



Phase Transformations in Materials

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Topics

- Thermodynamic Fundamentals
 - Component and Phase
 - Position Dependence of Properties P = P(x)
 - 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 d*U*, d*F*, d*H*, d*G*
 - 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, ... 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 mutli-phase.
- For general discussions, we use α, β, γ, ... as place holders for solid solutions and A_mB_n, ... as place holders for stoichiometric intermittent phases.





Revision: Position Dependence of Properties

Homogeneous:

- property P is not dependent on position x
- $\square P \neq P(\boldsymbol{x})$

Inhomogeneous:

- property P is a function of the position x
- $\square P = P(\boldsymbol{x})$

Heterogeneous:

property P is a inhomogeneous and exhibits jump discontinuities (like at phase boundaries)







Isotropic:

- Property P is not depending on the direction and the description simplifies to a scalar number
- $\blacksquare P_{klmn...} = P$
- Anisotropic:
 - Property P dependents on the direction and the description requests the use of tensors

•
$$P_{klmn...}$$
 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.

intensive		extensive		potential product			
tempe	erature	entropy					
symbol	unit	symbol	unit	symbol	differentials	units	
Т	К	S	J K	T S	T dS S dT	J = Nm = Ws	

 $dS = \frac{dQ}{T} = \frac{c_p dT}{T}$ 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*

intensive		extei	extensive		notontial product			
pres	sure	volume				potential product		
symbol	unit	symbol	unit	symbol	differentials	units		
p	$Pa = \frac{N}{m^2}$	V	m ³	p V	p dV V dp	J = Nm = Ws		

dp = K dV with K being the bulk modulus in Pa. Phase transformations might be associated with a volume change ΔV^{tr} .



Essential Quantities: μ , 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.

intensive		exter	extensive		notontial product			
chemical	potential	particle number						
symbol	unit	symbol	unit	symbol	differentials	units		
μ	J	Ν	1	μΝ	$\mu \ \mathrm{d}N \ N \ \mathrm{d}\mu$	J = Nm = Ws		

 $dG = \sum_i \mu_i dN_i$ 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: σ_{kl} , ε_{kl}



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

intensive		extensive		notontial product		
stre	ess	strain				
symbol	unit	symbol	unit	symbol	differentials	units
σ_{kl}	$Pa = \frac{N}{m^2}$	$arepsilon_{kl}$	1	$\sigma_{kl} \varepsilon_{kl} V$	$\sigma_{kl} \operatorname{d}\!arepsilon_{kl} V \ arepsilon_{kl} \operatorname{d}\!\sigma_{kl} V$	J = Nm = Ws

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

Note the similarity of σ_{kl} , ε_{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, $k, l, m, n \dots$ are direction indices! Einstein sum convention is used.

intensive extensive							
electric	cal field	electrical displacement			potential product		
symbol	unit	symbol	unit	symbol	differentials	units	
E_{k}	$\frac{V}{m}$	D_k	$\frac{C}{m^2}$	$E_k D_k V$	$E_k dD_k V \\ D_k dE_k V$	J = Nm = Ws	

 $D_k = \varepsilon_{kl} E_l + P_k$ with ε_{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, $k, l, m, n \dots$ are direction indices! Einstein sum convention is used.

intensive extensive		nsive		notontial pro	aduat		
magne	tic field	magnetic flux					
symbol	unit	symbol	unit	symbol	differentials	units	
H_k	$\frac{A}{m}$	B_k	$\frac{V s}{m^2}$	$H_k B_k V$	$egin{array}{ll} H_k & \mathrm{d}B_k & V \ B_k & \mathrm{d}H_k & V \end{array}$	J = Nm = Ws	

 $B_k = \mu_{kl} H_l + M_k$ with μ_{kl} being the permeability tensor components in $\frac{N}{m^2}$ 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

•
$$P_k^{\rm sp} = p_k \Delta T$$
 for the pyro-electric effect

•
$$D_k = d_{k,lm} \sigma_{lm}$$
 for the piezo-electric effect

etc.























