

5.2 Classical thermodynamics

Thermodynamic laws

Thermodynamic temperature ^a	$T \propto \lim_{p \rightarrow 0}(pV)$	(5.1)	T thermodynamic temperature V volume of a fixed mass of gas p gas pressure
Kelvin temperature scale	$T / \text{K} = 273.16 \frac{\lim_{p \rightarrow 0}(pV)_T}{\lim_{p \rightarrow 0}(pV)_{\text{tr}}}$	(5.2)	K kelvin unit tr temperature of the triple point of water
First law ^b	$dU = \delta Q + \delta W$	(5.3)	dU change in internal energy δW work done on system δQ heat supplied to system
Entropy ^c	$dS = \frac{\delta Q_{\text{rev}}}{T} \geq \frac{\delta Q}{T}$	(5.4)	S experimental entropy T temperature rev reversible change

^aAs 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.*

^bThe δ notation represents a differential change in a quantity that is not a function of state of the system.

^cAssociated 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	$\delta W = -p dV$	(5.5)	p (hydrostatic) pressure dV volume change
Surface tension	$\delta W = \gamma dA$	(5.6)	δW work done on the system γ surface tension dA change in area
Electric field	$\delta W = \mathbf{E} \cdot d\mathbf{p}$	(5.7)	$\mathbf{E}$ electric field $d\mathbf{p}$ induced electric dipole moment
Magnetic field	$\delta W = \mathbf{B} \cdot d\mathbf{m}$	(5.8)	$\mathbf{B}$ magnetic flux density $d\mathbf{m}$ induced magnetic dipole moment
Electric current	$\delta W = \Delta\phi dq$	(5.9)	$\Delta\phi$ potential difference dq charge moved

^aThe 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	$\eta = \frac{\text{work extracted}}{\text{heat input}} \leq \frac{T_h - T_l}{T_h}$	(5.10)	η efficiency T_h higher temperature T_l lower temperature
Refrigerator	$\eta = \frac{\text{heat extracted}}{\text{work done}} \leq \frac{T_l}{T_h - T_l}$	(5.11)	
Heat pump	$\eta = \frac{\text{heat supplied}}{\text{work done}} \leq \frac{T_h}{T_h - T_l}$	(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)

^aThe equalities are for reversible cycles, such as Carnot cycles, operating between temperatures T_h and T_l .

^bIdealised reversible “petrol” (heat) engine.

Heat capacities

Constant volume	$C_V = \left.\frac{\delta Q}{dT}\right _V = \left.\frac{\partial U}{\partial T}\right _V = T \left.\frac{\partial S}{\partial T}\right _V$	(5.14)	C_V heat capacity, V constant Q heat T temperature V volume U internal energy S entropy
Constant pressure	$C_p = \left.\frac{\delta Q}{dT}\right _p = \left.\frac{\partial H}{\partial T}\right _p = T \left.\frac{\partial S}{\partial T}\right _p$	(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
	$= \frac{VT\beta_p^2}{\kappa_T}$	(5.17)	κ_T isothermal compressibility
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

^aAlso called “cubic expansivity” or “volume expansivity.” The linear expansivity is $\alpha_p = \beta_p/3$.



Expansion processes

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

^aExpansion with no change in internal energy.

^bExpansion with no change in enthalpy. Also known as a “Joule–Thomson expansion” or “throttling” process.

Thermodynamic potentials^a

Internal energy	$dU = T dS - p dV + \mu dN$	(5.28)	U internal energy T temperature S entropy μ chemical potential N number of particles
Enthalpy	$H = U + pV$	(5.29)	H enthalpy
	$dH = T dS + V dp + \mu dN$	(5.30)	p pressure V volume
Helmholtz free energy ^b	$F = U - TS$	(5.31)	F Helmholtz free energy
	$dF = -S dT - p dV + \mu dN$	(5.32)	
Gibbs free energy ^c	$G = U - TS + pV$	(5.33)	G Gibbs free energy
	$= F + pV = H - TS$	(5.34)	
	$dG = -S dT + V dp + \mu dN$	(5.35)	
Grand potential	$\Phi = F - \mu N$	(5.36)	Φ grand potential
	$d\Phi = -S dT - p dV - N d\mu$	(5.37)	
Gibbs–Duhem relation	$-S dT + V dp - N d\mu = 0$	(5.38)	
Availability	$A = U - T_0 S + p_0 V$	(5.39)	A availability
	$dA = (T - T_0) dS - (p - p_0) dV$	(5.40)	T_0 temperature of surroundings p_0 pressure of surroundings

^a $dN=0$ for a closed system.

^bSometimes called the “work function.”

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

Phase transitions

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

^aPhase boundary gradient for a first-order transition. Equation (5.50) is sometimes called the "Clapeyron equation."

^bFor $V_2 \gg V_1$, e.g., if phase 1 is a liquid and phase 2 a vapour.

^cFor a second-order phase transition.

