Topics

- Thermodynamic Fundamentals
  - Component and Phase
  - Position Dependence of Properties $P = P(\chi)$
  - Direction Dependence of Properties $P_{klmn}$...
  - Quantities $T, S; p, V; \mu_i, N_i; \sigma_{kl}, \varepsilon_{kl}; E_k, D_k; H_k, B_k$
  - Composition, Concentration and Phase Fraction $x_i, w_i, c_i, x_i^j, w_i^j, x^j, w^j, v^j$
  - Thermodynamic Potentials $U, F, H, G$ and $dU, dF, dH, dG$
  - Thermodynamic Equilibrium
  - Stability: Stable, Metastable and Unstable
  - Driving Force
  - General Considerations on the Temperature Dependence of $G$
Components and Phases

- Components are **chemically independent constituents** of a system.
- For the lecture, these are **elements from the periodic table**. In some cases, components can also be compounds.
- For general discussions, we use $A, B, C, \ldots$ as place holders.

- Phases are **regions in materials that exhibit essentially uniform/homogeneous physical and chemical properties**. Regions of the same physical and chemical properties are considered the same phase and these are distinct from other parts of the system if the system is multi-phase.
- For general discussions, we use $\alpha, \beta, \gamma, \ldots$ as place holders for solid solutions and $A_m B_n, \ldots$ as place holders for stoichiometric intermittent phases.
Revision: Position Dependence of Properties

- Homogeneous:
  - property $P$ is **not dependent on position $x$**
  - $P \neq P(x)$

- Inhomogeneous:
  - property $P$ is **a function of the position $x$**
  - $P = P(x)$

- Heterogeneous:
  - property $P$ is a **inhomogeneous and exhibits jump discontinuities**
    (like at phase boundaries)
Revision: Direction Dependence of Properties

- **Isotropic:**
  - Property $P$ is **not depending on the direction** and the description simplifies to a scalar number
  - $P_{klnm...} = P$

- **Anisotropic:**
  - Property $P$ **depends on the direction** and the description requests the use of tensors
  - $P_{klnm...}$ with $k, l, m, n ... = \{1,2,3\}$
Essential Quantities

- In what follows, the **important physical quantities** used in the lecture are presented.

- In order to provide a profound structure to the **mathematics of thermodynamics**, the quantities are introduced as **pairs of matching intensive and extensive properties**.

- **Intensive properties do not change with the size or extent of a system** (whatever size is expressed with).

- **Extensive properties change with the size or extent of a system and are additive for subsystems**. Please note that normalizing extensive properties by the size of the system provides a size-independent *value* but does not convert the property into an intensive property as in the sense used in this lecture.

- The **pairs** of intensive and extensive properties are **connected by suitable materials properties and materials laws** (usually linear).
Essential Quantities: $T, S$

Note that we don't distinguish between the different notation of $c$ with respect to it's absolute, molar, weight-specific or volumetric description in the lecture. The representation follows from the structures of the equations and can easily be adopted.

<table>
<thead>
<tr>
<th>intensive</th>
<th>extensive</th>
<th>potential product</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature</td>
<td>entropy</td>
<td>symbol</td>
</tr>
<tr>
<td>$T$</td>
<td>$K$</td>
<td>$S$</td>
</tr>
</tbody>
</table>

$$dS = \frac{dQ}{T} = \frac{c_p}{T} dT$$ with $c$ being the heat capacity in $\frac{J}{K}$. $c_p$ can be determined under constant $p$ in comparison to $c_V$ under constant $V$. Phase transformations might be associated with an entropy change $\Delta S^{tr} = \frac{Q^{tr}}{T^{tr}}$ with $Q^{tr}$ being the latent heat of the reaction.
Essential Quantities: $p, V$

<table>
<thead>
<tr>
<th>intensive</th>
<th>extensive</th>
<th>potential product</th>
</tr>
</thead>
<tbody>
<tr>
<td>pressure</td>
<td>volume</td>
<td></td>
</tr>
<tr>
<td>symbol</td>
<td>unit</td>
<td>symbol</td>
</tr>
<tr>
<td>$p$</td>
<td>Pa = $\frac{N}{m^2}$</td>
<td>$V$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$m^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$p V$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$p , dV$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$V , dp$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$J = Nm = Ws$</td>
</tr>
</tbody>
</table>

\[ dp = K \, dV \] with $K$ being the bulk modulus in Pa. Phase transformations might be associated with a volume change $\Delta V^{\text{tr}}$. 
Essential Quantities: $\mu, N$

For the chemical considerations, the components and phases need to be considered during the thermodynamic treatment. Hence, $i$ and $j$ correspond to species and phases, respectively.

<table>
<thead>
<tr>
<th>intensive</th>
<th>extensive</th>
<th>potential product</th>
</tr>
</thead>
<tbody>
<tr>
<td>chemical potential</td>
<td>particle number</td>
<td></td>
</tr>
<tr>
<td>symbol</td>
<td>unit</td>
<td>symbol differentials</td>
</tr>
<tr>
<td>$\mu$</td>
<td>J</td>
<td>$\mu N$</td>
</tr>
</tbody>
</table>

$dG = \sum_i \mu_i \, dN_i$ is the change in Gibbs free energy when the particle numbers of the species $i$ are changed (at constant $p$ and $T$), for example by moving atoms from one phase to another.
Essential Quantities: $\sigma_{kl}, \varepsilon_{kl}$

Note that tensor properties are needed for the description of the following functional properties. Hence, $k, l, m, n ...$ are direction indices! Einstein sum convention is used.

