5. Thermodynamics

5.1. Basic concepts and definitions

<u>Definition</u>: Thermodynamics (TD) – science about transformation of heat into work (E. Fermi)

<u>Definition</u>: Thermodynamics –science that studies exchange of energy between macroscopic objects and the consequences of this exchange.

Object of thermodynamics: any system of *macroscopic* objects bound by the "dividing surface"

<u>Note</u>: macroscopic – is important. Don't apply TD to molecular systems!

<u>Classification of TD systems</u>:

- **Isolated** – exchange of energy and mass is prohibited
- **Closed** – exchange of energy is allowed, exchange of mass is prohibited
- **Open** – exchange of both energy and mass is allowed

<u>Definition</u>: **TD state** is defined is:

a) all parameters of state are given
b) the function (equation) of state is given

<u>Definition</u>: **TD variables** – the variables that characterize a system in its equilibrium

<u>Note</u>: we only work with TD variables!!!

TD parameters (variables) can be:

- **Extensive** = depend on size (volume, mass, etc.)
- **Intensive** = do not depend on size (temperature, pressure, etc)

a) **External** = depend on the position of external objects
b) **Internal** = depend on the internal properties of a system

<u>Definition</u>: **TD process** – a sequence of equilibrium states

<u>Note</u>: There is no time!

Mathematically, a TD process can be defined by the condition: $\dfrac{da}{dt} << \dfrac{\Delta a}{\tau}$, where $\dfrac{da}{dt}$ is the rate of change

of a TD variable a, τ is a characteristic relaxation time.

If the relaxation time is very small, then after each infinitesimal perturbation, the system returns to its equilibrium state very rapidly (e.g. Fig. 1).
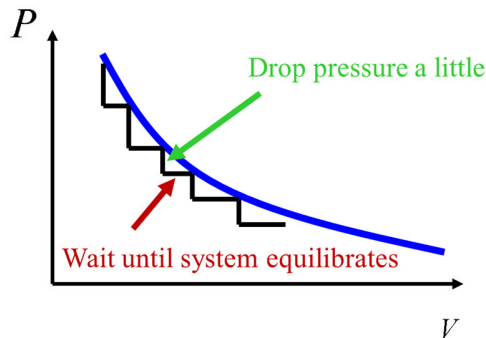

Figure 1. An isothermal process (T = const) for the ideal gas (PV = nRT). TD process is a sequence of equilibrium states.

5.2. Postulate of TD # 1 (we all will die ☺)

In any **isolated** system, after a certain time, the state of **thermodynamic equilibrium** will be reached, from which the system can not escape spontaneously.

Definition: **Equilibrium state** is the state in which TD parameters do not change in time, and there are no fluxes through any element of the dividing surface.

Note: If there are fluxes, one has a **steady-state**.

5.3. Postulate of TD #2 (existence of T)

There exists a function of state – temperature – which has the same value for all parts of a system that are in thermal equilibrium with each other.

In practice: Defined by an empirical scale for ideal gases: $V_t = V_0(1+\alpha t)$, where $\alpha = \dfrac{1}{273.16}$.

Convention: Triple point of water corresponds to $T = 273.16$

5.4. 0-th law of TD (transitivity of thermal equilibrium)

$A \Leftrightarrow B$ and $B \Leftrightarrow C$ then $A \Leftrightarrow C$

<u>In words</u>: If the system A is in thermal equilibrium with the system B, and the system B is in thermal equilibrium with the system C, then the system A is also in thermal equilibrium with the system C

5.5. Equation of state

A general approach. Lets say, we have a function of TD variables: $g(P,V,T)=0$. Assume, volume can be expressed explicitly, $V = f(P,T)$, then:

$$dV = df(P,T) = \left(\frac{\partial f}{\partial T}\right)_P dT + \left(\frac{\partial f}{\partial P}\right)_T dP$$

