Thermodynamic Laws

Zeroth Law: When two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other.

First Law (closed system): $Q = m\Delta u + W / J$
Heat entering a system can either increase temperature (internal energy) or be used to perform work on the surroundings. It is the law of energy conservation, i.e., energy cannot be created or destroyed.

Second Law (isolated system): $m\Delta s_{total} \geq 0$
The entropy change of any system and its surroundings, considered together, is positive, and approaches zero for any process that approaches reversibility. It is considered the fundamental law of natural science.

The two classical statements of the Second Law:
<u>Clausius statement</u>: It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.
<u>Kelvin-Plank statement</u>: It is impossible to construct a device that operates in a cycle and produces no effect other than the raising of a weight and the exchange of heat with a single reservoir.

Third Law: It is impossible to cool a body down to absolute zero.

Thermodynamic Laws (simplified)

First Law: You can't win, you can only break even.
Second Law: You can only break even at absolute zero.
Third Law: You can never reach absolute zero.

Thermodynamic Equations

Ideal Gas Law: $pV = nRT = NkT; V = mv; n = m/M; k = R / N_A$

The four thermodynamic potentials:

	→ - Ts	
↓	u	f
+ pv / J	h	g

Helmholtz Function: $f = u - Ts$
Gibbs Function: $g = h - Ts$

Equation of State: $p = -J\left(\frac{\partial f}{\partial v}\right)_T = J\rho^2\left(\frac{\partial f}{\partial \rho}\right)_T$

Enthalpy:

$$h = u + pv/J = \int\left[c_v + \frac{v}{J}\left(\frac{\partial p}{\partial T}\right)_v\right]dT + \frac{1}{J}\int\left[v\left(\frac{\partial p}{\partial v}\right)_T + T\left(\frac{\partial p}{\partial T}\right)_v\right]dv$$

$$= u + p/J\rho = \int\left[c_v + \frac{1}{J\rho}\left(\frac{\partial p}{\partial T}\right)_\rho\right]dT + \frac{1}{J}\int\frac{1}{\rho}\left[\left(\frac{\partial p}{\partial \rho}\right)_T - \frac{T}{\rho}\left(\frac{\partial p}{\partial T}\right)_\rho\right]d\rho$$

Entropy:

$$s = -\left(\frac{\partial f}{\partial T}\right)_v = -\left(\frac{\partial f}{\partial T}\right)_\rho = -\left(\frac{\partial g}{\partial T}\right)_p = \int\frac{c_v dT}{T} + \frac{1}{J}\int\left(\frac{\partial p}{\partial T}\right)_v dv = \int\frac{c_v dT}{T} - \frac{1}{J}\int\frac{1}{\rho^2}\left(\frac{\partial p}{\partial T}\right)_\rho d\rho$$

Isochoric Specific Heat:

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_\rho = T\left(\frac{\partial s}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_\rho = c_v^0 + \frac{1}{J}\int_\infty^v T\left(\frac{\partial^2 p}{\partial T^2}\right)_v dv = c_v^0 - \frac{1}{J}\int_0^\rho \frac{T}{\rho^2}\left(\frac{\partial^2 p}{\partial T^2}\right)_\rho d\rho$$

Isobaric Specific Heat: $c_p = \left(\frac{\partial h}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p = c_v - \frac{T\left(\frac{\partial p}{\partial T}\right)_v^2}{J\left(\frac{\partial p}{\partial v}\right)_T} = c_v + \frac{T\left(\frac{\partial p}{\partial T}\right)_\rho^2}{J\rho^2\left(\frac{\partial p}{\partial \rho}\right)_T}$

Specific Heat Ratio: $\gamma = c_p/c_v = \kappa/\kappa_s$

Velocity of Sound:

$$a = v\sqrt{Jg_c\gamma\left(\frac{\partial^2 f}{\partial v^2}\right)_T} = \rho\sqrt{Jg_c\gamma\left(\frac{\partial^2 f}{\partial \rho^2}\right)_T} = v\sqrt{-g_c\gamma\left(\frac{\partial p}{\partial v}\right)_T} = \sqrt{g_c\gamma\left(\frac{\partial p}{\partial \rho}\right)_T}$$

$$= v\sqrt{g_c\left[\frac{T\left(\frac{\partial p}{\partial T}\right)_v^2}{Jc_v} - \left(\frac{\partial p}{\partial v}\right)_T\right]} = \sqrt{g_c\left[\frac{T\left(\frac{\partial p}{\partial T}\right)_\rho^2}{J\rho^2 c_v} + \left(\frac{\partial p}{\partial \rho}\right)_T\right]}$$

