Thermodynamics

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Chapter 1

What is Thermodynamics?

In Thermodynamics you have *no model* like for example in statistical mechanics, you do not need to know, what is going on in your system[1]. What you do is you look for *related phenomena*, i.e. you try to predict the results of an experiment by looking for a similiar phenomenon (experiment) whose result you already know and try to transfer to your problem (system).

[1]For the definition of what is a *system* see next chapter.

Chapter 2

Definitions

System: a definite quantity of matter bounded by some closed surface

Surroundings: any systems which can interchange energy with a given system

State of System: determined by its *thermodynamic coordinates* or *state variables*, e.g. pressure, density or temperature

Thermodynamic equilibrium: the termodynamic coordinates of a homogeneous system are the same at all points

Process: any change in the thermodynamic coordinates of a system

Reversible process: chain of infinite slowly quasi-static processes; at every instant the system is infinitesimally near to equilibrium

Irreversible process: any non-reversible process

$\rightarrow$ *Example:* Consider a gas in a cylinder provided with a movable piston. If the piston ist pushed down very rapidly the process is irreversible. If it is pushed down very slowly to avoid turbulence and allow time for the pressure and temperature to become the same at all points, we'll get close to a reversible process.

Intensive variable: variable whose value is independent of the mass of a system, i.e. in a homogeneous system in equilibrium it is the same for the entire system as it is for any part of it
$\rightarrow$ e.g. pressure, temperature or density

Extensive variable: variable whose value is proportional to the mass of the system
→ e.g. volume, internal energy or entropy

Specific value of an extensive variable: the ratio of the extensive variable to the mass of the system
→ e.g. $v = \frac{V}{m}$

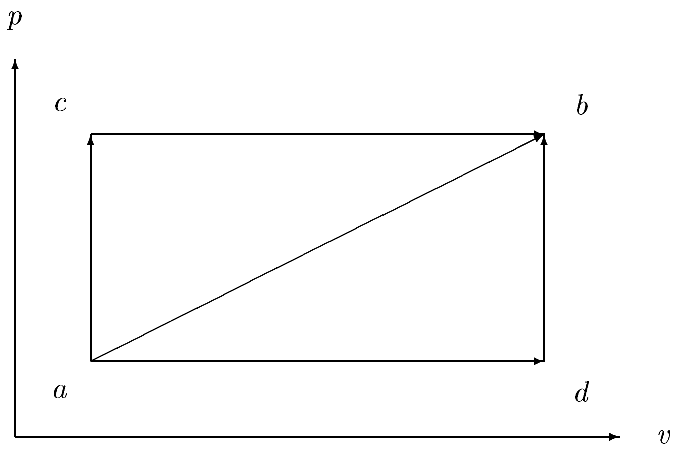
Equations of state: the relation between the pressure, specific volume and temperature of a system; a function $F(p, v, T) = 0$ exists for every substance
→ e.g. $pv = RT$ for ideal gas
→ or $(p + \frac{a}{v^2})(v - b) = RT$ for a van der Waals gas

Cyclic process: a process in which a system goes through certain changes and returns to its initial state

Work of a process: $w = \int p \, dv$

- *isometric*[1] process: $w_v = 0$, because $v = 0$
- *isobaric*[2] process: $w_p = p \int_{v_a}^{v_b} dv = p\,(v_b - v_a)$
- *isothermal*[3] process for an ideal gas[4]: $w_T = \int_{v_a}^{v_b} \frac{RT}{v} dv = RT \ln \frac{v_b}{v_a}$
- *work depends on the path*: it is *greatest* along the path *acb*, *least* along the path *adb*, and has some *intermediate value* along the third path

[1] I.e. $dv = 0$.
[2] I.e. $dp = 0$.
[3] I.e. $dT = 0$.
[4] $p = \frac{RT}{v}$


p
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Chapter 3

Zeroth and First Law of Thermodynamics

3.1 The Zeroth Law of Thermodynamics

If two systems A and B are in thermal equilibrium and the systems B and C are also in thermal equilibrium, then A and C are in thermal equilibrium:

$$A \sim B, \quad B \sim C \qquad \Rightarrow \qquad A \sim C \tag{3.1}$$

3.2 The First Law of Thermodynamics

$$dU = \delta Q - \delta W = \delta Q - p\, dV \tag{3.2}$$

For closed loops is

$$\oint dU = 0 \qquad \Rightarrow \qquad \oint \delta Q = \oint \delta W \tag{3.3}$$

or: $U =$ constant.

