

A GLOSSARY FOR THERMAL AND KINETIC PHYSICS

I gather together here some short definitions and explanations of many of the terms and concepts we use in TKP. I have ordered this version alphabetically.

-) ABSOLUTE TEMPERATURE: Also known as *thermodynamic temperature*, defined by Lord Kelvin in terms of the heat flows in a Carnot engine by

$$\frac{\Theta_2}{\Theta_1} = \frac{Q_2}{Q_1} .$$

The Θ scale is identical with the ideal gas temperature scale T .

-) ADIABATIC LAW: For an ideal gas undergoing an adiabatic change, we have $PV^\gamma = \text{constant}$ where γ is called the adiabatic constant for the gas. We can show that $\gamma = C_P/C_V$. We can re-express the law in terms of T and V or P and T by use of the equation of state.
-) ADIABATIC PROCESS: Any process where throughout there is no heat flow, that is, $dQ = 0$ at all points of the process. A process may be adiabatic because the system is heat insulated or because the process occurs so rapidly that there is no time for heat to flow.
-) ADIATHERMAL WALL: One which allows no heat exchange. Also called an *adiabatic* or insulating wall.
-) BLACK BODY: Any object that completely absorbs all electromagnetic radiation of any wavelength that falls on it.
-) CARNOT EFFICIENCIES: For any device operating in the Carnot cycle, the heat flow ratio is the same as the temperature ratio of the reservoirs, $Q_2/Q_1 = T_2/T_1$. Thus for Carnot engines, refrigerators and heat pumps the figures of merit (see below) may be expressed simply in terms of ratios of the reservoir temperatures.
-) CARNOT ENGINE: An ideal engine constructed with any material as working substance whose cycle of operation is isothermal expansion \rightarrow adiabatic expansion \rightarrow isothermal compression \rightarrow adiabatic compression back to the starting point.
-) DIATHERMAL WALL: One which allows a heat interchange. Also simply called a heat conducting wall.
-) DIFFUSION COEFFICIENT: Denoted by D , it is the constant of proportionality in Fick's Law. At the molecular level the mean squared displacement of a particle diffusing in three dimensions grows with time like $6Dt$ with the same coefficient D as occurs in Fick's Law.
-) EMPIRICAL TEMPERATURE: If X is any measurable property (the *thermometric property*) which varies with "hotness" of a system, then we can use that

system as a thermometer. We define the empirical temperature of a observed system as measured on the X scale by

$$T_X = 273.16 \frac{X}{X_{TP}} \quad ,$$

where X is the value when the thermometer is in thermal equilibrium with the observed system and X_{TP} is the value when the thermometer is in thermal equilibrium with water at its triple point.

-) ENGINE: A device operating in a cycle which takes in heat Q_1 from a high temperature source, expels heat Q_2 to a low temperature sink and produces useful work W .
-) ENTHALPY: A function of state denoted by H and defined as $H = U + PV$. The change in enthalpy of a system at constant pressure is equal to the heat absorbed by the system.
-) ENTROPY: A function of state denoted by S . *Changes* of entropy can be defined in terms of reversible heat flows by

$$\Delta S_{a \rightarrow b} = S_b - S_a = \int_a^b \frac{dQ_{REV}}{T} \quad .$$

Boltzmann showed that we can also define the entropy by the relation

$$S = k_B \ln \Omega \quad ,$$

where Ω is the number of microscopic arrangements of the system (microstates) that are compatible with the thermodynamic state (macrostate).