If V = const, then $dV = 0$, so: $\left(\frac{\partial f}{\partial T}\right)_P dT + \left(\frac{\partial f}{\partial P}\right)_T dP = 0 \Rightarrow \left(\frac{\partial f}{\partial T}\right)_P + \left(\frac{\partial f}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = 0$

Recall that $f(P,T) = V$, so we obtain:

$$\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = 0 \Rightarrow 1 + \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = 0$$

Introduce **thermal coefficients**:

$$\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P ;\ \beta = \frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_P \text{ and } \gamma = \frac{1}{P_0}\left(\frac{\partial P}{\partial T}\right)_V , \text{ we then obtain:}$$

$\alpha = \beta\gamma P_0$ - **thermal equation of state**

<u>Examples of equations of state for gases</u>:

Ideal gas: $PV = nRT$

1873, **van der Walls** $\left(P + \frac{an^2}{V^2}\right)(V - bn) = nRT \Leftrightarrow \left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$,

$V_m = \dfrac{V}{n}$ - molar volume.

1898, **Diterichi** $P(V_m - b) = RTe^{-\frac{a}{RTV_m}}$

1900, **Bertlo** $P = \dfrac{RT}{V_m - b} - \dfrac{a}{TV_m^2}$

1901, **virial** (Kamerling-Onnes) $P = \dfrac{RT}{V_m}\left(1 + \dfrac{B_2(T)}{V_m} + \dfrac{B_3(T)}{V_m^2} + ...\right)$

Here, $B_2(T)$ and $B_3(T)$ are called **virial coefficients**.

5.6. 1-st law of TD

A. Formulation

$$\delta Q_{ext} = dU + pdV - \sum_i p_i dq_i$$

<u>In words</u>: Heat transferred to the system (δQ_{ext}) is utilized to change the internal energy of the system and to perform work by the system against external forces.

<u>Essentially</u>: It is the law of energy conservation

<u>Sign convention</u>:

Heat is **positive** if it is transferred **to the system**

Work is **positive** if it is made **by the system**

<u>Notation</u>: Symbol δ signifies that the quantity is not a full differential.

B. Work and generalized forces

A – stands for German "Arbeit" = "work"

Here, the term $\delta A = pdV - \sum_i p_i dq_i$ stands for the work system performs on its environment.

The term $\delta A = pdV$ corresponds to the work gas expansion performs on the environment

The term $-\sum_i p_i dq_i$ accounts for other ways to perform work (e.g. charging, magnetization, etc.)

p_i are called **generalized forces**

q_i are called **generalized coordinates**

<u>Main examples</u>:

Table 1. Generalized forces and coordinates.		
q_i Coordinate (extensive)	p_i Force (intensive)	Description

V	P	Volume and pressure
q	φ	Charge and electric potential
Ω	σ	Surface area and surface tension
n	μ	Number of moles and chemical potential – for each component separately
D	E	Electrostatic induction and electric field intensity
B	H	Magnetic induction and magnetic field intensity
dS	T	Entropy and temperature

C. Alternative formulation of the 1-st law of TD. Functions of state:

$$\oint dU = 0$$

In words: internal energy is the function of state (mathematically, a potential function).

Definition: **Function of state** - its change in a TD process going from point A to point B does not depend on the path chosen, only on the initial and final states.

A consequence: Potential function is assumed to be additive.

This is applicable if:

1) for macrosystems (mole of a substance)
2) short-range interatomic forces.

C. Work of the gas expansion

Unlike potential energy, work is not a function of state. It depends on a selected path. For instance, Fig. 2 (left panel) shows two possible paths for gas expansion. Path **1** consists of an isobaric expansion (horizontal line) followed by a sudden change of the pressure (which is, by the way, not a process allowed in TD). According to $dA = pdV$ (change to a full differential, since all other parameters are kept fixed), we obtain:

$$A = \int_1^2 dA = \int_{V_1}^{V_2} pdV = p\int_{V_1}^{V_2} dV = p(V_2 - V_1)$$

The isochoric drop of the pressure (vertical line) contributes 0 to work (also using the same integral expression)