3.3 Partial Derivates and Jacobian Determinant

3.3.1 Jacobian Determinant

$$\frac{\partial(T,S)}{\partial(V,S)} := \begin{vmatrix} \left(\frac{\partial T}{\partial V}\right)_S & \left(\frac{\partial T}{\partial S}\right)_V \\ \left(\frac{\partial S}{\partial V}\right)_S & \left(\frac{\partial S}{\partial S}\right)_V \end{vmatrix} = \left(\frac{\partial T}{\partial V}\right)_S \tag{3.4}$$

3.3.2 The First Law of Thermodynamics expressed with Jacobian Determinant

$$\frac{\partial(T,S)}{\partial(p,V)} = 1 \tag{3.5}$$

Proof: with $dU = T\ dS - p\ dV$ the equation $\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$ is equivalent to $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \Leftrightarrow \frac{\partial(T,S)}{\partial(V,S)} = -\frac{\partial(p,V)}{\partial(S,V)} \Leftrightarrow \frac{\partial(T,S)}{\partial(V,S)} = \frac{\partial(p,V)}{\partial(V,S)}$. The above written equation follows.

3.3.3 Relation between Partial Derivatives

General relation for a functional dependence of x, y and z:

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \tag{3.6}$$

Proof: it follows from $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$ if $z =$ constant $\Rightarrow dz = 0$.

3.3.4 Jacobian Transformation

$$\frac{\partial(u,v,\ldots)}{\partial(x,y,\ldots)} = \frac{\partial(u,v,\ldots)}{\partial(\xi,\eta,\ldots)} \Big/ \frac{\partial(x,y,\ldots)}{\partial(\xi,\eta,\ldots)} \tag{3.7}$$

especially

$$\left(\frac{\partial u}{\partial x}\right)_{x,y,\ldots} = \frac{\partial(u,y,z,\ldots)}{\partial(x,y,z,\ldots)} \tag{3.8}$$

3.3.5 Definition of Coefficients

Expansion coefficient:

$$\beta := \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_x \tag{3.9}$$

For example: Isobaric expansion coefficient $\beta := \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

Compressibility:

$$\kappa := \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_x \tag{3.10}$$

For example: Isothermal kompressibility $\kappa := \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

Thermal coefficient of pressure:

$$\alpha := \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_x \tag{3.11}$$

For example: Thermal coefficient of the pressure at constant volume $\alpha := \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$

3.4 Ideal Gas

3.4.1 Equation of State

$$\boxed{\mathrm{p\ V = n\ R\ T}} \tag{3.12}$$

3.4.2 Internal Energy

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \Rightarrow \qquad U = U(T) = nC_V^o T \tag{3.13}$$

with $C_V^o = \frac{3}{2}R$ (for monatomic gas), $C_V^o = \frac{5}{2}R$ (for diatomic gas) and $C_V^o = 3R$ (for polyatomic gas)

3.4.3 Partial Pressure

$$p_i V := n_i RT \qquad \Rightarrow \qquad p = \sum_i p_i \tag{3.14}$$

3.5 Real Gas

3.5.1 Van der Waals Equation of State

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \qquad \text{with} \quad v := \frac{V}{m} \tag{3.15}$$

3.5.2 Kamerlingh-Onnes' Equation of State

$$pv = RT\left(1 + \frac{A_2}{v} + \frac{A_3}{v^2} + \ldots\right) \tag{3.16}$$

$A_2, A_3, \ldots$ are called *virial coefficients.*

Chapter 4

Second Law of Thermodynamics

4.1 Three equivalent Kinds to express the Second Law

1. **Clausius' principle:** A process which involves no change other than the transfer of heat from a hotter to a cooler boldy is irreversible; or: it is impossible for heat to transfer spontaneously from a colder to a hotter body without causing other damages[1].