-) EQUATION OF STATE: For any substance not all the functions of state are independent. Thus for a fixed quantity (fixed N) of a fluid, only two functions of state are independent and any third function of state will be dependent on these two. This is expressed by an *equation of state* relating together the three functions of state, for example, P , V , and T . For an ideal gas the equation of state is $PV = nRT$, for a van der Waals gas it is $(P + n^2a/V^2)(V - nb) = nRT$.
-) EQUILIBRIUM: A system has come to equilibrium if all functions of state are unchanging in time and there are no steady flows of energy, momentum or charge in the system.
-) FICK'S LAW: The statement that the flux of diffusing particles (number of particles per unit area per second) is proportional to the negative of the gradient of density.
-) FIGURES OF MERIT: For ideal engines, refrigerators and heat pumps that operate between a hot reservoir and a cold reservoir , we define a figure of merit to express how well they work. All involve work W and heat flows Q_1, Q_2 . The

primary definitions are

$$\begin{aligned}\eta &= \frac{\textit{What you want out}}{\textit{What you must put in}} \quad , \\ \eta_E &= \frac{W}{Q_1} = \frac{\textit{Work output}}{\textit{Heat input from hot reservoir}} \quad , \\ \eta_R &= \frac{Q_2}{W} = \frac{\textit{Heat removed from cold reservoir}}{\textit{Work input}} \quad , \\ \eta_{HP} &= \frac{Q_1}{W} = \frac{\textit{Heat delivered to hot reservoir}}{\textit{Work input}} = \frac{1}{\eta_E} \quad .\end{aligned}$$

Using the First Law we can write these as

$$\eta_E = 1 - \frac{Q_2}{Q_1} \quad , \quad \eta_R = \frac{1}{\frac{Q_1}{Q_2} - 1} \quad , \quad \eta_{HP} = \frac{1}{1 - \frac{Q_2}{Q_1}} \quad .$$

-) **FIRST LAW OF THERMODYNAMICS:** The universal law of energy conservation. For an infinitesimal change between equilibrium states of a system we express it as

$$dU = \delta Q + \delta W \quad ,$$

where dU (a perfect differential) is the infinitesimal change in the internal energy of the system, δQ (an imperfect differential) is the heat *absorbed BY* the system and δW (an imperfect differential) is the work *done ON* the system.

For a finite change from state a to state b we write it as

$$\Delta U_{a \rightarrow b} = \oint Q_{a \rightarrow b} + \oint W_{a \rightarrow b} \quad ,$$

where the sign conventions are the same for heat and work. Here $\Delta U_{a \rightarrow b} = U_b - U_a$, while

$$\oint Q_{a \rightarrow b} = \int_a^b \delta Q \quad , \quad \oint W_{a \rightarrow b} = \int_a^b \delta W \quad .$$

The heat absorbed by the system $\oint Q_{a \rightarrow b}$ and the work done on the system $\oint W_{a \rightarrow b}$ are path dependent while the change in internal energy $\Delta U_{a \rightarrow b}$ depends only on the initial and final states and not on the path joining them.

-) **FOURIER'S LAW:** The statement that the flux of heat (heat energy per unit area per second) is proportional to the negative of the gradient of temperature.
-) **FUNCTION OF STATE:** Any macroscopic variable which takes a unique value in each equilibrium state of a system. Examples of functions of state are P , V , T , N (the number of molecules in the system), n (the number of moles in the system), H , S , F , G . Derivatives of functions of state are also functions of state as in the heat capacities C_V , C_P and in K (bulk modulus), κ (compressibility), β (thermal expansion coefficient).
-) **GIBBS FREE ENERGY:** Also known as the Gibbs function. A function of state denoted by the letter G and defined, for a fluid, as $G = U - TS + PV$. For a paramagnetic system it would be defined as $G_{mag} = U - TS - B_0 M$.

-) HEAT CAPACITY AT CONSTANT VOLUME:

$$C_V = \lim_{\Delta T \rightarrow 0} \frac{dQ_{REV}}{\Delta T} \Big|_{V=constant} = \left(\frac{\partial U}{\partial T} \right)_V, \text{ and also } C_V = T \left(\frac{\partial S}{\partial T} \right)_V .$$

-) HEAT CAPACITY AT CONSTANT PRESSURE:

$$C_P = \lim_{\Delta T \rightarrow 0} \frac{dQ_{REV}}{\Delta T} \Big|_{P=constant} = \left(\frac{\partial H}{\partial T} \right)_P, \text{ and also } C_P = T \left(\frac{\partial S}{\partial T} \right)_P .$$

-) HEAT RESERVOIR: A body at temperature T with an essentially infinite heat capacity so that we may remove or inject heat energy without changing the temperature of the body.
-) HELMHOLTZ FREE ENERGY: A function of state denoted by the letter F and defined as $F = U - TS$.
-) IDEAL GAS TEMPERATURE: The empirical temperature measured by a constant volume gas thermometer in the limit that the density and pressure tend to zero.

$$T = \lim_{P_{TP} \rightarrow 0} 273.16 \frac{P}{P_{TP}} .$$

Its unit is the Kelvin K.