Alternatively, (assume) the path **2** describes isothermal expansion of the ideal gas. Then:

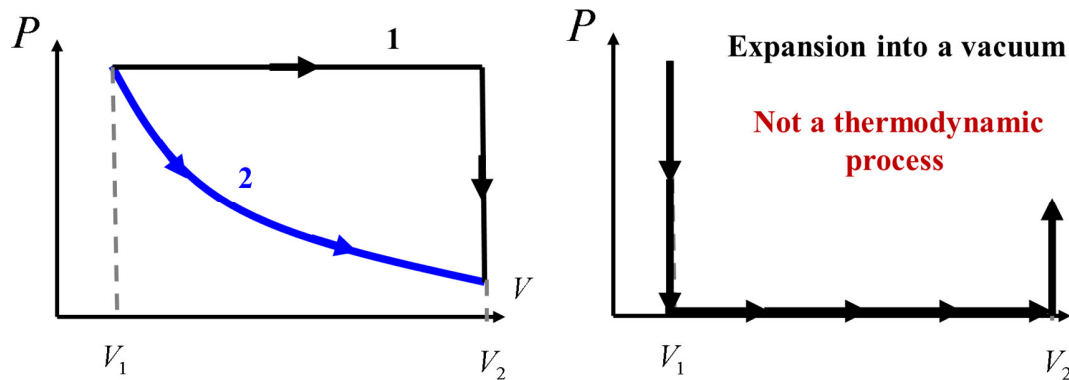$$A = \int_1^2 dA = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln \frac{V_2}{V_1}$$

Figure 2. To the discussion of a work produced by an expanding gas.

Finally, the right panel in Fig. 2 shows the path corresponding to a free expansion of a gas into a vacuum. Since there is no pressure against which the gas makes some efforts on changing the environment, the gas does not produce any work, $A = 0$.

5.7. Enthalpy and thermochemistry

A. General:

Definition: $H = U + PV$ is called **enthalpy**

$$dH = dU + d(PV) = dU + PdV + VdP$$

From the 1-st law we have:

$$\delta Q_{ext} = dU + pdV - \sum_i p_i dq_i$$

So: $\delta Q_{ext} = dH - Vdp - \sum_i p_i dq_i$

B. Natural variables:

$U = U(T, V, \{q_i\})$ - T, V, and generalized coordinates are said to be natural variables for U. This means, one usually use U if T, V and the corresponding generalized coordinates are fixed. For instance, it is typical to compute the internal energy (potential energy) in the MD calculations, since the simulation cell is usually fixed (e.g. NVE ensemble).

$H = H(T, P, \{q_i\})$ - T, P, and generalized coordinates are said to be natural variables for H. Again, if we work under constant temperature and pressure conditions (and all other generalized variables, I'm saying this

for the last time here), the use of H will be the most natural choice. Most of the experiments are performed under constant temperature and pressure (atmospheric) conditions. To maintain volume fixed is very difficult in experiment. Thus, H is the quantity one gets directly from the experiments. In the modeling: if you are running MD simulations under the conditions of NPT ensemble (the volume of your simulation cell may fluctuate), the potential energy you compute corresponds to enthalpy!

C. Heat capacity:

From $U = U(T, V, \{q_i\})$, we obtain:

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,\{q_i\}} dT + \left(\frac{\partial U}{\partial V}\right)_{T,\{q_i\}} dV + \sum_i \left(\frac{\partial U}{\partial q_i}\right)_{T,V,\{q_j\},j \neq i} dq_i$$