2. **Thomson's (or Kelvin's) principle:** A process in which work is transformed into heat without any other changes, is irreversible; or: it is impossible to convert all the heat taken from a body of uniform temperature into work without causing other changes.

3. **Principle of the impossibility of a perpetuum mobile of the second kind:** It is impossible to devise an engine operating in a *cycle* which does work by taking heat from a single heat reservoir without producing any other change.

[1] i.e. changes that remain after the process is completed.

4.2 Carnot's Cycle

4.2.1 Definition

A Carnot cycle is an engine that works between *two heat reservoirs* with the constant temperature T_1 and T_2 in a cycle which consists of *two isothermal* and *two adiabatic processes* absorbing the heat $Q_1 > 0$ and $Q_2 < 0$ and thus doing the work $W = Q_1 + Q_2$.

4.2.2 Efficiency

- **Reversible process:** $1 - \eta := \frac{|Q_2|}{Q_1} \quad \Rightarrow \quad \eta = \frac{W}{Q_1}$
- **Irreversible process:** $\eta' < \eta$

4.2.3 The Clausius Equation

For a Carnot cycle it true:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{4.1}$$

Proof: For the isothermal processes 1 and 2 the heat exchange is $Q_1 = \int_{V_1}^{V_2} nRT_1 \frac{dV}{V} = nRT_1 \log \frac{V_2}{V_1}$ and $Q_2 = nRT_2 \log \frac{V_4}{V_3}$. For the adiabatic procesess (with no heat exchange) we have $T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$ and $T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}$ from **Poisson's equation**

$$pV^\gamma = \text{constant} \qquad \text{or} \qquad TV^{\gamma-1} = \text{constant} \tag{4.2}$$

for adiabatic processes. From this we get $\frac{V_2}{V_1} = \frac{V_3}{V_4}$ and the Clausius equation follows.

4.2.4 Carnot's Principle

The efficiency of a *reversible* Carnot Cycle is *uniquely determined* by the temperatures T_1 and T_2 of the heat reservoirs and *independent* of the working substance.

With (4.1) we get an efficiency of $\eta\ (T_1, T_2) = 1 - \frac{|Q_2|}{Q_1} = 1 - \frac{T_2}{T_1}$ for a *reversible* Carnot cycle.

4.2.5 Clausius' Inequality for an Arbitrary Cycle

For an engine that absorbs the heats $Q_i (i = 1, 2, \dots, n)$ at the temperatures $T_i^{(e)}$ the following holds:

$$\sum_{i=1}^{n} \frac{Q_i}{T_i^{(e)}} \leq 0 \tag{4.3}$$

For continuous change we get:

$$\oint \frac{\delta Q}{T^{(e)}} \leq 0 \tag{4.4}$$

with equality when the process is *reversible*.

Proof: Let the i-th cycle absorb the heat Q_i' from a reservoir with T_0 doing the work W_i' by giving the heat Q_i to reservoir with T_i. Then we have $Q_i' = Q_i \frac{T_0}{T_i^{(e)}}$ and $W_i' = Q_i - Q_i' = Q_i \left(1 - \frac{T_0}{T_i^{(e)}}\right)$. When all cycles work together the heat $(Q_1' + \dots + Q_n')$ is taken from the reservoir with T_0 and the work $\sum Q_i - \sum W_i' = T_0 \sum \frac{Q_i}{T_i^{(e)}}$ is done *on* the environment. According to Thomson's principle[2] this must be equal to zero or negative.

4.3 Entropy

4.3.1 Definition

A given thermal equilibrium stat α_0 is chosen as the standard state of a system. The *entropy* $S(\alpha)$ of the system in another equilibrium state, α, is defined by

$$S(\alpha) := \int_{\alpha_0}^{\alpha} \frac{\delta Q}{T} \tag{4.5}$$

where the integration is done along any *quasi-static* process which connects α to α_0. In differential form:

$$dS = \frac{\delta Q}{T} \tag{4.6}$$

[2]see 4.1, page 10.