<table>
<thead>
<tr>
<th>intensive</th>
<th>extensive</th>
<th>potential product</th>
</tr>
</thead>
<tbody>
<tr>
<td>stress</td>
<td>strain</td>
<td></td>
</tr>
<tr>
<td>symbol</td>
<td>unit</td>
<td>symbol</td>
</tr>
<tr>
<td>$\sigma_{kl}$</td>
<td>Pa = $\frac{N}{m^2}$</td>
<td>$\varepsilon_{kl}$</td>
</tr>
</tbody>
</table>

$\sigma_{kl} = C_{klmn} \varepsilon_{mn}$ with $C_{klmn}$ being the stiffness tensor components in Pa. Phase transformations might be associated with a transformation strain $\varepsilon_{kl}^{tr}$.

Note the similarity of $\sigma_{kl}, \varepsilon_{kl}$ to $p, V$ which individually account for multi-axial and hydrostatic stress/strain, respectively.
Essential Quantities: $E_k, D_k$

Note that tensor properties are needed for the description of the following functional properties. Hence, $k, l, m, n ...$ are direction indices! Einstein sum convention is used.

<table>
<thead>
<tr>
<th>intensive</th>
<th>extensive</th>
<th>potential product</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrical field</td>
<td>electrical displacement</td>
<td>symbol</td>
</tr>
<tr>
<td>$E_k$</td>
<td>$D_k$</td>
<td>$E_k , D_k , V$</td>
</tr>
</tbody>
</table>

$D_k = \varepsilon_{kl} \, E_l + P_k$ with $\varepsilon_{kl}$ being the permittivity tensor components in $\frac{C}{Vm}$ and $P_k$ the electric polarization. Phase transformations might be associated with a spontaneous polarization $P_k^{sp}$.

Note that for electromagnetism, several naming conventions and unit systems exist where the equations might differ.
Essential Quantities: $H_k, B_k$

Note that tensor properties are needed for the description of the following functional properties. Hence, $k, l, m, n ...$ are direction indices! Einstein sum convention is used.

<table>
<thead>
<tr>
<th>intensive</th>
<th>extensive</th>
<th>potential product</th>
</tr>
</thead>
<tbody>
<tr>
<td>magnetic field</td>
<td>magnetic flux</td>
<td></td>
</tr>
<tr>
<td>symbol</td>
<td>unit</td>
<td>symbol</td>
</tr>
<tr>
<td>$H_k$</td>
<td>$\frac{A}{m}$</td>
<td>$B_k$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$B_k = \mu_{kl} H_l + M_k$ with $\mu_{kl}$ being the permeability tensor components in $\frac{\text{N}}{\text{m}^2}$ and $M_k$ the magnetization. Phase transformations might be associated with a spontaneous polarization $M_k^{sp}$.

Note that for electromagnetism, several naming conventions and unit systems exist where the equations might differ.
Essential Quantities

The benefit of treating the subject in the aforementioned, generalized way is that many different materials science problems can be treated in a unique framework.

Similar to what is seen for the direct coupling of the intensive and extensive quantities in the previous cases, cross-coupling of different properties is possible in special materials, for example by:

- $\varepsilon_{kl} = \alpha_{kl} \Delta T$ for the thermal expansion
- $P_{k}^{sp} = p_{k} \Delta T$ for the pyro-electric effect
- $D_{k} = d_{k,lm} \sigma_{lm}$ for the piezo-electric effect
- etc.
Overview with Heckmann Diagrams

direct coupling:
- heat capacity
- elastic compliance/stiffness
- electric permittivity

extensive

intensive
Overview with Heckmann Diagrams

cross coupling:
- thermal expansion
- piezocaloric effect
- thermal stress
- heat of deformation

Note that some cross-coupling effects don't have common names.
Overview with Heckmann Diagrams

cross coupling:
- direct and converse piezoelectric effect
Overview with Heckmann Diagrams

cross coupling:
- pyroelectric effect
- heat of polarization

cross coupling:
- pyroelectric effect
- heat of polarization

extensive

intensive
Overview with Heckmann Diagrams

direct coupling:
- heat capacity
- elastic compliance/stiffness
- magnetic permeability

cross coupling:
- magnetocaloric effect
- magnetostriction
- magnetoelectricity
- etc.
Ferro Effects

- Apart from the (linear) coupling effects, spontaneous polarization, transformation strain, heat of transformation, and spontaneous magnetization are possible due to phase transitions.
- For the cases of elasticity, electricity, and magnetism, a ferro-phase can be defined:
  - ferro-elasticity
  - ferro-electricity
  - ferro-magnetism
- Depending on the mathematical structure of the tensor properties, only certain substances with specific crystal structures can exhibit the required properties.
- Depending on the elementary structure of the material, related properties are also possible:
  - **ferro**: all elementary units are parallel coupled (charge, magnetic moment, lattice parameter)
  - **anti-ferro**: all elementary units are anti-parallel coupled and, hence, cancel out each other and result in no net polarization or magnetization
  - **ferri**: the elementary units are anti-parallel coupled but different in magnitude and, hence, they only partially cancel out
### Ferro Effects

<table>
<thead>
<tr>
<th>Dielectricity (all insulators)</th>
<th>Piezoelectricity</th>
<th>Pyroelectricity</th>
<th>Ferroelectricity</th>
</tr>
</thead>
<tbody>
<tr>
<td>• can belong to all 32 point groups</td>
<td>• need to belong to the 20 non-centrosymmetric point groups (one exception)</td>
<td>• need to belong to the 10 polar point groups</td>
<td>• only when polarization is reversible by electric field</td>
</tr>
</tbody>
</table>
Essential Quantities: $x_i, w_i$

Most of the phase transformations presented in this lecture are of chemical nature. Hence, composition is an important quantity to be expressed.