Then:

$$\delta Q_{ext} = dU + pdV - \sum_i p_i dq_i = \left(\frac{\partial U}{\partial T}\right)_{V,\{q_i\}} dT + \left[\left(\frac{\partial U}{\partial V}\right)_{T,\{q_i\}} + P\right] dV + \sum_i \left[\left(\frac{\partial U}{\partial q_i}\right)_{T,V,\{q_j\},j \neq i} - p_i\right] dq_i$$

$$\frac{\delta Q_{ext}}{dT} = \left(\frac{\partial U}{\partial T}\right)_{V,\{q_i\}} + \left[\left(\frac{\partial U}{\partial V}\right)_{T,\{q_i\}} + P\right]\frac{\partial V}{\partial T} + \sum_i \left[\left(\frac{\partial U}{\partial q_i}\right)_{T,V,\{q_j\},j \neq i} - p_i\right]\frac{\partial q_i}{\partial T}$$

<u>Definition</u>: $C_V \equiv \left(\dfrac{\delta Q_{ext}}{dT}\right)_{V,\{q_i\}}$ - **isochoric heat capacity**

<u>Definition</u>: $C_P \equiv \left(\dfrac{\delta Q_{ext}}{dT}\right)_{P,\{q_i\}}$ - **isobaric heat capacity**

From the above derivations, we see:

$$C_V \equiv \left(\frac{\delta Q_{ext}}{dT}\right)_{V,\{q_i\}} = \left(\frac{\partial U}{\partial T}\right)_{V,\{q_i\}}$$

$$C_P \equiv \left(\frac{\delta Q_{ext}}{dT}\right)_{P,\{q_i\}} = \left(\frac{\partial U}{\partial T}\right)_{V,\{q_i\}} + \left[\left(\frac{\partial U}{\partial V}\right)_{T,\{q_i\}} + P\right]\left(\frac{\partial V}{\partial T}\right)_{P,\{q_i\}}, \text{ or}$$

$$C_P \equiv C_V + \left[\left(\frac{\partial U}{\partial V}\right)_{T,\{q_i\}} + P\right]\left(\frac{\partial V}{\partial T}\right)_{P,\{q_i\}}$$

<u>For the ideal gas</u>:

$\left(\dfrac{\partial U}{\partial V}\right)_{T,\{q_i\}} = 0$ and $\left(\dfrac{\partial V}{\partial T}\right)_{P,\{q_i\}} = \dfrac{R}{P}$, so:

$$C_P \equiv C_V + R$$

Working with enthalpy:

$$H = H(T, P, \{q_i\}) \Rightarrow dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP + \sum_i \left(\frac{\partial H}{\partial q_i}\right)_{T,P,\{q_j\},j \neq i} dq_i$$

$$\delta Q_{ext} = dH - Vdp - \sum_i p_i dq_i = \left(\frac{\partial H}{\partial T}\right)_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP + \sum_i \left[\left(\frac{\partial H}{\partial q_i}\right)_{T,P,\{q_j\},j \neq i} - p_i\right] dq_i$$

Now:

$$\frac{\delta Q_{ext}}{dT} = \left(\frac{\partial H}{\partial T}\right)_P + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\frac{\partial P}{\partial T} + \sum_i \left[\left(\frac{\partial H}{\partial q_i}\right)_{T,P,\{q_j\},j \neq i} - p_i\right]\frac{\partial q_i}{\partial T}$$

So:

$$C_V = \left(\frac{\delta Q_{ext}}{dT}\right)_{V,\{q_i\}} = \left(\frac{\partial H}{\partial T}\right)_P + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\left(\frac{\partial P}{\partial T}\right)_V$$

$$C_P = \left(\frac{\delta Q_{ext}}{dT}\right)_{P,\{q_i\}} = \left(\frac{\partial H}{\partial T}\right)_P$$

<u>Note</u>: Enthalpy is related to C_P as internal energy is related to C_V

D. Major types of TD processes

Consider a **simple system** = no external forces

$$\delta Q_{ext} = dU + pdV = \left(\frac{\partial U}{\partial T}\right)_{V,\{q_i\}} dT + \left[\left(\frac{\partial U}{\partial V}\right)_{T,\{q_i\}} + P\right]dV = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_{T,\{q_i\}} + P\right]dV$$