-) INTERNAL ENERGY: A function of state denoted by U . It is the total energy in a system arising from the average value of all forms of molecular energy (translational kinetic energy, rotational kinetic energy, potential energy).
-) KINETIC TEMPERATURE: The temperature as measured by the mean kinetic energy of the molecules in a system,

$$\frac{\overline{mv^2}}{2} = \frac{3}{2} k_B T .$$

-) LATENT HEAT: When a substance undergoes a change of phase (*solid* \leftrightarrow *liquid*, *liquid* \leftrightarrow *vapour* or *solid* \leftrightarrow *vapour*) there is an input or output of heat from the substance which occurs without change of temperature until the phase change is complete.
-) MEAN FREE PATH: In a gas or liquid the average distance travelled by a molecule between successive collisions with other molecules.
-) PARAMAGNET: Any material composed of molecules with a permanent magnetic moment. In the absence of an external magnetic field thermal agitation means that the molecules are disordered so that there is no net macroscopic magnetization.
-) REFRIGERATOR or HEAT PUMP: A device operating in a cycle which takes in heat Q_2 from a low temperature source and delivers heat Q_1 to a high temperature sink at the cost of work W input to the device. It is an engine whose cycle has been reversed.

-) SECOND LAW OF THERMODYNAMICS:
 - (Kelvin-Planck) It is impossible to construct a device which, operating in a cycle, has no other effect than to extract heat from a single body at uniform temperature and convert it to an equivalent amount of work.
 - (Clausius) It is impossible to construct a device which, operating in a cycle, has no other effect than to transfer heat from a cooler to a warmer body.
 - (Entropy Form) For any thermally isolated system, the entropy can only increase or stay the same, $\Delta S \geq 0$, it can never decrease. For any spontaneous irreversible process it will increase while for reversible processes only it stays the same.
-) STATE VARIABLES: In the case of a fixed quantity of uniform fluid we are free to choose any two functions of state to be the independent variables. These two which are regarded as independent are called the *state variables* and all others may be regarded as functions of these two.
-) STEFAN-BOLTZMANN LAW: Any black body at temperature T spontaneously emits electromagnetic radiation from all parts of its surface. The flux of energy (amount of energy radiated per unit area per second) is given by σT^4 where σ is a universal constant called the Stefan-Boltzmann constant.
-) TEMPERATURE: The common property of all systems that are in thermal equilibrium with each other.
-) THERMAL CONDUCTIVITY COEFFICIENT: Denoted by κ it is the constant of proportionality that occurs in Fourier's law.
-) THERMAL EQUILIBRIUM: Two systems are in *thermal equilibrium* with each other if each is itself in equilibrium and if, when we place the two systems in thermal contact through a diathermal or conducting wall, there is no change in either system.
-) THIRD LAW OF THERMODYNAMICS:
 - (Macroscopic form) It is impossible to reduce the temperature of a macroscopic system to absolute zero in a finite number of processes.
 - (Simon form) The entropy contribution from each aspect of a system which is in internal thermodynamic equilibrium tends to zero at absolute zero.
 - (Nernst form) For two distinct equilibrium states of a substance corresponding to some difference in an external parameter, the entropy difference of the two states tends to zero as the temperature approaches absolute zero.
-) TRIPLE POINT: For all simple substances there is a unique value of P, T at which all three phases (solid, liquid, vapour) can co-exist in thermodynamic equilibrium. The values of P_{TP}, T_{TP} are different for each material.
-) ZEROTH LAW OF THERMODYNAMICS: Two systems, each in thermal equilibrium with a third system are in thermal equilibrium with each other.