

Thermodynamics

Fundamental Concepts

Properties and State

Intensive Properties: Independent of mass (T, P, ρ , 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:

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

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 ω increase

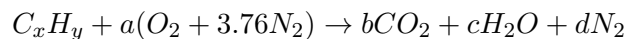
Cooling with Dehumidification: - Both T and ω decrease - Process line intersects saturation curve

Evaporative Cooling (Adiabatic Saturation): - $h = \text{constant}$ (approximately) - ω 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°):

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