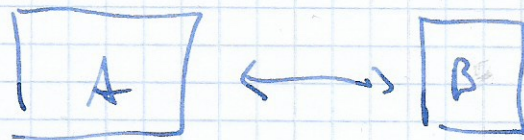


# I BASICS OF THERMODYNAMICS

## § 1. THERMODYNAMIC LAWS

Phenomenological thermodynamics studies equilibrium properties of matter and energy exchange between thermodynamic systems



In equilibrium - a system is sufficiently described by a small number of parameters corresponding to its physical properties, which do not change in time.  
e.g. temperature, pressure, etc.

Df. Thermodynamic state (macrostate) is described by a specific values of thermodynamic parameters describing this system and they are called thermodynamic variables.

In equilibrium the thermodynamic state does not change in time, there is no gradients of thermodynamic variables and no stationary flows. Equilibrium state is treated as a stable equilibrium. A small change returns to the equilibrium. ①

## Extensive thermodynamic variables -

proportional to the number of particles  $N$

e.g. volume  $V \sim N$   
energy  $U \sim N$

## Intensive thermodynamic variables -

do not depend on  $N$

e.g. temperature  $T$   
pressure  $P$

Equation of state - a functional relationship between thermodynamic variables, at equilibrium

e.g.  $f(P, V, T) = 0$

## Example - Ideal gas

$$PV = N k_B T$$

$$k_B = 1,380648 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$$

This equation defines a universal temperature scale - temperature of ideal gas

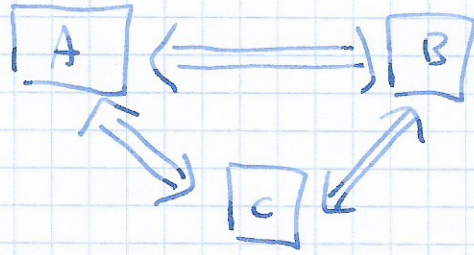
at  $T=0$ ,  $P=0$

at triple point of water  $T = 273,16 \text{ K}$

D

## Zero law of thermodynamics

Two systems A and B in equilibrium with a system C are in equilibrium between each other



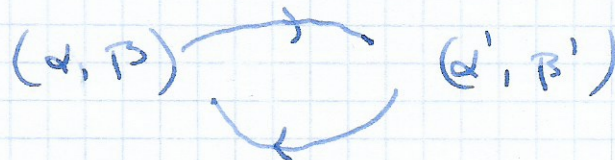
⇒ There exists a thermometer

df. Thermodynamic process - a change of equilibrium thermodynamic state by a change of external constraints, conditions.



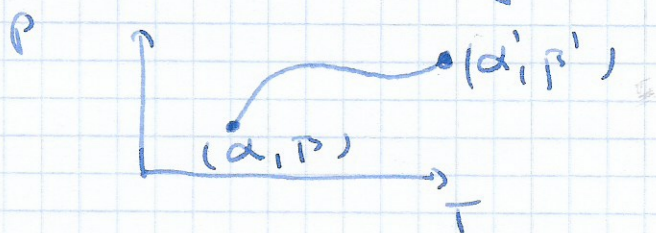
df. If ~~initial~~ <sup>external</sup> conditions return to the initial one the process is cyclic.

df. A process, when the system's parameters go from  $\alpha$  to  $\alpha'$  and the environment's parameters from  $\beta$  to  $\beta'$  is called reversible (in general sense) if there exists any process in which the system and the environment return to the initial conditions  $(\alpha, \beta)$



Df. A process is reversible (in a narrow sense) if one can revert its direction by infinitesimal change of a factor yielding this process.

Df. Pseudostatic process - a process going on through a continuum of equilibrium states. There is a curve in a parameter space corresponding to this process.



Df. Quasistatic process - a system and an environment are in equilibrium states and the corresponding parameters in the system and the environment, responsible for this process, are equal.

e.g.

$$\delta W = -p(\text{ext}) dV = -p dV$$

Fact: ~~Quasistatic process is reversible~~

Reversible process is always quasistatic

(not vice versa!)