For the **ideal gas**!!! (note – for other types of systems, this may be not true): $\left(\frac{\partial U}{\partial V}\right)_{T,\{q_i\}} = 0$, so:

$$\delta Q_{ext} = C_V dT + PdV = C_V dT + \frac{RT}{V}dV$$

Condition $\delta Q_{ext} = 0$ defines an **adiabatic process** (slow, so all internal energy is converted to work)

Condition $\delta Q_{ext} = CdT$ defines a **polythermal process** (slow, so all internal energy is converted to work)

Adiabatic:

$$0 = C_V \frac{dT}{T} + \frac{R}{V} dV \Rightarrow C_V \ln T + R \ln V = const \Rightarrow T^{C_V} V^R = const \Rightarrow$$

$$\left(\frac{PV}{R} \right)^{C_V} V^R = const \Rightarrow P^{C_V} V^{C_V + R} = const \Rightarrow PV^{\gamma} = const$$

,

where $\gamma = \dfrac{C_P}{C_V}$

Polythermal:

$$C \frac{dT}{T} = C_V \frac{dT}{T} + \frac{R}{V} dV \Rightarrow (C_V - C) \ln T + R \ln V$$

so, analogously, one obtains:

$$PV^n = const \text{, but with } \gamma = \frac{C_P - C}{C_V - C}.$$

Isothermal process:

$$\delta Q_{ext} = C_V dT + PdV \Rightarrow \delta Q_{ext} = \frac{RT}{V} dV \Rightarrow Q_{ext} = A = RT \ln \frac{V_2}{V_1}$$

in this case: $dU = C_V dT = 0$

Isobaric process:

$$A = P(V_2 - V_1)$$

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} C_P dT$$

E. Thermochemistry. Hess law.

Heat of reaction, δQ , is determined by the conditions under which the reaction takes place:

If under constant volume – use internal energy: $\delta Q_V = \Delta U$

If under constant pressure – use enthalpy: $\delta Q_P = \Delta H$

Hess law:

The amount of heat released or adsorbed during chemical reaction (thermal effect of chemical reaction) that takes place under constant volume or pressure does not depend on the reaction path. It depends only on the initial (reactants) and final (product) states.

Note: in thermochemistry, heat is taken as positive if it is released into the environment, that is when $\Delta H < 0$ and $\Delta U < 0$.

Relationships between ΔH and ΔU :

In solution or solid phase: $\Delta H = \Delta U + \Delta(PV) \approx \Delta U$

In gas phase: $\Delta H = \Delta U + \Delta(PV) \approx \Delta U + \Delta n \cdot RT$

Definition: **Standard state** – a state of a pure substance at pressure of 1 bar (= 10^5 Pa) and given temperature.

Reaction	Formation/Combustion
$\Delta_r H_T^0$ - enthalpy of reaction between substances in standard states at temperature T	$\Delta_f H_T^0$ - enthalpy of **formation** at given temperature T of 1 mole of a substance from elements, in their most stable state Reference point: $\Delta_f H_T^0(H^+) = 0$ (H$^+$ in water solution) Tabulated for T = 298 K. For other temperatures use: $$H_T - H_0 = \int_0^T C_P dT$$ $\Delta_c H_T^0$ - enthalpy of **combustion** at given temperature T – is the enthalpy of reaction of oxidation of 1 mole of a substance
For the reaction $\displaystyle\sum_i v_i A_i = \sum_j v_j B_j$	
Enthalpy of formation = Formation Products – Formation Reactant $\displaystyle\Delta_r H_T^0 = \sum_j v_j \Delta_f H_T^0(B_j) - \sum_i v_i \Delta_f H_T^0(A_i)$	
Enthalpy of formation = Combustion Reactants – Combustion Products $\displaystyle\Delta_r H_T^0 = \sum_i v_i \Delta_c H_T^0(A_i) - \sum_j v_j \Delta_c H_T^0(B_j)$	

5.8. 2-nd law of TD

The law consists of two parts:

1. $\exists S : dS = \dfrac{\delta Q_{ext}}{T}$ for equilibrium processes. S – **entropy**

2. $dS > \dfrac{\delta Q_{ext}}{T}$ for non-equilibrium processes.