4.3.2 The Combined First and Second Law (Gibbs' Relation)

$$dU = T\,dS - p^{(e)}dV + \sum_i X_i^{(e)} dx_i + \sum_{j=1}^{c} \mu_j^{(e)} dN_j \tag{4.7}$$

with:

$$\begin{aligned} \delta Q &= T\,dS, &(4.8)\\ \delta W &= -p^{(e)}dV + \sum_i X_i^{(e)} dx_i, &(4.9)\\ \delta Z &= \sum_{j=1}^{c} \mu_j^{(e)} dN_j, &(4.10) \end{aligned}$$

$p^{(e)}$ = pressure of the surroundings, $X_i^{(e)}$ = i-th type force on the system due to the surroundings, dx_i = the coordinate of the system cooresponding to the force $X_i^{(e)}$, dN_j = number of molecules or the mole number of the j-th component in the system, and $\mu_j^{(e)}$ = the chemical potential per molecule or mole of the j-th component in the surroundings.
The law is given in a Paffian form[3].

For a closed system (only volume changes) (4.7) becomes:

$$dU = T\,dS - p\,dV \tag{4.11}$$

4.3.3 The Entropy: An Extensive State Quantity

If we have two quasi-static processes L and L' connected to a reversible cycle, $\alpha_0 \overset{L}{\to} \alpha \overset{L'}{\to} \alpha_0$, we get $\int_{\alpha_0(L)}^{\alpha} \frac{\delta Q}{T} + \int_{\alpha(L')}^{\alpha_0} \frac{\delta Q}{T} = 0$ or $\int_{\alpha_0(L)}^{\alpha} \frac{\delta Q}{T} = \int_{\alpha_0(L')}^{\alpha} \frac{\delta Q}{T}$. Thus if α_0 is fixed, $S(\alpha)$ is *independent of the process* $(\alpha_0 \to \alpha)$ and is *uniquely defined* for a given α.
Therefore dS as given in (4.6) is a *total differential*[4].

Additivity of the Entropy: The entropy of a system is also proportional to its mass or volume, because the heat absorbed to bring it from one state to another is proportional to the mass. Therefore the entropy of a thermodynamical system is the sum of its subsystems:

$$S = S_A(\alpha) + S_B(\beta) + \ldots \tag{4.12}$$

$\Rightarrow$ the entropy is an *extensive* state variable.

[3] $dU = \sum_i y_i\,dY_i$.
[4] In other words T is the *integrating denominator* of δQ.

4.3.4 Total Entropy Change

The *total entropy change* is the sum of change of entropy of the system (ΔS) and of the environment (i.e. the heat reservoir; ΔS_r):

$$\Delta S_t = \Delta S - \Delta S_r = \Delta S - \frac{Q}{T} \geq 0 \tag{4.13}$$

4.4 General Expression of the Second Law

$$\int_{\alpha'(L)}^{\alpha''} \sum \frac{\delta Q}{T^{(e)}} \leq \Delta S, \qquad \text{where} \quad \Delta S = S(\alpha'') - S(\alpha') \tag{4.14}$$

with "=" for reversible process and "<" for irreversible process.
Here δQ is the infinitesimal heat received by the various parts of the system from the environment at temperature $T^{(e)}$; $\sum$ indicates the summation over the various parts of the system and the integration is carried along the process L. If the temperature is uniform throughout the system, $T^{(e)}$ is replaced by the temperature T of the system.

4.5 The Direction of an Actual Change

A process cannot be realized between two states α' and α'' of a given system if it violates inequality (4.14). This determines the possible direction of a change.
For example for an *adiabatic system* ($\delta Q = 0$) the left side disappears and we get $\Delta S \geq 0$. For a *closed adiabatic system* we get

$$(\Delta S)_{U,V,M} \geq 0 \tag{4.15}$$

that is the *principle of the increase of entropy*. The system will reach equilibrium (*equilibrium condition*) if

$$S = \max. \tag{4.16}$$

4.6 Maximum Work and Minimum Work

If W is the work *done by* the environment on the system other than $-p^{(e)}\Delta V$ due to the change in volume, we have

$$Q = \Delta U + p^{(e)}\Delta V - \sum_u \mu_j^{(e)} \Delta N_j - W. \tag{4.17}$$