Atomic concentration $x_i$ of a component $i$ in material:

$$x_i = \frac{N_i}{N} = \frac{N_i}{\sum_i N_i} = \frac{n_i}{n} = \frac{n_i}{\sum_i n_i}$$

with $N_i = N_A n_i$

Weight (mass) concentration $w_i$ of a component $i$ in a phase or material:

$$w_i = \frac{m_i}{m} = \frac{m_i}{\sum_i m_i} = \frac{n_i M_i}{\sum_i n_i M_i} = \frac{x_i M_i}{\sum_i x_i M_i}$$

with $m_i = M_i n_i$ and $M_i$ of $i$ being the molar mass in g/mol.

The boundary conditions $\sum_i x_i = 1$ and $\sum_i w_i = 1$ need to be fulfilled.
Essential Quantities: $x_i, w_i$

Consider a perlitic C80 alloy:

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w_i / m%$</td>
<td>99.20 m%</td>
<td>0.80 m%</td>
</tr>
<tr>
<td>$M_i / g/mol$</td>
<td>55.845 g/mol</td>
<td>12.001 g/mol</td>
</tr>
<tr>
<td>$x_i / at%$</td>
<td>96.38 at%</td>
<td>3.62 at%</td>
</tr>
</tbody>
</table>

When atomic weights are different, it is important to indicate how the composition is noted!

$$x_i = \frac{n_i}{n} = \frac{m_i}{\sum_i M_i} = \frac{w_i}{\sum_i M_i}$$
Essential Quantities: $x_i^j, w_i^j$

- Compositions might be specific to phases $j$ as well.
- Again, consider a perlitic C80 alloy:

* taken from the phase diagram

<table>
<thead>
<tr>
<th>$j$</th>
<th>alloy</th>
<th>ferrite $\alpha$Fe</th>
<th>cementite $\text{Fe}_3\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$</td>
<td>Fe</td>
<td>C</td>
<td>Fe</td>
</tr>
<tr>
<td>$w_i^j , / , \text{m%}$</td>
<td>99.20</td>
<td>0.80</td>
<td>99.98</td>
</tr>
<tr>
<td>$M_i , \text{or} , M_j , / , \text{g/mol}$</td>
<td>55.845</td>
<td>12.001</td>
<td>55.804</td>
</tr>
<tr>
<td>$x_i^j , / , \text{at%}$</td>
<td>96.38</td>
<td>3.62</td>
<td>99.91</td>
</tr>
</tbody>
</table>

$$M^j = \frac{m^j}{n^j} = \frac{\sum_i n_i^j M_i}{n^j} = \sum_i \frac{n_i^j}{n^j} M_i = \sum_i x_i^j M_i$$

is the molar mass of the phase $j$. 
Essential Quantities: $x^j, w^j, v^j$

- For the phases $j$, their content can be expressed in terms of number of atoms, mass and volume:

\[
v^j = \frac{V^j}{V} = \frac{V^j}{\sum_j V^j} \quad m^j = \frac{\rho^j}{\rho^j} \frac{w^j}{\sum_i w^j} \quad \text{with } \rho^j = \frac{m^j}{v^j} \text{ being the mass density of } j \text{ in kg/m}^3.
\]

- The phase contents need to fulfill the boundary conditions:

\[
x_i = \sum_j x^j x_i^j \quad w_i = \sum_j w^j w_i^j \quad \sum_j v^j = 1
\]

Essentially corresponds to the lever rule when two phases are considered.
Consider a perlitic C80 alloy including its phases:

<table>
<thead>
<tr>
<th>$j$</th>
<th>alloy</th>
<th>ferrite $\alpha$Fe</th>
<th>cementite $\text{Fe}_3\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$</td>
<td>Fe</td>
<td>C</td>
<td>Fe</td>
</tr>
<tr>
<td>$w_i^j$ / m%</td>
<td>99.20</td>
<td>99.98</td>
<td>Fe</td>
</tr>
<tr>
<td>$w^j$ / m%</td>
<td>100.00</td>
<td>88.29</td>
<td></td>
</tr>
<tr>
<td>$x_i^j$ / at%</td>
<td>96.38</td>
<td>3.62</td>
<td>99.91</td>
</tr>
<tr>
<td>$x^j$ / at%</td>
<td>100.00</td>
<td>85.83</td>
<td></td>
</tr>
<tr>
<td>$\rho^j$ / kg/m$^3$</td>
<td>7853</td>
<td>7874</td>
<td></td>
</tr>
<tr>
<td>$v^j$ / vol%</td>
<td>100.00</td>
<td>88.06</td>
<td></td>
</tr>
</tbody>
</table>

$$x^{\alpha\text{Fe}} = \frac{x^\text{Fe}_3\text{C} - x_C}{x_C^{\text{Fe}_3\text{C}} - x^{\alpha\text{Fe}}}, \quad w^{\alpha\text{Fe}} = \frac{w^\text{Fe}_3\text{C} - w_C}{w_C^{\text{Fe}_3\text{C}} - w^{\alpha\text{Fe}}}$$

$$\rho = \frac{m}{V} = \frac{\sum_j \rho^j V^j}{\sum_j V^j} = \sum_j \rho^j \frac{V^j}{\sum_j V^j} = \sum_j \rho^j v^j$$