If Mechanical work in a reversible process,

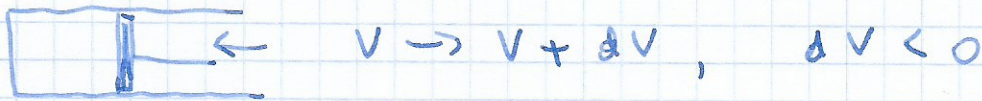
$$\boxed{dW = F dx}$$

$x$  - changed parameter  
 $F$  - force  
 $dx$  - infinitesimal change

where  $d$  means infinitesimal work, but not an exact derivative

$$dW \neq \frac{dW}{dx} dx \quad (!)$$

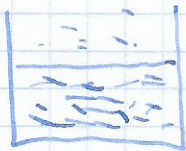
Example: a gas at pressure  $P$  in a cylinder with a moving piston



$$dW = -p dV > 0$$

work "on" the system ↑ pressure □

Example: A system with a varying number of particles (evaporation)



$$dW = \mu dN$$

↑ chemical potential

In multi species systems

$$dW = \sum_i \mu_i dN_i$$

□

Example: equilibrium

$T_1$	$T_2$
$P_1$	$P_2$
$\mu_1$	$\mu_2$

$$T_1 = T_2 - \text{thermal eq.}$$

$$P_1 = P_2 - \text{mechanical eq.}$$

$$\mu_1 = \mu_2 - \text{chemical eq.}$$

□

Generalized coordinates

$$x_i = V, N, \dots$$

generalized forces

$$F_i = P, \mu, \dots$$

Experimental fact - energy of a system can be changed without any change of generalized coordinates (!)

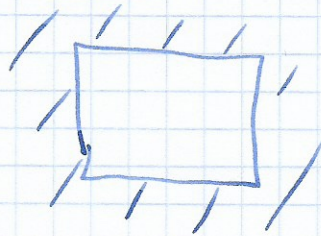
df.

The energy, which is transferred to the system and is not a work  $W$ , is named a heat  $Q$ .

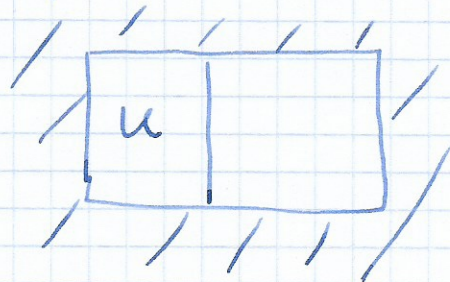
Df. A macrostate can be described by an internal energy - a state function

$$u = u(T, V, N, \dots)$$

For an isolated system  $u = \text{const.}$  - energy conservation law



If two systems can exchange an energy



$$du = \delta W + \delta Q$$

The infinitesimal change of internal energy is given by the work on the system and the heat transferred into the system.

First thermodynamic law

For infinitesimal processes

$$du = \delta W + \delta Q$$

energy conservation law

exact  
differential  
state function

It works for reversible and irreversible processes.

In reversible processes  $\delta W = -pdV + \dots$  etc.  
 $\delta Q$  - is still unknown!

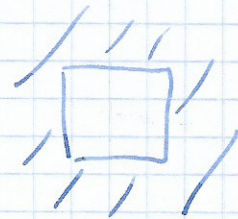
## Second thermodynamic law -

equilibrium state is characterized by a state function  $S$ , called entropy,

which is continuous, extensive, and

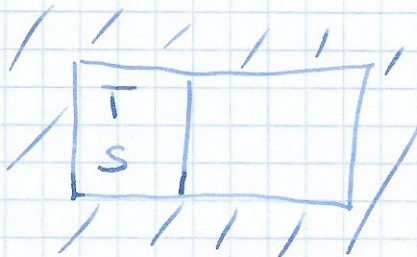
i) In an arbitrary process in isolated system the entropy never decreases

$$\Delta S \geq 0$$



$\Delta S = 0$  only in reversible processes

ii) In an arbitrary system (not isolated) when there is a heat exchange  $dQ$ ,



$$dQ \leq T dS$$

$T$  - absolute temperature

$dS$  - exact derivative



Therefore, for both reversible and irreversible processes, a <sup>small</sup> change in the internal energy

$$dU(x_1, x_2, \dots, S) = \sum_k \left( \frac{\partial U}{\partial x_k} \right)_{x_i \neq x_k, S} dx_k + \left( \frac{\partial U}{\partial S} \right)_{x_i} dS$$

generalized coordinates

$$dU = T dS - \sum_k F_k dx_k$$

Fundamental relation for infinitesimal processes.

where

$$T := \left( \frac{\partial U}{\partial S} \right)_{x_i} - \text{absolute temperature}$$

or

$$F_k := - \left( \frac{\partial U}{\partial x_k} \right)_{x_i \neq x_k, S} - \text{generalized force}$$

Example  $dU = T dS - p dV, \quad p = - \left( \frac{\partial U}{\partial V} \right)_S$

□

Fundamental relation is valid for quasistatic (reversible or irreversible) processes. Quasistatic condition  $\rightarrow$   $U$  and  $S$ , as state functions, are well defined at any moment.