With the second law (4.14), $Q \leq T^{(e)}\Delta S$, we get

$$i) \quad W_{min} \equiv \Delta U - T^{(e)}\Delta S + p^{(e)}\Delta V - \sum_{u} \mu_j^{(e)} \Delta N_j \leq W \tag{4.18}$$

If $W_{min} > 0$ then W, the work that must be *done by* the environment in order to make this change is always *greater* than W_{min}. $W = W_{min}$ is only the case if the change is *reversible*.

$$ii) \quad W_{max} \equiv -(\Delta U - T^{(e)}\Delta S + p^{(e)}\Delta V - \sum_{u} \mu_j^{(e)} \Delta N_j) \geq -W \tag{4.19}$$

If $W_{max} > 0$ then $-W$, the work that can be *extracted by* the change is always *less* than W_{max}. $-W = W_{max}$ is only the case if the change is *reversible*.

Chapter 5

Thermodynamical potentials

5.1 Definitions

A system in thermal equilibrium is characterized by *thermodynamic potentials* (or: *thermodynamic functions*) which are *extensive quantities* expressed as functions of suitable independent variables. There is a particular set of variables which is convenient for each thermodynamic function. These are called the *natural independent variables*. If a thermodynamic potential is given as a function of its natural independent variables, the thermodynamic properties are completely determined.

Here are the most important thermodynamic potentials with their natural independent variables and total differential:

Internal energy: $U := U(S, V, N_i)$

$$\Rightarrow \quad dU = T\ dS - p\ dV + \sum \mu_i\ dN_i \tag{5.1}$$

Free energy: $F := F(T, V, N_i) \quad \rightarrow \quad F = U - TS$

$$\Rightarrow \quad dF = -S\ dT - p\ dV + \sum \mu_i\ dN_i \tag{5.2}$$

Enthalpy: $H := H(S, p, N_i) \quad \rightarrow \quad H = U + pV$

$$\Rightarrow \quad dH = T\ dS + V\ dp + \sum \mu_i\ dN_i \tag{5.3}$$

Gibbs potential[1]**:** $G := G(T, p, N_i) \quad \rightarrow \quad G = F + pV = \sum \mu_\mathbf{i} \mathbf{N_i}$

$$\Rightarrow \quad dG = -S\ dT + V\ dp + \sum \mu_i\ dN_i \tag{5.4}$$

[1]Sometimes called *free enthalpy*; in some books the symbol of the Gibbs potential (free enthalpy) is φ, not G.

5.2 How to get the Equation of a certain Potential

5.2.1 For Example: Free energy

$$\begin{aligned} dU &= T\,dS - p\,dV && (5.5)\\ \Leftrightarrow dU - d(TS) &= T\,dS - d(TS) - p\,dV && (5.6)\\ \Leftrightarrow d(U-TS) &= -S\,dT - p\,dV && (5.7)\\ \Leftrightarrow dF &= -S\,dT - p\,dV && (5.8) \end{aligned}$$

From this you can get the partial derivations

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \qquad ; \qquad \left(\frac{\partial F}{\partial V}\right)_T = -p \tag{5.9}$$

This kind of transformation is called *Legendre Transformation:*

5.2.2 Legendre Transformations

Take a thermodynamical function L with its natural independent variables $x, y, z, \ldots$. Then it has a total differential (Pfaffian form):

$$dL = X\ dx + Y\ dy + Z\ dz + \ldots, \tag{5.10}$$

where $X, Y, Z, \ldots$ are all functions of $x, y, z, \ldots$.
Then the following transformation is called *Legendre transformation:*

$$\begin{aligned} L \rightarrow \bar{L} &= L - Xx, && (5.11)\\ x, y, z, \ldots &\rightarrow X, y, z, \ldots && (5.12)\\ \Rightarrow \quad d\bar{L} &= -x\ dX + Y\ dy + Z\ dz + \ldots && (5.13) \end{aligned}$$

si With Legendre transformations you can calculate every thermodynamical potential.