Note that densities are always averaged by using volume fractions, never mass or atomic fractions!
**Essential Quantities: \( x_i^j, w_i^j \)**

- Compare to a eutectic, gray cast iron including its phases:

<table>
<thead>
<tr>
<th>( j )</th>
<th>alloy</th>
<th>ferrite ( \alpha_{\text{Fe}} )</th>
<th>graphite ( C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( i )</td>
<td>Fe</td>
<td>C</td>
<td>Fe</td>
</tr>
<tr>
<td>( w_i^j ) / m%</td>
<td>95.70</td>
<td>4.30</td>
<td>99.98</td>
</tr>
<tr>
<td>( w^j ) / m%</td>
<td>100.0</td>
<td></td>
<td>95.72</td>
</tr>
<tr>
<td>( x_i^j ) / at%</td>
<td>82.72</td>
<td>17.28</td>
<td>99.91</td>
</tr>
<tr>
<td>( x^j ) / at%</td>
<td>100.0</td>
<td></td>
<td>82.80</td>
</tr>
<tr>
<td>( \rho^j ) / kg/m(^3)</td>
<td>7119</td>
<td>7874</td>
<td>2260</td>
</tr>
<tr>
<td>( v^j ) / vol%</td>
<td>100.00</td>
<td></td>
<td>86.51</td>
</tr>
</tbody>
</table>

\( \rho \) in g/cm\(^3\)
Essential Quantities

*x*<sub>A</sub>, *x*<sub>B</sub>, *x*<sub>C</sub>, ...

*w*<sub>A</sub>, *w*<sub>B</sub>, *w*<sub>C</sub>, ...

\[ x_\alpha, x_\alpha, x_\alpha, \ldots \]

\[ w_\alpha, w_\alpha, w_\alpha, \ldots \]

\[ x_\beta, x_\beta, x_\beta, \ldots \]

\[ w_\beta, w_\beta, w_\beta, \ldots \]

\[ x_\gamma, x_\gamma, x_\gamma, \ldots \]

\[ w_\gamma, w_\gamma, w_\gamma, \ldots \]

\[ x_A + x_B + x_C + \cdots = 1 \]

\[ w_A + w_B + w_C + \cdots = 1 \]
Essential Quantities

\[ x^\beta, w^\beta, v^\beta \]

\[ x^\alpha + x^\beta + x^\gamma + \cdots = 1 \]
\[ w^\alpha + w^\beta + w^\gamma + \cdots = 1 \]
\[ v^\alpha + v^\beta + v^\gamma + \cdots = 1 \]

\[ x_A = x^\alpha x_A^\alpha + x^\beta x_A^\beta + x^\gamma x_A^\gamma + \cdots \]
\[ w_A = w^\alpha w_A^\alpha + w^\beta w_A^\beta + w^\gamma w_A^\gamma + \cdots \]
\[ \cdots \]
Essential Quantities: \( c_i, c_i^j \)

- The aforementioned properties are used to describe
  - the *composition* (relative amount of an element, either with respect to number of atoms or mass) or
  - the *phase fraction* (relative amount of a phase, either with respect to number of atoms, mass or volume).

- This needs to be distinguished from
  - the *concentration* \( c \) that is a *volume-specific* content of substance as it is used for example when diffusion is concerned.
  - For this lecture, we only focus on the molar concentration:
    \[
    c_i = \frac{n_i}{V}, \quad c_i^j = \frac{n_i^j}{V^j}
    \]
    Hence, \( c \) has a physical unit, e.g. the molar concentration \( \left[ c_i, c_i^j \right] = \frac{\text{mol}}{\text{l}} \)
Thermodynamic Potentials

- Thermodynamic potentials are scalar quantities representing the state of a thermodynamic system.
- Many different potentials can be defined but only few are useful to be used for specific problems.

In order to outline the mathematical structure of the theory, we introduce the necessary potentials for a system defined by only $S, T$ and $p, V$. 
# Thermodynamic Potentials

<table>
<thead>
<tr>
<th>Potential</th>
<th>Symbol</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal energy</td>
<td>$U = U(S, V)$</td>
<td>Capacity to do work and release heat.</td>
</tr>
<tr>
<td>Helmholtz (free) energy</td>
<td>$F = F(T, V)$</td>
<td>Capacity to do mechanical and non-mechanical work.</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>$H = H(S, p)$</td>
<td>Capacity to do non-mechanical work and release heat.</td>
</tr>
<tr>
<td>Gibbs (free) energy</td>
<td>$G = G(T, p)$</td>
<td>Capacity to do non-mechanical work.</td>
</tr>
</tbody>
</table>
Thermodynamic Potentials

The starting point: **the internal energy is always a function of all extensive properties of a system.** Anyhow, in most cases internal energy remains unknown and impossible to be calculated. A transformation to more suitable potentials is possible by the Legendre transform. It allows for obtaining potentials with reasonable “natural variables”.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Transformation</th>
<th>Differentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U = U(S,V)$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$F = F(T,V)$</td>
<td>$F = U - TS$</td>
<td>$dF = dU - T dS - S dT$</td>
</tr>
<tr>
<td>$H = H(S,p)$</td>
<td>$H = U + pV$</td>
<td>$dH = dU + p dV + V dp$</td>
</tr>
<tr>
<td>$G = G(T,p)$</td>
<td>$G = U - TS + pV$</td>
<td>$dG = dU - T dS - S dT$ + $p dV + V dp$</td>
</tr>
</tbody>
</table>
Thermodynamic Potentials

When the **thermodynamic laws** are applied:

\[
dU = dQ - dW
\]

with \(dQ = T \, dS\) and \(dW = p \, dV\) and \(dU = 0\) for a **closed system**. Hence, \(T \, dS = p \, dV\).

\[
dU = dQ - dW\] refers to heat flowing *in* and work done *on* the system!

