5.2 Classical thermodynamics

Thermodynamic laws

Thermodynamic temperature[a]	$T \propto \lim_{p\to 0}(pV)$	(5.1)	T V p	thermodynamic temperature volume of a fixed mass of gas gas pressure
Kelvin temperature scale	$T/\mathrm{K} = 273.16\dfrac{\lim_{p\to 0}(pV)_T}{\lim_{p\to 0}(pV)_{\mathrm{tr}}}$	(5.2)	K tr	kelvin unit temperature of the triple point of water
First law[b]	$\mathrm{d}U = đQ + đW$	(5.3)	$\mathrm{d}U$ $đW$ $đQ$	change in internal energy work done on system heat supplied to system
Entropy[c]	$\mathrm{d}S = \dfrac{đQ_{\mathrm{rev}}}{T} \geq \dfrac{đQ}{T}$	(5.4)	S T rev	experimental entropy temperature reversible change

[a]As determined with a gas thermometer. The idea of temperature is associated with the zeroth law of thermodynamics: *If two systems are in thermal equilibrium with a third, they are also in thermal equilibrium with each other.*

[b]The đ notation represents a differential change in a quantity that is not a function of state of the system.

[c]Associated with the second law of thermodynamics: *No process is possible with the sole effect of completely converting heat into work* (Kelvin statement).

Thermodynamic work[a]

Hydrostatic pressure	$đW = -p\,\mathrm{d}V$	(5.5)	p $\mathrm{d}V$	(hydrostatic) pressure volume change
Surface tension	$đW = \gamma\,\mathrm{d}A$	(5.6)	$đW$ γ $\mathrm{d}A$	work done on the system surface tension change in area
Electric field	$đW = \boldsymbol{E}\cdot\mathrm{d}\boldsymbol{p}$	(5.7)	$\boldsymbol{E}$ $\mathrm{d}\boldsymbol{p}$	electric field induced electric dipole moment
Magnetic field	$đW = \boldsymbol{B}\cdot\mathrm{d}\boldsymbol{m}$	(5.8)	$\boldsymbol{B}$ $\mathrm{d}\boldsymbol{m}$	magnetic flux density induced magnetic dipole moment
Electric current	$đW = \Delta\phi\,\mathrm{d}q$	(5.9)	$\Delta\phi$ $\mathrm{d}q$	potential difference charge moved

[a]The sources of electric and magnetic fields are taken as being outside the thermodynamic system on which they are working.

Cycle efficiencies (thermodynamic)[a]

Heat engine	$\eta = \frac{\text{work extracted}}{\text{heat input}} \le \frac{T_\mathrm{h}-T_\mathrm{l}}{T_\mathrm{h}}$	(5.10)	η efficiency T_h higher temperature T_l lower temperature
Refrigerator	$\eta = \frac{\text{heat extracted}}{\text{work done}} \le \frac{T_\mathrm{l}}{T_\mathrm{h}-T_\mathrm{l}}$	(5.11)	
Heat pump	$\eta = \frac{\text{heat supplied}}{\text{work done}} \le \frac{T_\mathrm{h}}{T_\mathrm{h}-T_\mathrm{l}}$	(5.12)	
Otto cycle[b]	$\eta = \frac{\text{work extracted}}{\text{heat input}} = 1-\left(\frac{V_2}{V_1}\right)^{\gamma-1}$	(5.13)	$\frac{V_1}{V_2}$ compression ratio γ ratio of heat capacities (assumed constant)

[a]The equalities are for reversible cycles, such as Carnot cycles, operating between temperatures T_h and T_l.
[b]Idealised reversible "petrol" (heat) engine.

Heat capacities

Constant volume	$C_V = \left.\frac{đQ}{\mathrm{d}T}\right\|_V = \left.\frac{\partial U}{\partial T}\right\|_V = T\left.\frac{\partial S}{\partial T}\right\|_V$	(5.14)	C_V heat capacity, V constant Q heat T temperature V volume U internal energy S entropy
Constant pressure	$C_p = \left.\frac{đQ}{\mathrm{d}T}\right\|_p = \left.\frac{\partial H}{\partial T}\right\|_p = T\left.\frac{\partial S}{\partial T}\right\|_p$	(5.15)	C_p heat capacity, p constant p pressure H enthalpy
Difference in heat capacities	$C_p - C_V = \left(\left.\frac{\partial U}{\partial V}\right\|_T + p\right)\left.\frac{\partial V}{\partial T}\right\|_p$	(5.16)	β_p isobaric expansivity κ_T isothermal compressibility
	$= \frac{VT\beta_p^2}{\kappa_T}$	(5.17)	
Ratio of heat capacities	$\gamma = \frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}$	(5.18)	γ ratio of heat capacities κ_S adiabatic compressibility

Thermodynamic coefficients

Isobaric expansivity[a]	$\beta_p = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right\|_p$	(5.19)	β_p isobaric expansivity V volume T temperature
Isothermal compressibility	$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right\|_T$	(5.20)	κ_T isothermal compressibility p pressure
Adiabatic compressibility	$\kappa_S = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right\|_S$	(5.21)	κ_S adiabatic compressibility
Isothermal bulk modulus	$K_T = \frac{1}{\kappa_T} = -V\left.\frac{\partial p}{\partial V}\right\|_T$	(5.22)	K_T isothermal bulk modulus
Adiabatic bulk modulus	$K_S = \frac{1}{\kappa_S} = -V\left.\frac{\partial p}{\partial V}\right\|_S$	(5.23)	K_S adiabatic bulk modulus

[a]Also called "cubic expansivity" or "volume expansivity." The linear expansivity is $\alpha_p = \beta_p/3$.

