

USEFUL FORMULAE

Physical constants

Avagadro's number	N_A	6.022×10^{23} /mol
Boltzmann constant	k_B	1.38×10^{-23} J/K 8.617×10^{-5} eV/K
Ideal gas constant	R	8.314 J/mol K 8.206×10^{-2} l atm / mol K $k_B N_A$
Gravity at sea level	g	9.8 m/s ²
One atmosphere		1.013×10^5 Pa (J/m ³)
speed of light	c	2.998×10^8 m/s
Planck constant	h	6.626×10^{-34} J s 4.135×10^{-15} eV s
	\hbar	1.054×10^{-34} J s 0.658×10^{-15} eV s
electron volt	eV	1.602×10^{-19} J
electron charge	e	1.602×10^{-19} C
electron mass	m_e	9.109×10^{-31} kg
electron mag moment	μ_e	9.2848×10^{-24} J/T
proton mass	m_p	1.673×10^{-27} kg
proton mag moment	μ_p	1.4106×10^{-26} J/T
neutron mass	m_n	1.675×10^{-27} kg 939.6 MeV/c ²

Molecular masses

Particle	g/mol
N ₂	28
O ₂	32
He	4
Ar	40
CO ₂	44
H ₂	2
Si	28
Ge	73
Cu	64
Al	27

Symbol	meaning
T	Temperature
U	Internal energy
S	Entropy
Ω	Number of equally probable states
C_V	Heat capacity at constant volume
C_p	Heat capacity at constant pressure
V	Volume
p	Pressure
μ	Chemical potential
N	Number of particles
n	Number of moles of particles ($n = N/N_A$)
dW_{on}	Work on $-pdV$
dW_{by}	Work by pdV
H	Enthalpy $U + pV$

Mathematical identities and combinatorics

N distinguishable particles with M possible states each

N indistinguishable particles with M possible states each

Choose q from N options without replacement

$$\begin{aligned} M^N \\ M^N/N! \\ \binom{N}{q} = \frac{N!}{q!(N-q)!} \end{aligned}$$

$$\ln(A) - \ln(B) = \ln(A/B)$$

$$e^{A+B} = e^A e^B$$

Derivatives and differentials

Thermodynamic derivative notation.

$$\left(\frac{dS}{dU}\right)_{V,N} \equiv \frac{\partial S(U, V, N)}{\partial U}$$

Integration to find changes

$$\Delta x = \int dx$$

Chain rule

$$\frac{dz}{dx} = \frac{dz}{dy} \frac{dy}{dx}$$

Entropy

$$S = k_B \ln \Omega$$

Definition of temperature, pressure, and chemical potential

$$\frac{1}{T} \equiv \left(\frac{dS}{dU}\right)_{V,N}$$

$$\frac{p}{T} \equiv \left(\frac{dS}{dV}\right)_{U,N}$$

$$\frac{\mu}{T} \equiv -\left(\frac{dS}{dN}\right)_{U,V}$$

Heat capacity

Always true

Constant volume

Constant pressure

$$\begin{aligned} C &\equiv \frac{dQ}{dT} \\ C_V &= \frac{dU}{dT} \\ C_p &= \frac{dU}{dT} + p \frac{dV}{dT} \end{aligned}$$

Heat conduction

$$q = -k \frac{T_2 - T_1}{d}$$

Combine heat conductivity k same as electrical conductivity.

Ideal gas

Equation of state

$$pV = NkT$$

Isothermal processes

$$p = \frac{NkT}{V}$$

Adiabatic processes

$$p = \frac{C}{V^\gamma},$$

C constant, $\gamma = \frac{2}{N_{DOF}} + 1$

Kinetic ideal gas assumption:

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$$

Equipartition

$$U = \frac{N_{DOF}}{2} NkT + \text{constant}$$

Translational and rotational motion counts as 1 degree of freedom each, vibrational counts as 2 degrees of freedom each.

Thermodynamic processes

First law of thermodynamics (division into work and heat)

$$dU = dQ - pdV$$

Second law of thermodynamics

$$\int_{S_i}^{S_f} dS \geq 0$$

Fundamental relation of thermodynamics

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

At constant number,

$$dS = \frac{dQ}{T} = \frac{C}{T}dT$$

Typical processes:

Isothermal	T constant	reversible
Isobaric	p constant	irreversible
Isochoric	V constant	irreversible
Adiabatic	$Q = 0$	reversible

Maximum Carnot efficiency between two reservoirs at T_H, T_C

$$\frac{W}{Q_H} \leq 1 - \frac{T_C}{T_H}$$

Coefficient of performance

- Refrigeration: Q_C/W
- Heat pump: Q_H/W

Boltzmann factors and quantum systems

Boltzmann factor for state i

$$f_i = e^{-E_i/kT}$$

Probability of state i

$$P(i) = \frac{f_i}{\sum_j f_j}$$

Average internal energy

$$U = \sum_i P_i E_i$$

Heat capacity of a collection of harmonic oscillators with energy separation hf

$$C_V = 3Nk \frac{x^2 e^x}{(e^x - 1)^2}, x = \frac{hf}{kT}$$

Number of ways to distribute q quanta in N oscillators

$$\Omega = \binom{N+q-1}{q}$$

Helmholtz free energy (T,V,N)

$$F = U - T_{env}S$$

- Equilibrium occurs at minimum F
- $W_{max} = -\Delta F$

Chemical potential

$$\mu = \left(\frac{dF}{dN} \right)_{T,V}$$

Solutions

$$\frac{N_{solute}}{N_{solvent}} = C e^{-\Delta/kT}$$

Semiconductors

$$\frac{N_{conductors}}{N_{atoms}} = C e^{-\Delta/2kT}$$

Conductivity is proportional to the number of conductors.

Gibbs free energy (T,p,N)

$$G = U - TS + pV = \mu(p, T)N$$

- Equilibrium occurs at minimum G
- $W_{max} = -\Delta G$

Phases and phase transitions

Only exist at fixed pressure and temperature (otherwise coexistence of phases). Lowest $\mu \rightarrow$ equilibrium phase.

Latent heat:

$$L = \Delta H = T\Delta S$$

Variation of the chemical potential of phase X as a function of pressure and temperature:

$$d\mu_X = \frac{V_X}{N_X} dp - \frac{S_X}{N_X} dT$$

- Number Density: N_X/V_X
- Entropy per particle: S_X/N_X