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Transformation</th>
<th>Differentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>(U = U(S,V))</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>(F = F(T,V))</td>
<td>(F = U - T , S)</td>
<td>(dF = 0 - p , dV - S , dT)</td>
</tr>
<tr>
<td>(H = H(S,p))</td>
<td>(H = U + p , V)</td>
<td>(dH = 0 + T , dS + V , dp)</td>
</tr>
<tr>
<td>(G = G(T,p))</td>
<td>(G = U - T , S + p , V)</td>
<td>(dG = 0 - T , dS - S , dT + T , dS + V , dp)</td>
</tr>
</tbody>
</table>
Thermodynamic Potentials

- The „natural variables“ \( x, y, z, \ldots \) of a function \( f(x, y, z, \ldots) \) are obtained by comparing the gained differentials with the total differential of the function.

\[
\frac{df}{dx} \bigg|_{y,z,\ldots} \, dx + \frac{df}{dy} \bigg|_{x,z,\ldots} \, dy + \frac{df}{dz} \bigg|_{x,y,\ldots} \, dz + \ldots
\]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Transformation</th>
<th>Differentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>( U = U(S, V) )</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>( F = F(T, V) )</td>
<td>( F = U - T , S )</td>
<td>( dF = -p , dV - S , dT )</td>
</tr>
<tr>
<td>( H = H(S, p) )</td>
<td>( H = U + p , V )</td>
<td>( dH = T , dS + V , dp )</td>
</tr>
<tr>
<td>( G = G(T, p) )</td>
<td>( G = U - T , S + p , V )</td>
<td>( dG = -S , dT + V , dp )</td>
</tr>
</tbody>
</table>
Thermodynamic Potentials

The "natural variables" $x, y, z, ...$ of a function $f(x, y, z, ...)$ are obtained by comparing the gained differentials with the total differential of the function

$$df = \frac{\partial f}{\partial x} |_{y,z,...} dx + \frac{\partial f}{\partial y} |_{x,z,...} dy + \frac{\partial f}{\partial z} |_{x,y,...} dz + \cdots$$

Note that the partial differentials also become physically reasonable:

<table>
<thead>
<tr>
<th>Differentials</th>
<th>Partial differentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>$dU = dQ - dW = T , dS - p , dV$</td>
<td>$T = \frac{\partial U}{\partial S}</td>
</tr>
<tr>
<td>$dF = -p , dV - S , dT$</td>
<td>$-p = \frac{\partial F}{\partial V}</td>
</tr>
<tr>
<td>$dH = T , dS + V , dp$</td>
<td>$T = \frac{\partial H}{\partial S}</td>
</tr>
<tr>
<td>$dG = -S , dT + V , dp$</td>
<td>$-S = \frac{\partial G}{\partial T}</td>
</tr>
</tbody>
</table>
### Guggenheim Mnemonic

<table>
<thead>
<tr>
<th>$-S$</th>
<th>$U$</th>
<th>$V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td></td>
<td>$F$</td>
</tr>
<tr>
<td>$-\rho$</td>
<td>$G$</td>
<td>$T$</td>
</tr>
</tbody>
</table>

*Good Physicists Have Studied Under Very Fine Teachers*

*SUV-Fahrer tragen gerne pinke Hemden*
Guggenheim Mnemonic

Good Physicists Have Studied Under Very Fine Teachers
SUV-Fahrer tragen gerne pinke Hemden

<table>
<thead>
<tr>
<th>−S</th>
<th>U</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>−p</td>
<td>G</td>
<td>T</td>
</tr>
</tbody>
</table>

$U = U(S, V)$
Guggenheim Mnemonic

\[ dU = T \, dS - p \, dV \]

Note that the sign only affects the pre-differential factor, not the differential itself.

Good Physicists Have Studied Under Very Fine Teachers
SUV-Fahrer tragen gerne pinke Hemden
## Thermodynamic Potentials

<table>
<thead>
<tr>
<th>Potential</th>
<th>Symbol</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal energy</td>
<td>$U = U(S, V)$</td>
<td>When potential energies in vacuum are of interest because then it becomes accessible</td>
</tr>
<tr>
<td>Helmholtz (free) energy</td>
<td>$F = F(T, V)$</td>
<td>For thermodynamic systems considered at $T = \text{const.}$, e.g. in a immersion cooler or heater</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>$H = H(S, p)$</td>
<td>For thermodynamic systems considered at $p = \text{const.}$, e.g. chemical reactions in a test tube</td>
</tr>
<tr>
<td>Gibbs (free) energy</td>
<td>$G = G(T, p)$</td>
<td>For thermodynamic systems considered at $T, p = \text{const.}$, e.g. materials undergoing phase transitions</td>
</tr>
</tbody>
</table>
Thermodynamic Potentials

The aforementioned structure can be extended to many more physical effects by incorporating the respective extensive and intensive variables. Of course, the number of possible potentials increases:

<table>
<thead>
<tr>
<th>Potential</th>
<th>Transformation</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal energy</td>
<td>$-\ U = U(S, V, N_i, \varepsilon_{kl}, D_k, B_k, ...)$</td>
<td></td>
</tr>
<tr>
<td>Helmholtz (free) energy</td>
<td>$F = U - T S$</td>
<td>$F = F(T, V, N_i, \varepsilon_{kl}, D_k, B_k, ...)$</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>$H = U + p V$</td>
<td>$H = H(S, p, N_i, \varepsilon_{kl}, D_k, B_k, ...)$</td>
</tr>
<tr>
<td>Gibbs (free) energy</td>
<td>$G = U - T S + p V$</td>
<td>$G = G(T, p, N_i, \varepsilon_{kl}, D_k, B_k, ...)$</td>
</tr>
<tr>
<td>Grand potential</td>
<td>$\Omega = U - T S - \sum_i \mu_i N_i$</td>
<td>$\Omega = \Omega(T, p, \mu_i, \varepsilon_{kl}, D_k, B_k, ...)$</td>
</tr>
</tbody>
</table>

etc.
Thermodynamic Equilibrium

- Thermodynamic equilibrium corresponds to a stationary condition where no macroscopic flow of energy or atoms occurs.
- Hence, no macroscopic change of the system occurs (while it continuously changes between the various microscopic realizations of the system).
Stability: Stable

stable state with absolute minimum energy

Fluctuations do not lead to a transition.
Stability: Metastable

*metastable* state with local minimum energy

Fluctuations do not lead to an *immediate* transition.
Stability: Metastable

metastable state with local minimum energy

Note that critical fluctuations exist that lead to transition by overcoming the energy barrier.

These fluctuations are statistical in nature and occur with a certain probability. Hence, the transition is controlled by sufficient time or increased temperature (that increases the probability of sufficiently large fluctuations).
Stability: unstable

Any fluctuation always leads to a transition.

Note that from mechanical point of view, the system may obtain force balance. This is not equivalent to thermodynamic stability (since it involves thermal, mechanical, chemical and radiative equilibrium).
Thermodynamic Equilibrium

For a simple thermodynamic system, following formalism for transitions of the system can be done based on the aforementioned statements:

\[ dU = dQ - dW \]

\[ dH = d(U + p V) = dU + p \, dV + V \, dp = T \, dS - p \, dV + p \, dV + V \, dp \]
\[ = T \, dS + V \, dp \]

at \( p = \text{const.} \): \( dH = T \, dS = dQ \) corr. to the heat involved

\[ dF = d(U - T \, S) = dU - T \, dS - S \, dT = T \, dS - p \, dV - T \, dS - S \, dT \]
\[ = -p \, dV - S \, dT \]

at \( T = \text{const.} \): \( dF = -p \, dV = -dW \) corr. to the work done on the system

\[ dG = d(U - T \, S + p \, V) = V \, dp - S \, dT \]

at \( T, p = \text{const.} \): \( dG = 0 \)
For a system maintained at constant $p$ and $T$ during the transformation (as typical of materials science related problems), $G$ becomes minimal: $dG = 0$.

Hence, focus during the lecture will be on interpretation of the dependence of $G$ on various parameters in order to obtain the thermodynamically feasible states.
Driving Force

- When $G$ is not minimal, the Gibbs free energy difference $\Delta G^{\text{tr}}$ to the minimal $G$ state is the driving force to promote the transformation from the high $G$ state to the minimal $G$ state.

- If there is a barrier $\Delta G^{\text{act}}$ to overcome and achieve the minimal $G$ state, the initial configuration is metastable and the activation of the transformation needs fluctuation or perturbation.

- If there is no barrier to overcome, the transformation occurs spontaneously (sometimes referred to as “continuous” due to the respective spatial and temporal process, see later in the lecture).

- A driving force is necessary but not sufficient for the transformation to occur. There needs to be a temporal/spatial/chemical/etc. reaction path to mediate the transformation from one state into the other. This is subject of kinetics as the sufficient requisite of the transformation.
Driving Force

\[ \Delta G^{tr} \text{ is the driving force} \]

\[ \Delta G^{act} \text{ is the activation energy} \]
Driving Force

\[ \Delta G^{tr} \text{ is the driving force} \]
Temperature Dependence of $G$

As seen on the slide before, the temperature dependence of $G$ is of central interest in the following chapters in order to assess temperature-depending phase transformations.

The temperature dependence can be estimated by following temperature dependence of the enthalpy and entropy contribution:

$$G = H - TS$$
Temperature Dependence of $H$

- $H$ has a zero-K term $H_0$. The absolute magnitude of $H_0$ remains unknown and is not important.

- From experiments, the relative stability of certain material’s states are known and allow to estimate the ratios of $H_0$. All metallic elements are for example solid at 0 K, liquid above $T_m$ and gaseous above $T_b$. Hence, $H_{0,S} < H_{0,L} < H_{0,G}$. Note that this information is put into the following considerations, not a result of it!

- Another contribution arises from heating up the system to the temperature under consideration:

$$H = H_0 + \int_0^T c_p(T) \, dT$$
Temperature Dependence of $H$

- The heat capacity $c_p(T) = \frac{\partial H}{\partial T} \mid_p$ as a function of temperature can be determined by using calorimetric setups (see Ch. 3).
- As mentioned earlier in the chapter, phase transformations might be associated with a latent heat (discontinuous transformations) due to sudden change in entropy. These heats are equivalent to
  \[ \Delta S^{\text{tr}} = \frac{Q^{\text{tr}}}{T^{\text{tr}}} = \frac{\Delta H^{\text{tr}}}{T^{\text{tr}}} \]
and need to be added to $H$. In case of phase transformations, the integration must be performed stepwise for each phase.
Temperature Dependence of $c$

- In order to assess the temperature contributions to heat capacity, the thermally induced motion of particles needs to be considered.
- Contributions in materials arise from:
  - phonons (quasiparticles corresponding to a collective excitations of an elastic lattice)
  - magnons (quasiparticles corresponding to a collective excitations of magnetic lattice)
  - electrons
Temperature Dependence of $c$

- The contribution by phonons is properly described by the Debye model

$$c_V \approx \frac{12 \pi^4}{5} N k_B \left( \frac{T}{\Theta_D} \right)^3 \propto T^3 \text{ for } T < \Theta_D$$

$$c_V = 3 N k_B \text{ for } T \gg \Theta_D$$

- The Debye model considers a linear dispersion relation of phonons $\omega \propto k$ below $\omega_D$ with a continuous population of phonon states with increasing temperature. One linear and two transversal oscillation modes are considered. The Debye temperature is provided by a maximum angular frequency $\omega_D$ of the lattice – the total number of phonon modes is limited by $3N$ with the number of particles in the system $N$.