Nomenclature	I-P	S-I
a = velocity of sound	ft/sec	m/sec
c_p = isobaric specific heat	Btu/lb_m-°R	kJ/kg-°K
c_v = isochoric specific heat	Btu/lb_m-°R	kJ/kg-°K
f = Helmholtz function	Btu/lb_m	kJ/kg
g = Gibbs function	Btu/lb_m	kJ/kg
g_c = gravitational conversion factor	32.174 lb_m-ft/lb_f-sec^2	1.0

h = enthalpy	Btu/lb_m	kJ/kg
J = Joule's constant	778.16926 ft-lb_f/Btu	1.0
m = mass	lb_m	kg
M = molecular weight	---	---
N = no. of molecules	---	---
n = no. of moles	lb mol	kg mol
p = pressure	lb_f/ft^2	kPa
Q = heat	Btu	kJ
s = entropy	Btu/lb_m-°R	kJ/kg-°K
T = temperature	°R	°K
u = internal energy	Btu/lb_m	kJ/kg
v = specific volume	ft^3/lb_m	m^3/kg
V = volume	ft^3	m^3
W = work	ft-lb_f	kJ
κ = isothermal compressibility	ft^2/lb_f	$(kPa)^{-1}$
κ_S = adiabatic compressibility	ft^2/lb_f	$(kPa)^{-1}$
γ = specific heat ratio	---	---
ρ = density	lb_m/ft^3	kg/m^3

Superscript: 0 = heat capacity at zero pressure

Fluid Flow Equations

Bernoulli equation: $\frac{p_1 g_c}{\gamma} + \frac{v_1^2}{2g} + z_1 = \frac{p_2 g_c}{\gamma} + \frac{v_2^2}{2g} + z_2 ; \gamma = \rho g$

Reynolds Number: $R_e = \frac{vD}{\nu} = \frac{vD\rho}{\mu g_c}$

Colebrook's natural roughness function:

$$\frac{1}{\sqrt{f}} = 1.14 + 2\log_{10}\left(D/\varepsilon\right) - 2\log_{10}\left[1 + \frac{9.3}{R_e\left(\varepsilon/D\right)\sqrt{f}}\right]$$

Colebrook equation:

$$\frac{1}{\sqrt{f}} = -2\log_{10}\left[\frac{\varepsilon/D}{3.7} + \frac{2.51}{R_e\sqrt{f}}\right]$$

Darcy-Weisbach equation: $h_f = f\frac{L_e}{D}\frac{v^2}{2g}$

Orifice equation (incompressible flow): $m = C_f A_o \sqrt{2 g_c \rho \Delta p}; R_e > 250$

Orifice equation (vapor flow):

$$m = C_f A_o \sqrt{\frac{2k}{k-1} p_u g_c \rho_u \left(\frac{p_d}{p_u}\right)\left[1-\left(\frac{p_d}{p_u}\right)^{(k-1)/k}\right]}; \frac{p_d}{p_u} > \text{critical pressure ratio}$$

$$\text{Critical pressure ratio } = \left(\frac{2}{k+1}\right)^{k/(k-1)}$$

<u>Nomenclature</u>	<u>I-P</u>	<u>S-I</u>
A_o = orifice area	ft^2	m^2
C_f = flow coefficient	---	---
D = diameter	ft	m
f = friction factor	---	---
g_c = gravitational conversion factor	32.174 lb_m-ft/lb_f-sec^2	1.0
k = specific heat ratio	---	---
h_f = head loss due to friction	ft	m
L_e = equivalent length	ft	m
m = mass flow rate	lb_m/sec	kg/sec
p = pressure	lb_f/ft^2	Pa
R_e = Reynold's Number	---	---
v = velocity	ft/sec	m/sec
z = height	ft	m
ε = effective roughness	ft	m
γ = specific weight	lb_m/ft^2-sec^2	N/m^3
μ = absolute viscosity	lb_f-sec/ft^2	Pa-sec
ν = kinematic viscosity	ft^2/sec	m^2/sec
ρ = density	lb_m/ft^3	kg/m^3

Subscripts: u = upstream; d = downstream

<u>Physical Constants</u>	<u>I-P</u>	<u>S-I</u>
g = standard acceleration due to gravity	32.1740 ft/sec^2	9.80665 m/sec^2
k = Boltzmann's constant	5.657308×10^{-24} ft-lb_f/°R	1.380650×10^{-26} kJ/°K
N_A = Avogadro's constant	$2.73159766 \times 10^{26}$ / lb mol	$6.02214199 \times 10^{26}$ / kg mol
R = universal gas constant	1545.349 ft-lb_f/lb mol-°R	8.314471 kJ/kg mol-°K