\circ}F) + 459.67$$

$$T(^{\circ}F) = \frac{9}{5}T(^{\circ}C) + 32$$

## Properties of Pure Substances

### Phase Diagram and Saturation

**Saturation Temperature:**  $T_{sat}$  at given pressure

**Saturation Pressure:**  $P_{sat}$  at given temperature

**Quality (for two-phase mixture):**

$$x = \frac{m_{vapor}}{m_{total}} = \frac{m_g}{m_f + m_g}$$

**Properties in Two-Phase Region:**

$$v = v_f + x \cdot v_{fg}$$

$$u = u_f + x \cdot u_{fg}$$

$$h = h_f + x \cdot h_{fg}$$

$$s = s_f + x \cdot s_{fg}$$

where subscript  $f$  denotes saturated liquid,  $g$  denotes saturated vapor, and  $fg$  denotes difference ( $v_{fg} = v_g - v_f$ )

**Ideal Gas Law**

$$PV = mRT$$

or

$$Pv = RT$$

where  $R$  is specific gas constant

**Universal Gas Constant:**

$$R_u = 8.314 \text{ kJ}/(\text{kmol} \cdot \text{K}) = 1.986 \text{ Btu}/(\text{lbmol} \cdot \text{R})$$

**Specific Gas Constant:**

$$R = \frac{R_u}{M}$$

where  $M$  is molar mass

**Ideal Gas Relations:**

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

**First Law of Thermodynamics**

**Energy Balance**

**General Form:**

$$\Delta E_{system} = E_{in} - E_{out}$$

**Total Energy:**

$$E = U + KE + PE = U + \frac{1}{2}mv^2 + mgz$$

**Per Unit Mass:**

$$e = u + \frac{v^2}{2} + gz$$

**Closed System**

**Energy Balance:**

$$Q - W = \Delta U + \Delta KE + \Delta PE$$

For stationary system (negligible KE, PE):

$$Q - W = \Delta U = m(u_2 - u_1)$$

**Boundary Work (moving boundary):**

$$W_b = \int_{V_1}^{V_2} P dV$$

For constant pressure (isobaric):

$$W_b = P(V_2 - V_1)$$

For polytropic process ( $Pv^n = C$ ):

$$W_b = \frac{P_2 V_2 - P_1 V_1}{1 - n} = \frac{mR(T_2 - T_1)}{1 - n} \quad (n \neq 1)$$

For isothermal process of ideal gas:

$$W_b = P_1 V_1 \ln \left( \frac{V_2}{V_1} \right) = mRT \ln \left( \frac{V_2}{V_1} \right)$$

**Open System (Control Volume)**

**Mass Balance (Conservation of Mass):**

$$\frac{dm_{cv}}{dt} = \sum \dot{m}_{in} - \sum \dot{m}_{out}$$

Steady flow:  $\sum \dot{m}_{in} = \sum \dot{m}_{out}$

**Energy Balance:**

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \sum \dot{m}_{in} \left( h + \frac{v^2}{2} + gz \right)_{in} - \sum \dot{m}_{out} \left( h + \frac{v^2}{2} + gz \right)_{out}$$

### Steady-Flow Energy Equation (SFEE):

$$\dot{Q} - \dot{W} = \sum \dot{m}_{out} \left( h + \frac{v^2}{2} + gz \right)_{out} - \sum \dot{m}_{in} \left( h + \frac{v^2}{2} + gz \right)_{in}$$

For single inlet/outlet:

$$\dot{Q} - \dot{W} = \dot{m} \left[ (h_2 - h_1) + \frac{v_2^2 - v_1^2}{2} + g(z_2 - z_1) \right]$$

### Enthalpy:

$$H = U + PV$$

$$h = u + Pv$$

## Specific Heats

### Constant Volume Specific Heat:

$$c_v = \left( \frac{\partial u}{\partial T} \right)_v$$

### Constant Pressure Specific Heat:

$$c_p = \left( \frac{\partial h}{\partial T} \right)_p$$

### Ideal Gas Relations:

$$c_p = c_v + R$$

$$k = \frac{c_p}{c_v}$$

### Internal Energy Change (Ideal Gas):

$$\Delta u = c_v \Delta T$$

### Enthalpy Change (Ideal Gas):

$$\Delta h = c_p \Delta T$$

## Second Law of Thermodynamics

### Kelvin-Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce net work.

## Clausius Statement

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.