Expansion processes

Joule expansion[a]	$\eta = \left.\frac{\partial T}{\partial V}\right\vert_U = -\frac{T^2}{C_V}\left.\frac{\partial(p/T)}{\partial T}\right\vert_V$ (5.24) $= -\frac{1}{C_V}\left(T\left.\frac{\partial p}{\partial T}\right\vert_V - p\right)$ (5.25)	η Joule coefficient T temperature p pressure U internal energy C_V heat capacity, V constant
Joule–Kelvin expansion[b]	$\mu = \left.\frac{\partial T}{\partial p}\right\vert_H = \frac{T^2}{C_p}\left.\frac{\partial(V/T)}{\partial T}\right\vert_p$ (5.26) $= \frac{1}{C_p}\left(T\left.\frac{\partial V}{\partial T}\right\vert_p - V\right)$ (5.27)	μ Joule–Kelvin coefficient V volume H enthalpy C_p heat capacity, p constant

[a]Expansion with no change in internal energy.
[b]Expansion with no change in enthalpy. Also known as a "Joule–Thomson expansion" or "throttling" process.

Thermodynamic potentials[a]

Internal energy	$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$ (5.28)	U internal energy T temperature S entropy μ chemical potential N number of particles
Enthalpy	$H = U + pV$ (5.29) $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N$ (5.30)	H enthalpy p pressure V volume
Helmholtz free energy[b]	$F = U - TS$ (5.31) $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$ (5.32)	F Helmholtz free energy
Gibbs free energy[c]	$G = U - TS + pV$ (5.33) $= F + pV = H - TS$ (5.34) $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N$ (5.35)	G Gibbs free energy
Grand potential	$\Phi = F - \mu N$ (5.36) $\mathrm{d}\Phi = -S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu$ (5.37)	Φ grand potential
Gibbs–Duhem relation	$-S\,\mathrm{d}T + V\,\mathrm{d}p - N\,\mathrm{d}\mu = 0$ (5.38)	
Availability	$A = U - T_0S + p_0V$ (5.39) $\mathrm{d}A = (T - T_0)\,\mathrm{d}S - (p - p_0)\,\mathrm{d}V$ (5.40)	A availability T_0 temperature of surroundings p_0 pressure of surroundings

[a]$\mathrm{d}N = 0$ for a closed system.
[b]Sometimes called the "work function."
[c]Sometimes called the "thermodynamic potential."

Maxwell's relations

Maxwell 1	$\left.\frac{\partial T}{\partial V}\right\|_S = -\left.\frac{\partial p}{\partial S}\right\|_V \quad \left(= \frac{\partial^2 U}{\partial S \partial V}\right)$	(5.41)	U T V	internal energy temperature volume
Maxwell 2	$\left.\frac{\partial T}{\partial p}\right\|_S = \left.\frac{\partial V}{\partial S}\right\|_p \quad \left(= \frac{\partial^2 H}{\partial p \partial S}\right)$	(5.42)	H S p	enthalpy entropy pressure
Maxwell 3	$\left.\frac{\partial p}{\partial T}\right\|_V = \left.\frac{\partial S}{\partial V}\right\|_T \quad \left(= \frac{\partial^2 F}{\partial T \partial V}\right)$	(5.43)	F	Helmholtz free energy
Maxwell 4	$\left.\frac{\partial V}{\partial T}\right\|_p = -\left.\frac{\partial S}{\partial p}\right\|_T \quad \left(= \frac{\partial^2 G}{\partial p \partial T}\right)$	(5.44)	G	Gibbs free energy

Gibbs–Helmholtz equations

$U = -T^2 \left.\frac{\partial (F/T)}{\partial T}\right\|_V$	(5.45)	F U	Helmholtz free energy internal energy
$G = -V^2 \left.\frac{\partial (F/V)}{\partial V}\right\|_T$	(5.46)	G H T	Gibbs free energy enthalpy temperature
$H = -T^2 \left.\frac{\partial (G/T)}{\partial T}\right\|_p$	(5.47)	p V	pressure volume

Phase transitions

Heat absorbed	$L = T(S_2 - S_1)$	(5.48)	L T S	(latent) heat absorbed ($1 \rightarrow 2$) temperature of phase change entropy
Clausius–Clapeyron equation[a]	$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_2 - S_1}{V_2 - V_1}$ $= \frac{L}{T(V_2 - V_1)}$	(5.49) (5.50)	p V 1,2	pressure volume phase states
Coexistence curve[b]	$p(T) \propto \exp\left(\frac{-L}{RT}\right)$	(5.51)	R	molar gas constant
Ehrenfest's equation[c]	$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\beta_{p2} - \beta_{p1}}{\kappa_{T2} - \kappa_{T1}}$ $= \frac{1}{VT}\frac{C_{p2} - C_{p1}}{\beta_{p2} - \beta_{p1}}$	(5.52) (5.53)	β_p κ_T C_p	isobaric expansivity isothermal compressibility heat capacity (p constant)
Gibbs's phase rule	$\mathsf{P} + \mathsf{F} = \mathsf{C} + 2$	(5.54)	P F C	number of phases in equilibrium number of degrees of freedom number of components

[a]Phase boundary gradient for a first-order transition. Equation (5.50) is sometimes called the "Clapeyron equation."
[b]For $V_2 \gg V_1$, e.g., if phase 1 is a liquid and phase 2 a vapour.
[c]For a second-order phase transition.