5.3 Euler's Equation and the Gibbs-Duhem Relation

The Gibbs free energy (see 5.1, p. 16) has the particle numbers $N_1, N_2, \ldots$ as extensive variables, therefore

$$G(T, p, \alpha N_1, \alpha N_2, \ldots) = \alpha\ G(T, p, N_1, N_2, \ldots). \tag{5.14}$$

Differentiate this with respect to α and setting $\alpha = 1$ we get

$$\sum_j N_j \left(\frac{\partial G}{\partial N_j}\right)_{T,p,N'_j} = G \qquad \textbf{Euler's equation} \tag{5.15}$$

With $\left(\frac{\partial G}{\partial N_j}\right)_{T,p,N'_j} = \mu_j$ we get $G = \sum N_j \mu_j$. By substituting this into dG (see 5.1, p. 16) we get the *Gibbs-Duhem relation***:**

$$S\ dT - V\ dp + \sum_j N_j\ d\mu_j = 0 \tag{5.16}$$

5.4 The Connection between the Calorical and the Thermical Equation of State

Calorical equation of state: $U := U(V,T)$

Thermical equation of state: $p := p(V,T)$

Connection: For example with the *internal energy***:**

$$dU = T\ dS - p\ dV \ \Rightarrow\ U = U(S,V) \quad (*)$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V \Rightarrow T = T(S,V) \Rightarrow S = S(T,V) \quad (**)$$

$$\overset{\textbf{in}(*)}{\Rightarrow} U = U(S(T,V),V) \qquad \textbf{calorical equation of state} \tag{5.17}$$

$$(*) \Rightarrow \quad -p = \left(\frac{\partial U}{\partial V}\right)_S = -p(S,V)$$

$$\overset{(**)}{\Rightarrow} -p = -p(S(T,V),V) \qquad \textbf{thermical equation of state} \tag{5.18}$$

5.5 The Third Law of Thermodynamics (Nernst-Planck-Theorem)

The entropy of a chemically uniform body of finite density approaches a limiting value as the temperature goes to absolute zero regardless of pressure, density or phase.

Therefore it is convenient to take the state $0°K$ as the standard state by assuming

$$\lim_{T\to 0} S = S_0 \equiv 0 \tag{5.19}$$

Then the *entropy of any state* **is** *uniquely determined***.**

5.6 Equilibrium Conditions

5.6.1 Equilibrium between Two Systems

Main condition for equilibrium:

$$S_A + S_B = max. \quad \Rightarrow \quad \delta S_A + \delta S_B = 0 \tag{5.20}$$

Auxiliary conditions:

$$U_A + U_B = const. \quad \Rightarrow \quad \delta U_A + \delta U_B = 0 \tag{5.21}$$
$$V_A + V_B = const. \quad \Rightarrow \quad \delta V_A + \delta V_B = 0 \tag{5.22}$$
$$N_j^A + N_j^B = const. \quad \Rightarrow \quad \delta N_j^A + \delta N_j^B = 0, \quad j = 1, 2, \ldots \tag{5.23}$$

With $dS = \frac{dU}{T} + \frac{p}{T}dV - \sum \frac{\mu_j}{T}\, dN_j$ **and (5.20) we get:**

$$\left(\frac{1}{T_A} - \frac{1}{T_B}\right)\delta U_A + \left(\frac{p_A}{T_A} - \frac{p_B}{T_B}\right)\delta V_A - \sum \left(\frac{\mu_j^A}{T_A} - \frac{\mu_j^B}{T_B}\right)\delta N_j^A = 0 \tag{5.24}$$

From this equation you can obtain the conditions for certain restrictions, e.g.

1. **Mechanical equilibrium:** $p_A = p_B$
2. **Heat exchange:** $T_A = T_B$
3. **Material exchange:** $\mu_j^A = \mu_j^B$

5.6.2 General Equilibrium Condition

If a system is in contact with the environment at the temperature $T^{(e)}$**, pressure** $p^{(e)}$**, chemical potential** $\mu_j^{(e)} (j = 1, 2, \ldots)$ **and is acted by the forces** $X_i^{(e)}$**, the first law gives**

$$\delta' Q = \delta U + p^{(e)}\delta V - \sum_i X_i^{(e)}\delta x_i - \sum_j \mu_j^{(e)}\delta N_j \tag{5.25}$$

where $\delta U, \delta V, \ldots$ **are virtual displacements. By the second law, such a displacement will be unrealizable if**

$$\delta U - T^{(e)}\delta S + p^{(e)}\delta V - \sum_i X_i^{(e)}\delta x_i - \sum_j \mu_j^{(e)}\delta N_j > 0 \tag{5.26}$$

5.6.3 Stabiblity of Thermal Equilibrium

The condition for thermal equilibrium is, that the first-order variation is zero, but stability is only guaranteed if also the second (or higher) order variations are zero.
If a thermodynamical potential has more than one minimum, the state which gives the least value of the minima is the *most stable equilibrium state*. **The others are** *metastable*.