In words: $\forall$ system $\exists$ an additive state function – entropy – which in **isolated system** reaches its maximal value ($dS > 0$). $\forall$ **spontaneous nonequilibrium** process is associated with increase of entropy, which reaches its maximum in equilibrium state.

$\forall$ virtual deviation of the system from equilibrium state leads to decrease of entropy.

Fundamental Gibbs equation: $TdS = dU + pdV - \sum\limits_{i} p_i dq_i$ (this is only true for equilibrium processes)

Ideal gas without generalized forces, 2-nd law can be proven rigorously:

$$\delta Q_{ext} = dU + pdV = C_v dT + pdV \Rightarrow \frac{\delta Q_{ext}}{T} = \frac{C_v dT}{T} + \frac{RdV}{V}$$

Since: $\dfrac{\partial}{\partial V}\left(\dfrac{C_v dT}{T} \right) = 0$ and $\dfrac{\partial}{\partial T}\left(\dfrac{RdV}{V} \right) = 0$, then the expression $\dfrac{\delta Q_{ext}}{T}$ is a full differential, call it dS, then $\exists S$ - which is a state function.

Postulate: assume the above result is also true for all other gases and systems

2-nd law states that there are no perpetuum mobile of the second kind.

Classification:

Perpetuum mobile of the 1-st kind: Indefinitely (infinitely) can produce work without consuming any energy resources (1-st law of TD)

Perpetuum mobile of the 2-nd kind: converts heat extracted from all surroundings into a useful work.

(it doesn't violate the 1-st law, but violates the 2-nd one)

5.9. Approaches for computing entropy

Below, we will consider only simple systems.

$$TdS = dU + pdV$$

$$TdS = dH - Vdp$$

$$U = U(T,V) \Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$H = H(T,P) \Rightarrow dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

So:

$$TdS = dH - Vdp = \left(\frac{\partial H}{\partial T}\right)_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP = C_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

$$TdS = dU + pdV = \left(\frac{\partial U}{\partial T}\right)_{V,\{q_i\}} dT + \left[\left(\frac{\partial U}{\partial V}\right)_{T,\{q_i\}} + P\right]dV = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_{T,\{q_i\}} + P\right]dV$$

Then, considering

$$S = S(T,V) \Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \text{ or}$$

$$S = S(T,P) \Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Comparing the terms, we obtain:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P \text{ and } \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

Because the second derivatives do not depend on the order of differentiation, we further obtain:

$$\left(\frac{\partial^2 S}{\partial T \partial V}\right) = \left(\frac{\partial^2 S}{\partial V \partial T}\right)$$

$$\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right) = \frac{\partial}{\partial T}\left[\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\right] = -\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] + \frac{1}{T}\left[\frac{\partial^2 U}{\partial V \partial T} + \left(\frac{\partial P}{\partial T}\right)_V\right]$$

$$\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right) = \frac{\partial}{\partial V}\left[\frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_V\right] = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T}$$

So: $-\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] + \frac{1}{T}\left[\left(\frac{\partial P}{\partial T}\right)_V\right] = 0 \Rightarrow T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T + P$

This is one of the achievements of the 2-nd law of TD

By analogy, we derive:

$$T\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial H}{\partial P}\right)_T + V$$

From $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$ and from $\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P$, we can compute the absolute values of entropy

$$S_T^0 = S_T^0 + \int_0^{T_{ph.tr.,1}} \frac{C_P}{T}dT + \frac{\Delta H_{ph.tr.,1}}{T_{ph.tr.,1}} + ...$$

5.10. Charachteristic functions. Thermodynamic potentials. Maxwell's equations.

<u>Definition #1</u>: **Charachteristic function** – is a function of state of a system that (function) can be used, together with its derivatives, to determine all parameters of the system.