For reversible processes

$$\begin{aligned} \delta Q &= T dS \\ \delta W &= - \sum_k F_k dx_k \end{aligned}$$

For irreversible processes

$$dU = T ds - \sum_k F_k dx_k \quad \text{holds but}$$

its terms can not be identified as heat and work!

In adiabatic process  $dQ = 0$ .

Equations of state

$$T = \left( \frac{\partial U}{\partial S} \right)_{x_i}$$

$$F_k = - \left( \frac{\partial U}{\partial x_k} \right)_{S, x_{i \neq k}}$$

$S$  - generalized coordinate

$T = F_k$  - generalized force

Thermodynamics invented a new generalized coordinate - entropy (a common name for a motion in microscopic scale) and a generalized force - temperature (yields a change of the generalized coordinate  $S$ ).

From  $T = \left( \frac{\partial U}{\partial S} \right)_{x_i}$  - absolute temperature is the same as the temperature of an ideal gas.

Third thermodynamic law


lim  $S' = S_0$  - a universal constant  
 $T \rightarrow 0^+$  (independent on microscopic parameters of the system)

## § 2. THERMODYNAMIC RESPONSE FUNCTIONS

Def. heat capacity

$$C_x = \left( \frac{\delta Q}{dT} \right)_x \quad \left[ \frac{J}{K} \right]$$

↑ constant parameters

$\delta Q \rightarrow$    $T \rightarrow T + dT$

extensive

specific heat - intensive, heat capacity per unit mass, per mole, etc.

This is example of thermodynamic response functions - how the system responds to a small external stimulus

Using  $dU = \delta Q + \delta W$ ,  $\delta W = -p \delta V$

$$\delta Q = \left( \frac{\partial U}{\partial T} \right)_V dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + p \right] \delta V \quad (V, T) \text{ indep. variables}$$

$$\delta Q = \left[ \left( \frac{\partial U}{\partial T} \right)_P + p \left( \frac{\partial V}{\partial T} \right)_P \right] dT + \left[ \left( \frac{\partial U}{\partial P} \right)_T + p \left( \frac{\partial V}{\partial P} \right)_T \right] \delta P$$

Setting  $\delta V = 0$  or  $\delta P = 0$  we get

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

$$U = U(V, T)$$

$$H = U + pV \quad \text{enthalpy} \quad (P, T)$$

One can use other state functions

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V$$

$$C_P = T \left( \frac{\partial S}{\partial T} \right)_P = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_P$$

tutorials

Th. From 3<sup>rd</sup> law of thermodynamics it follows  
that  $C_x \xrightarrow{T \rightarrow 0} 0$ .

Proof for  $C_V$ :  $C_V = T \left( \frac{\partial S}{\partial T} \right)_V$

$$\rightarrow S(T_2, V) = S(T_1, V) + \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

taking the limit  $T_1 \rightarrow 0$ , by  $\lim_{T \rightarrow 0} S = S_0$ , the  
integral on RHS is finite if  $C_V \xrightarrow{T \rightarrow 0} 0$

$$\int_0^{T_2} \frac{C_V}{T} dT < \infty \quad \text{if } C_V(T=0) = 0.$$

□

### Other response functions

Compressibility - how the volume changes on  
varying the pressure

#### isothermal compressibility

intensive

$$\alpha_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{\partial^2 G}{\partial P^2} \right)_T$$

$$V = \left( \frac{\partial G}{\partial P} \right)_T \quad G = G(T, P)$$

#### adiabatic compressibility

intensive

$$\alpha_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S = -\frac{1}{V} \left( \frac{\partial^2 H}{\partial P^2} \right)_S$$

$$V = \left( \frac{\partial H}{\partial P} \right)_S \quad H = H(S, P)$$

Coefficient of thermal expansion - how volume changes in response to varying temperature at constant pressure

intensive

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

Note:  $T, P$  are good control parameters.

