

# USEFUL FORMULAE

## Physical constants

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

## Molecular masses

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

Symbol	meaning
$T$	Temperature
$U$	Internal energy
$S$	Entropy
$\Omega$	Number of equally probable states
$C_V$	Heat capacity at constant volume
$C_p$	Heat capacity at constant pressure
$V$	Volume
$p$	Pressure
$\mu$	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

$$M^N$$

$$M^N/N!$$

$$\binom{N}{q} = \frac{N!}{q!(N-q)!}$$

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

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

## 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

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

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

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

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.

## Heat capacity

Always true

$$C \equiv \frac{dQ}{dT}$$

Constant volume

$$C_V = \frac{dU}{dT}$$

Constant pressure

$$C_p = \frac{dU}{dT} + p \frac{dV}{dT}$$

## Heat conduction

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

## 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  $T_H, T_C$

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

Coefficient of performance

- Refrigeration:  $Q_C/W \leq \frac{T_C}{T_H - T_C}$
- Heat pump:  $Q_H/W \leq \frac{1}{1 - T_C/T_H}$

## 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

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

Semiconductors

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

Conductivity is proportional to the number of conductors.

**Gibbs free energy (T,p,N)**

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

Chemical potential

$$\mu = \left( \frac{dG}{dN} \right)_{T,p}$$

- 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:  $S_X/N_X$