## Carnot Principles

1. No heat engine can be more efficient than a reversible engine operating between the same two reservoirs
2. All reversible heat engines operating between the same two reservoirs have the same efficiency

## Entropy

### Definition:

$$dS = \left( \frac{\delta Q}{T} \right)_{rev}$$

### Entropy Change:

$$\Delta S = \int_1^2 \left( \frac{\delta Q}{T} \right)_{rev}$$

### Clausius Inequality:

$$\oint \frac{\delta Q}{T} \leq 0$$

Equality for reversible process, inequality for irreversible

### Entropy Balance (Control Volume):

$$\frac{dS_{cv}}{dt} = \sum \frac{\dot{Q}_k}{T_k} + \sum \dot{m}_i s_i - \sum \dot{m}_e s_e + \dot{S}_{gen}$$

where  $\dot{S}_{gen} \geq 0$  (entropy generation)

### Isentropic Process:

$$\Delta s = 0$$

(reversible and adiabatic)

## Entropy Change for Different Processes

### Ideal Gas:

$$\Delta s = c_p \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{P_2}{P_1} \right)$$

$$\Delta s = c_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2}{v_1} \right)$$

**Incompressible Substance:**

$$\Delta s = c \ln \left( \frac{T_2}{T_1} \right)$$

**Isentropic Relations (Ideal Gas):**

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{(k-1)/k} = \left( \frac{v_1}{v_2} \right)^{k-1}$$

$$\frac{P_2}{P_1} = \left( \frac{v_1}{v_2} \right)^k$$

## Exergy (Availability)

**Exergy (Flow):**

$$\psi = (h - h_0) - T_0(s - s_0) + \frac{v^2}{2} + gz$$

**Exergy (Non-Flow):**

$$\phi = (u - u_0) + P_0(v - v_0) - T_0(s - s_0) + \frac{v^2}{2} + gz$$

**Exergy Destruction:**

$$X_{dest} = T_0 S_{gen}$$

**Second Law Efficiency:**

$$\eta_{II} = \frac{\text{Exergy recovered}}{\text{Exergy supplied}}$$

## Power Cycles

**Cycle Efficiency and COP**

**Thermal Efficiency (Heat Engine):**

$$\eta_{th} = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

**Coefficient of Performance (Refrigerator):**

$$COP_R = \frac{Q_L}{W_{net}} = \frac{Q_L}{Q_H - Q_L}$$

**Coefficient of Performance (Heat Pump):**

$$COP_{HP} = \frac{Q_H}{W_{net}} = \frac{Q_H}{Q_H - Q_L}$$

Note:  $COP_{HP} = COP_R + 1$

## Carnot Cycle

### Carnot Efficiency:

$$\eta_{Carnot} = 1 - \frac{T_L}{T_H}$$

### Carnot COP (Refrigerator):

$$COP_{Carnot,R} = \frac{T_L}{T_H - T_L}$$

### Carnot COP (Heat Pump):

$$COP_{Carnot,HP} = \frac{T_H}{T_H - T_L}$$

## Air-Standard Cycles

### Otto Cycle (Spark Ignition):

Compression ratio:  $r = v_1/v_2$

Efficiency:

$$\eta_{Otto} = 1 - \frac{1}{r^{k-1}}$$

### Diesel Cycle (Compression Ignition):

Compression ratio:  $r = v_1/v_2$

Cutoff ratio:  $r_c = v_3/v_2$

Efficiency:

$$\eta_{Diesel} = 1 - \frac{1}{r^{k-1}} \left[ \frac{r_c^k - 1}{k(r_c - 1)} \right]$$

### Brayton Cycle (Gas Turbine):

Pressure ratio:  $r_p = P_2/P_1$

Efficiency:

$$\eta_{Brayton} = 1 - \frac{1}{r_p^{(k-1)/k}}$$

With regeneration:

$$\eta_{regen} = 1 - \left( \frac{T_1}{T_3} \right) \left( \frac{1}{r_p^{(k-1)/k}} \right)$$