These response functions are not all independent

$$\begin{aligned} \Delta T (C_p - C_v) &= T V \alpha^2 \\ C_p (\Delta T - \Delta S) &= T V \alpha^2 \end{aligned}$$

trivial

$$\frac{C_p}{C_v} = \frac{\Delta T}{\Delta S}$$

# §3. MAGNETIC AND ELECTRIC SYSTEMS

## Magnetic systems



noninteracting  
turbine

$$dW = \mu_0 H dM$$

magnetic  
permeability  
of vacuum

magnetic  
field  
strength (intensive)

the work performed by the generator to set up a magnetic field  $H$  and increase the total magnetic moment is  $dM$

$$\mu_0 = 4\pi \cdot 10^{-7} \left[ \frac{H}{m} \right] \text{ heavy per meter}$$

magnetization (extensive)  
magnetic moment

Fundamental thermodynamic relations

$$dU = T dS + \mu_0 H dM$$

$$V \rightarrow -M$$

$$P \rightarrow \mu_0 H$$

$H$ -control parameters in experiments

Heat capacities

$$C_H = \left( \frac{\partial U}{\partial T} \right)_M = T \left( \frac{\partial S}{\partial T} \right)_M = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_M$$

$$H^* = U - \mu_0 M H$$

$$C_H^* = \left( \frac{\partial H^*}{\partial T} \right)_H = T \left( \frac{\partial S}{\partial T} \right)_H = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_H$$

$$G = U - TS - \mu_0 M H$$

turbine

magnetic susceptibility

$$\mathcal{M} = \frac{1}{V} M - \text{magnetization (intensive)}$$

$$\chi_T = \frac{1}{\mu_0} \left( \frac{\partial \mathcal{M}}{\partial H} \right)_T = \frac{1}{V \mu_0} \left( \frac{\partial M}{\partial H} \right)_T = -\frac{1}{V \mu_0^2} \left( \frac{\partial^2 G}{\partial H^2} \right)_T \quad \text{isothermal}$$

$$\chi_S = \frac{1}{\mu_0} \left( \frac{\partial \mathcal{M}}{\partial H} \right)_S = \frac{1}{V \mu_0} \left( \frac{\partial M}{\partial H} \right)_S = -\frac{1}{V \mu_0^2} \left( \frac{\partial^2 H^*}{\partial H^2} \right)_S \quad \text{adiabatic}$$

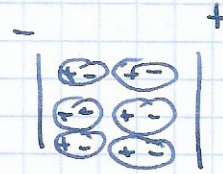
$$\alpha_H = \left( \frac{\partial \mathcal{M}}{\partial T} \right)_H \quad \text{thermal coefficient}$$

$$\chi_T (C_H - C_M) = T \alpha_H^2 \quad \text{turbine}$$

$$C_H (\chi_T - \chi_S) = T \alpha_H^2$$

# Electric systems (dielectrics)

$$\delta W = E \delta D$$



$$D = \epsilon E + P$$

total dipole moment

$$\nabla \cdot E = \text{wurt.}, \quad \delta D = \delta P$$

heat capacity

$$\delta W = E \delta P$$

$$\delta U = T \delta S + E \delta P$$

$$V \rightarrow -P \\ P \rightarrow E$$

$$C_P = \left( \frac{\partial U}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_P$$

$$H^* = U - PE$$

$$C_E = \left( \frac{\partial H^*}{\partial T} \right)_E = T \left( \frac{\partial S}{\partial T} \right)_E = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_E$$

$$G = U - TS - PE$$

electric susceptibility

$$\chi_T = \frac{1}{V} \left( \frac{\partial P}{\partial E} \right)_T = \frac{1}{V} \left( \frac{\partial P}{\partial E} \right)_T = - \frac{1}{V} \left( \frac{\partial^2 G}{\partial E^2} \right)_T$$

$$\chi_S = \frac{1}{V} \left( \frac{\partial P}{\partial E} \right)_S = \frac{1}{V} \left( \frac{\partial P}{\partial E} \right)_S = - \frac{1}{V} \left( \frac{\partial^2 H^*}{\partial E^2} \right)_S$$