- In the high temperature limit, it approaches the thermodynamic expectation for a solid (Dulong-Petit law).
Temperature Dependence of $c$

The scheme of the Debye model can easily be adopted for other Bosonian particles, e.g. magnons, when the dispersion relation, integration and number boundary conditions are modified. For ferromagnetic materials, a proportionality of:

$$c_V \propto T^{3/2}$$

is observed.
Temperature Dependence of \( c \)

- The contribution of electrons was one of the most challenging subjects of solid state physics in the early 20\textsuperscript{th} century – together with the vanishing electrical resistivity of perfect metallic crystals at 0 K and misleading predictions for the Hall coefficient.

- According to the Drude model of fully delocalized electrons, they should provide a similar contribution to heat capacity as an atomic gas with \( \frac{3}{2} k_B \) per electron, but they don’t!

- Occupation of electronic states in solids occurs according to the Pauli exclusion principle since electrons are Fermions. The occupation of the states is described by the Fermi-Dirac distribution (rather than a Boltzmann distribution). Only a small fraction of electrons at about the Fermi level contribute to \( c \) (and conduction). At low temperatures, the contribution of electrons in metals is:

\[
c_V \propto T
\]
Temperature Dependence of $c$

$c/\text{J mol K}$

$c_p$, $c_V$

$\Theta_D$, $T_m$

$3R = 24.942 \text{ J mol K}$

Copper Cu

Temperature Dependence of $c$

The experimental determination of $c$ is usually performed for $p = \text{const.}$ as $c_p = \frac{\partial H}{\partial T} |_p$, while $c_v$ is of theoretical importance since it corresponds to $c_v = \frac{\partial U}{\partial T} |_V$. The relation between the two is:

$$c_p = c_v (1 + \beta \gamma T)$$

$\gamma$ is the Grüneisen parameter

$$\gamma = \frac{\beta K_T V_m}{c_v} = \frac{\beta K_S V_m}{c_p}$$

$\beta$ is the volume expansion coefficient. $K_T$ and $K_S$ are the isothermal and adiabatic bulk moduli. $V_m$ is the molar volume.

For solids, the difference is usually considered small. In general, $c_p > c_v$. 

Phase Transformations
Temperature Dependence of $c$

![Graph showing the temperature dependence of $c$ for Tungsten W.](image)

Temperature Dependence of \( c \)

Note the discontinuity at the phase transformation. This is indicative of a discontinuous phase transformation!

\[ c_p / \frac{J}{\text{mol K}} \]

\[ 3R \]

Silicon Si

Temperature Dependence of $c$

Again, discontinuities for discontinuous phase transformations are observed. For the magnetic transition between ferro- and paramagnetic state at Curie temperature $T_C$, a huge anomaly of $c$ is observed indicative of continuous phase transformation.

Iron Fe

At Néel temperature where the transition from antiferro- to paramagnetism occurs, a similar but much smaller anomaly occurs.

Manganese Mn

Temperature Dependence of $S$

- The entropy $S$ is similarly found by integration with:

$$S = S_0 + \int_0^T \frac{c_p(T)}{T} \,dT$$

- And similar to $H$, entropy changes due to transformations $\Delta S^{\text{tr}}$ need to be added to $S$. 

Phase Transformations
Temperature Dependence of $G$

If we consider a polynomial function $c_p(T) = \sum_n A_n T^n$ with $n \geq 1$ and $A_n \geq 0$, the integration of $H(T)$ and $S(T)$ yields:

$$G(T) = H(T) - T S(T)$$

$$= H_0 + \int_0^T \sum_n A_n T^n \, dT - T S_0 - T \int_0^T \sum_n \frac{A_n T^n}{T} \, dT$$

$$= H_0 - T S_0 + \sum_n \frac{A_n}{n+1} T^{n+1} - T \sum_n \frac{A_n}{n} T^n$$

$$= H_0 - T S_0 + \sum_n \frac{A_n}{n+1} T^{n+1} - \sum_n \frac{A_n}{n} T^{n+1}$$

$$= H_0 - T S_0 - \sum_n \frac{A_n}{n(n+1)} T^{n+1}$$

Phase Transformations
Temperature Dependence of $G$

$G$, $H$, $-T \, S$

$G$ continuously decreases with increasing temperature $T$! The slope of $G$ is indicative of the entropy $S$.

$H_0 = G_0$

$-S = \left. \frac{\partial G}{\partial T} \right|_p$
Temperature Dependence of $G$

- In many cases, it is useful to assess the entropy $S$ not just by the phenomenological treatment as shown on the slides before but also by its statistical interpretation as quantification for the state of disorder, randomness, or uncertainty.