5.7 Inequalities of Thermodynamics

Chapter 6

Phase Equilibrium and Chemical Equilibrium

6.1 Equilibrium between Different Phases of a Pure Substance

6.1.1 Plane Interface which Transmits Pressure

For phase equilibrium we must have[1]

$$\begin{aligned} & p' = p'' = p \quad \textbf{and} \quad T' = T'' = T \\ \Rightarrow \quad & \mu'(p,T) = \mu''(p,T) \quad \Rightarrow \quad \bar{G}'(p,T) = \bar{G}''(p,T) \end{aligned} \tag{6.1}$$

what means that the two planes $\mu'(p,T)$ **and** $\mu''(p,T)$ **have a intersection line in the space** (μ, p, T)**.**
A *phase transition* **occurs when this line is crossed.**

A) First-Order Phase Transition

Conditions for first-order transition[2]**:**

1. $\Delta\mu := \mu' - \mu'' = 0$
2. $\frac{\partial \Delta\mu}{\partial T} \neq 0$

[1] $\bar{G}' = \bar{G}''$ follows, because $\bar{G}_j$ is defined as $\bar{G}_j := \frac{\partial G}{\partial N_j}$ (partial molar free energy of the j-th component) and $G = \sum \mu_j N_j = \sum \bar{G}_j N_j$ (cf. 5.1, S. 16) what means that $\bar{G}_j = \mu_j$ and $\Delta\bar{G} = \Delta\mu$.

[2] That means we really cross the coexinstence line and do not move along it.

3. $\frac{\partial \Delta\mu}{\partial p} \neq 0$

From this we get with (6.1) $\Delta \frac{\partial \bar{G}}{\partial p} dp + \Delta \frac{\partial \bar{G}}{\partial T} dT = 0$ **or**[3]**:**

$$\frac{dp}{dT} = \frac{\Delta \bar{S}}{\Delta \bar{V}} = \frac{\Lambda}{T \Delta \bar{V}} \tag{6.2}$$

which is the *Clausius-Clapeyron equation*, **where** $\Lambda := T\Delta\bar{S} = T(\bar{S}' - \bar{S}'')$ **is the heat of transition per mole.**

B) Second-Order Phase Transition

Here we move along the coexistence line. The conditions are:

1. $\Delta\mu = 0$
2. $\frac{\partial \Delta\mu}{\partial T} = 0$
3. $\frac{\partial \Delta\mu}{\partial p} = 0$

From this we get[4]

$$\left.\begin{array}{ll} \Delta \frac{\partial \bar{V}}{\partial p}\, dp + \Delta \frac{\partial \bar{V}}{\partial T}\, dT = 0 & \left(\frac{\partial \Delta \bar{G}}{\partial p} = \Delta \bar{V} = 0\right), \\ \Delta \frac{\partial \bar{V}}{\partial T}\, dp - \frac{\Delta C_p}{T}\, dT = 0 & \left(\frac{\partial \Delta \bar{G}}{\partial T} = \Delta \bar{S} = 0\right). \end{array}\right\} \tag{6.3}$$

[3] Because $\left(\frac{\partial G}{\partial T}\right)_{p,N} = -S$ and $\left(\frac{\partial G}{\partial p}\right)_{T,N} = V$, cf. 5.1, S. 16.

[4] Note that $T\left(\frac{\partial S}{\partial T}\right)_p = C_p$ and $\left(\frac{\partial \bar{S}}{\partial p}\right)_T = \frac{\partial(S,T)}{\partial(p,T)} = \frac{\partial(V,p)}{\partial(p,t)} = -\left(\frac{\partial V}{\partial T}\right)_p$.