<u>Definition #2</u>: **Characteristic function** – any function of state with the following 3 properties:

   a) It allows determining the **direction of spontaneous process** under the conditions when natural variables are fixed
   b) Necessary variables are determined by the first partial derivatives
   c) Thermal and caloric coefficients are determined by the second partial derivatives

<u>Definition</u>: Thermodynamic potential – is a characteristic function having the dimension of energy

A. Entropy

$$S = S(U, V, q_i)$$

<u>Note</u>: here and below the variables given in the parenthesis in such definition are the natural variables

1) $TdS = dU + pdV - \sum_i p_i dq_i$

If all natural variables are fixed, we obtain: $dU = dV = dq_i = 0$, so one gets $dS = 0$, but this is not the full picture. Since we are looking at the irreversible process (spontaneous, unidirectional), we should extend out

space beyond the normal TD space and include the internal variables. Then, the entropy will consist of two components – one is due to TD variables, dS_e, and one is due to internal variables, $dS_i = dS_i(X_i)$:

$dS = dS_e + dS_i$, Here, X_i stands for all internal variables. The entropy due to internal variables is non-decreasing in **any** process: $dS_i \geq 0$.

Now, return to our equation:

$$TdS = TdS_e + TdS_i = dU + pdV - \sum_i p_i dq_i + TdS_i$$

So, for the spontaneous process:

$$dS_{U,V,q_i} = dS_i(X_i) \geq 0$$

2) 1-st derivatives,

$$\left(\frac{\partial S}{\partial U}\right)_{V,q_i} = \frac{1}{T} \; ; \; \left(\frac{\partial S}{\partial V}\right)_{U,q_i} = \frac{P}{T} \; ; \; \left(\frac{\partial S}{\partial q_i}\right)_{V,U,q_j} = \frac{p_i}{T}$$

3) 2-nd derivatives,

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,q_i} = \frac{\partial}{\partial U}\frac{1}{T} = -\frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_V = -\frac{1}{T^2 C_V}$$

B. Internal energy

$$U = U(S,V,q_i)$$

1) $dU = TdS_e - pdV + \sum_i p_i dq_i = TdS - pdV + \sum_i p_i dq_i - TdS_i$

Then, $dU_{S,V,q_i} = -TdS_i < 0$

2) 1-st derivatives

$$\left(\frac{\partial U}{\partial S}\right)_{V,q_i} = T \; ; \; \left(\frac{\partial U}{\partial V}\right)_{S,q_i} = -P \; ; \; \left(\frac{\partial U}{\partial q_i}\right)_{V,S,q_j} = p_i$$

3) 2-nd derivatives

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,q_i} = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} \; ;$$

1-st Maxwell equation:

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}, \text{so}$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_{V,q_i} = \left(\frac{\partial T}{\partial V}\right)_{S,q_i} \text{ and } \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_{S,q_i} = -\left(\frac{\partial P}{\partial S}\right)_V, \text{ leading to:}$$

$$\left(\frac{\partial T}{\partial V}\right)_{S,q_i} = -\left(\frac{\partial P}{\partial S}\right)_V$$

C. Enthalpy

1)

$$H = U + PV \Rightarrow dH = dU + pdV + Vdp = TdS_e + Vdp + \sum_i p_i dq_i =$$

$$= TdS + Vdp + \sum_i p_i dq_i - TdS_i$$

So: $H = H(S, P, q_i)$

Then, $dH_{S,P,q_i} = -TdS_i < 0$

2) 1-st derivatives

$$\left(\frac{\partial H}{\partial S}\right)_{P,q_i} = T \; ; \; \left(\frac{\partial H}{\partial P}\right)_{S,q_i} = V \; ; \; \left(\frac{\partial H}{\partial q_i}\right)_{P,S,q_j} = p_i$$

3) 2-nd derivatives

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,q_i} = \left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P} \; ;$$

2-nd Maxwell equation:

$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial^2 H}{\partial P \partial S} \Rightarrow \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S ,$$