### Stirling and Ericsson Cycles:

Both have Carnot efficiency:  $\eta = 1 - T_L/T_H$

## Rankine Cycle (Vapor Power)

**Basic Components:** 1. Pump (1→2):  $w_p = v_1(P_2 - P_1) \approx v_f(P_2 - P_1)$  2. Boiler (2→3):  $q_{in} = h_3 - h_2$  3. Turbine (3→4):  $w_t = h_3 - h_4$  4. Condenser (4→1):  $q_{out} = h_4 - h_1$

**Efficiency:**

$$\eta_{Rankine} = \frac{w_t - w_p}{q_{in}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2}$$

**With Reheat:**

Turbine work increases, efficiency increases

**With Regeneration:**

Extract steam from turbine to preheat feedwater

Increases efficiency by reducing  $q_{in}$

**Back Work Ratio:**

$$bwr = \frac{w_p}{w_t}$$

Typically very small for vapor cycles (1-2%)

## Refrigeration Cycles

**Ideal Vapor-Compression Cycle:**

1. Evaporator (1→4):  $q_L = h_1 - h_4$  2. Compressor (1→2):  $w_{in} = h_2 - h_1$  3. Condenser (2→3):  $q_H = h_2 - h_3$  4. Throttling valve (3→4):  $h_4 = h_3$

**COP:**

$$COP_R = \frac{q_L}{w_{in}} = \frac{h_1 - h_4}{h_2 - h_1}$$

**Cascade Systems:**

Multiple cycles in series for large temperature differences

**Multistage Compression:**

Reduces compressor work with intercooling

## Gas Mixtures

### Composition

**Mass Fraction:**

$$mf_i = \frac{m_i}{m_{total}}$$



**Mole Fraction:**

$$y_i = \frac{N_i}{N_{total}}$$

**Conversion:**

$$mf_i = \frac{y_i M_i}{\sum y_j M_j}$$

**Dalton's Law (Ideal Gases)**

$$P = \sum P_i$$

where  $P_i = y_i P$  is partial pressure

**Amagat's Law:**

$$V = \sum V_i$$

where  $V_i = y_i V$  is partial volume

**Properties of Mixtures**

**Apparent Molar Mass:**

$$M_m = \sum y_i M_i$$

**Gas Constant:**

$$R_m = \frac{R_u}{M_m} = \sum mf_i R_i$$

**Specific Heat:**

$$c_{p,m} = \sum mf_i c_{p,i}$$

$$c_{v,m} = \sum mf_i c_{v,i}$$

**Psychrometrics (Gas-Vapor Mixtures)**

**Humidity Ratios**

**Absolute Humidity (Specific Humidity):**

$$\omega = \frac{m_v}{m_a} = 0.622 \frac{P_v}{P - P_v}$$

where  $P_v$  is partial pressure of water vapor,  $P$  is total pressure

**Relative Humidity:**

$$\phi = \frac{P_v}{P_g} = \frac{\text{actual vapor density}}{\text{saturation vapor density}}$$

where  $P_g$  is saturation pressure at given temperature

**Degree of Saturation:**

$$\mu = \frac{\omega}{\omega_s}$$

## Psychrometric Properties

**Dry-Bulb Temperature ( $T_{db}$ ):** Actual temperature

**Wet-Bulb Temperature ( $T_{wb}$ ):** Temperature with adiabatic saturation

**Dew-Point Temperature ( $T_{dp}$ ):** Temperature at which condensation begins

**Enthalpy of Moist Air:**

$$h = c_p T + \omega(h_g + c_{pv}T)$$

where  $h_g$  is enthalpy of vaporization at 0°C

Simplified:

$$h \approx c_p T + \omega h_g$$

## Air-Conditioning Processes

**Simple Heating/Cooling:** -  $\omega = \text{constant}$  - Horizontal line on psychrometric chart

**Heating with Humidification:** - Both  $T$  and  $\omega$  increase

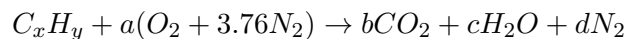
**Cooling with Dehumidification:** - Both  $T$  and  $\omega$  decrease - Process line intersects saturation curve