- In this representation, entropy depends on the number of microscopic realizations $\omega$ of a macro system in one and the same macro state:

$$S = k_B \ln \omega$$

- Any macro state of the systems treated in this lecture can be achieved by many different microscopic arrangements of the atoms, molecules and defects without any noticeable change in the state of the macro system. The number of different realizations is decisive for the entropy $S$.  

Application of $G$

As an example for the application of $G$, the concentration of vacancies in thermodynamic equilibrium is considered in what follows since they are of utmost importance for Ch. 1b.

The incorporation of empty lattice sites, namely vacancies, results in disorder of the system and, hence, generally leads to a reduction in $G$. Since bonds remain unsaturated, a certain enthalpy is needed to form the vacancies and, thus, an equilibrium vacancy concentration is obtained by the balance of the two factors.
Thermal Vacancies

The Gibb’s free energy change due to $N^V$ vacancies in a crystal of $N$ atoms is:

$$\Delta G^V = \Delta H^V - T \cdot \Delta S^V$$

State 1: perfect crystal with $\omega = 1$

State 2: crystal containing vacancies with $\omega = \frac{N!}{N^V! \cdot (N-N^V)!}$ realizations and some distortion around the vacancies.
Thermal Vacancies

- In order to form $N^V$ vacancies, $N^V \Delta H^{V,F}$ enthalpy is needed due to unsaturated bonds. $\Delta H^{V,F}$ denotes the formation enthalpy per vacancy. It typically ranges between 0.5 eV (low $T_m$ metals) up to 4.0 eV (high $T_m$ metals).

- Due to distortion around vacancies and the changes in vibration states (higher vibration frequency before the vacancy is formed), the disorder of the system increases over the perfect crystal by $N_V \Delta S^{V,F}$. $\Delta S^{V,F}$ denotes the formation entropy per vacancy. It ranges between $(1-2)k_B$ at low temperatures and $(4-5)k_B$ at high temperatures.

- Due to the incorporation of vacancies, the number of realizations of the crystal increases since the exact positioning of the vacancies does not change the macro state of the system. Hence, the so-called configurational entropy change needs to be considered

$$\Delta S^{V, config} = S^{faulted} - S^{perfect} = k_B \cdot \ln \frac{N!}{N^V! \cdot (N - N^V)!} - k_B \cdot \ln 1$$

$$= k_B \cdot \left( \ln N! - \ln N^V! - \ln(N - N^V)! \right)$$
Thermal Vacancies

- Using Stirling's approximation for factorials $x! \approx x \ln x - x$ for $x > 751$:
  \[ \Delta S_{\text{V,config}} \approx k_B \cdot \left( N \ln N - N - N^V \ln N^V + N^V - (N - N^V) \ln(N - N^V) + (N - N^V) \right) \]
  \[ = k_B \cdot \left( N \ln N - N^V \ln N^V - (N - N^V) \ln(N - N^V) \right) \]

- Hence, $G$ is:
  \[ \Delta G^V = N^V \Delta H^{V,F} - T \left( N^V \Delta S^{V,F} + \Delta S_{\text{V,config}} \right) \]

- with \( \frac{d\Delta G^V}{dN^V} \bigg|_{N^V,0} = 0 \) for thermodynamic equilibrium:
  \[ \frac{d\Delta G^V}{dN^V} \bigg|_{N^V,0} = \Delta H^{V,F} - T \Delta S^{V,F} - T \frac{d\Delta S_{\text{V,config}}}{dN^V} \]
  \[ \Delta H^{V,F} - T \Delta S^{V,F} + T \left( k_B \cdot \ln \frac{N^V,0}{N - N^V,0} \right) \approx \Delta H^{V,F} - T \Delta S^{V,F} + T \left( k_B \cdot \ln \frac{N^V,0}{N} \right) = 0 \]
The equilibrium vacancy concentration is:

$$x^{V,0} = \frac{N^{V,0}}{N} = \exp\left(\frac{T \Delta S^{V,F} - \Delta H^{V,F}}{k_B T}\right) = \exp\left(\frac{\Delta S^{V,F}}{k_B}\right) \exp\left(-\frac{\Delta H^{V,F}}{k_B T}\right)$$

$$x^{V,0} \propto \exp\left(-\frac{\Delta H^{V,F}}{k_B T}\right)$$

Close to melting temperature $x^{V,0}$ can reach $10^{-4}$ to $10^{-3}$. 

Thermal Vacancies
Thermal Vacancies

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta H_{V,F}^{\text{eV}}$</th>
<th>$\Delta S_{V,F}^{\text{eV}} / k_B$</th>
<th>$x_{V,0} / 10^{-4}$ @ $T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.7</td>
<td>0.6</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>1.2</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>Au</td>
<td>1.0</td>
<td>1.1</td>
<td>7</td>
</tr>
<tr>
<td>Ag</td>
<td>1.1</td>
<td>–</td>
<td>2</td>
</tr>
<tr>
<td>Pb</td>
<td>0.5</td>
<td>0.7</td>
<td>2</td>
</tr>
<tr>
<td>Pt</td>
<td>1.5</td>
<td>1.3</td>
<td>–</td>
</tr>
<tr>
<td>Ni</td>
<td>1.7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mo</td>
<td>3.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>W</td>
<td>4.0</td>
<td>2.3</td>
<td>1</td>
</tr>
</tbody>
</table>

Note that these numbers are intended to give you some impression. For a detailed and critical assessment of the various methods to obtain such numbers, please see: Y. Kraftmakher: Lecture Notes on Equilibrium Point Defects and Thermophysical Properties of Metals, Singapore, New Jersey, London, Hong Kong: World Scientific (2000)