**Evaporative Cooling (Adiabatic Saturation):** -  $h = \text{constant}$  (approximately) -  $\omega$  increases,  $T$  decreases - Follows constant wet-bulb temperature line

## Combustion

### Stoichiometry

**General Hydrocarbon Combustion:**



For complete combustion: -  $b = x$  (carbon balance) -  $c = y/2$  (hydrogen balance) -  $d = 3.76a$  (nitrogen balance) -  $a = x + y/4$  (oxygen balance)

**Air-Fuel Ratio (AF):**

$$AF = \frac{m_{air}}{m_{fuel}}$$

**Fuel-Air Ratio:**

$$FA = \frac{m_{fuel}}{m_{air}} = \frac{1}{AF}$$

**Percent Theoretical Air:**

$$\%TA = \frac{\text{actual air}}{\text{theoretical air}} \times 100\%$$

**Percent Excess Air:**

$$\%EA = \%TA - 100\%$$

**Enthalpy of Formation and Combustion****Enthalpy of Formation ( $\bar{h}_f^\circ$ ):**

Enthalpy change when compound is formed from elements at standard state (25 °C, 1 atm)

For elements in standard state:  $\bar{h}_f^\circ = 0$

**Enthalpy of Combustion ( $\bar{h}_{RP}$ ):**

Enthalpy of reaction (negative for exothermic)

**First Law for Reacting Systems:**

$$Q - W = \sum_{\text{products}} N_i(\bar{h}_f^\circ + \Delta\bar{h})_i - \sum_{\text{reactants}} N_j(\bar{h}_f^\circ + \Delta\bar{h})_j$$

**Adiabatic Flame Temperature**

For adiabatic combustion ( $Q = 0$ ,  $W = 0$ ):

$$\sum_{\text{reactants}} N_j(\bar{h}_f^\circ + \Delta\bar{h})_j = \sum_{\text{products}} N_i(\bar{h}_f^\circ + \Delta\bar{h})_i$$

Solve iteratively for product temperature.

**Higher Heating Value (HHV):**

Water in products is liquid

**Lower Heating Value (LHV):**

Water in products is vapor

$$HHV = LHV + m_{H_2O} \cdot h_{fg}$$

**Entropy Change of Reacting Systems**

$$\Delta S = \sum_{\text{products}} N_i \bar{s}_i - \sum_{\text{reactants}} N_j \bar{s}_j + \Delta S_{\text{mixing}}$$

For ideal gases:

$$\bar{s}_i(T, P) = \bar{s}_i^\circ(T) - R_u \ln \left( \frac{P_i}{P_{ref}} \right)$$

## Thermodynamic Relations

### Maxwell Relations

From  $dU = TdS - PdV$ :

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

From  $dH = TdS + VdP$ :

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

From  $dF = -SdT - PdV$  (Helmholtz):

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

From  $dG = -SdT + VdP$  (Gibbs):

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

### Clapeyron Equation

$$\frac{dP_{sat}}{dT} = \frac{h_{fg}}{Tv_{fg}}$$

Relates slope of saturation curve to properties

**Clausius-Clapeyron Equation (for vapor):**

$$\ln \left( \frac{P_2}{P_1} \right) = - \frac{h_{fg}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

### Joule-Thomson Coefficient

$$\mu_J = \left( \frac{\partial T}{\partial P} \right)_h$$

For ideal gas:  $\mu_J = 0$

For real gas: can be positive or negative

## Quick Reference

**Common Values:** - Standard temperature:  $25^{\circ}\text{C} = 298\text{ K} = 77^{\circ}\text{F}$  - Standard pressure:  $1\text{ atm} = 101.325\text{ kPa} = 14.7\text{ psi}$  - Air:  $R = 0.287\text{ kJ}/(\text{kg} \cdot \text{K})$ ,  $c_p = 1.005\text{ kJ}/(\text{kg} \cdot \text{K})$ ,  $c_v = 0.718\text{ kJ}/(\text{kg} \cdot \text{K})$ ,  $k = 1.4$  - Water:  $c_p \approx 4.18\text{ kJ}/(\text{kg} \cdot \text{K})$

**Sign Conventions:** - Heat in: positive - Work out: positive -  $Q > 0$ : to system -  $W > 0$ : by system