Heckmann Diagrams

direct coupling:

- heat capacity
- elastic compliance/stiffness
- magnetic permeability

cross coupling:

- magnetocaloric effect
- magnetostriction
- magnetoelectricity

etc.











- 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



dielectricity (all insulators)	 can belong to all 32 point groups exhibit at least a scalar ε_{ik}
piezoelectricity	 need to belong to the 20 non-centrosymmetric point groups (one exception)
pyroelectricity	 need to belong to the 10 polar point groups
ferroelectricity	 only when polarization is reversible by electric field



Essential Quantities: *x*_{*i*}, *w*_{*i*}



• Atomic concentration x_i of a component *i* in material:

$$x_{i} = \frac{N_{i}}{N} = \frac{N_{i}}{\sum_{i} N_{i}}$$
 with $N_{i} = N_{A} n_{i}$
$$= \frac{n_{i}}{n} = \frac{n_{i}}{\sum_{i} n_{i}}$$

• 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 pearlitic C80 alloy:

	Fe	С
<i>w_i</i> / m%	99.20 m%	0.80 m%
<i>M_i</i> / g/mol	55.845 g/mol	12.001 g/mol
x_i / at%	96.38 at%	3.62 at%

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

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



Essential Quantities: x_i^j , w_i^j



Compositions might be specific to phases *j* as well.
 Again, consider a pearlitic C80 alloy:

* taken from the phase diagram

j	alloy		ferrit	e αFe	cementite Fe ₃ C		
i	Fe	С	Fe	С	Fe	С	
w_i^j / m%	99.20	0.80	99.98	0.02*	93.32	6.68	
M _i or M ^j ∕g/mol	55.845	12.001	55.804		44.8	384	
x_i^j / at%	96.38	3.62	99.91	0.09	75.00	25.00*	

$$M^{j} = \frac{m^{j}}{n^{j}} = \frac{\sum_{i} n_{i}^{j} M_{i}}{n^{j}} = \sum_{i} \frac{n_{i}^{j}}{n^{j}} M_{i} = \sum_{i} x_{i}^{j} M_{i}$$

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:

$$v^{j} = \frac{V^{j}}{V} = \frac{V^{j}}{\sum_{j} V^{j}}$$
with $\rho^{j} = \frac{m^{j}}{V^{j}}$ being the

$$= \frac{\frac{m^{j}}{\rho^{j}}}{\sum_{i} \frac{w^{j}}{\rho^{j}}} = \frac{\frac{w^{j}}{\rho^{j}}}{\sum_{i} \frac{w^{j}}{\rho^{j}}}$$
kg/m³.

The phase contents need to fulfill the boundary conditions:

$$x_{i} = \sum_{j} x^{j} x_{i}^{j}$$
$$w_{i} = \sum_{j} w^{j} w_{i}^{j}$$
$$\sum_{j} v^{j} = 1$$

Essentially corresponds to the lever rule when two phases are considered.



Essential Quantities: x_i^j , w_i^j



Consider a perlitic C80 alloy including its phases:

j	a	lloy	ferrite αFe		cementite Fe ₃ C	
i	Fe	С	Fe	С	Fe	С
w_i^j / m%	99.20	0.80	99.98	0.02	93.32	6.68
<i>w^j /</i> m%	100.00		88.29		11.71	
x_i^j / at%	96.38	3.62	99.91	0.09	75.00	25.00
x^j / at%	10	0.00	85.83		14.17	
$ ho^{j}$ / kg/m 3	78	853	7874		7700	
v^j / vol%	100.00		88.06		11.	94
$x^{\alpha Fe} = \frac{x_C^{Fe_3C} - x_C}{x_C^{Fe_3C} - x_{\alpha}^{\alpha Fe}}, w^{\alpha Fe} = \frac{w_C^{Fe_3C} - w_C}{w_C^{Fe_3C} - w_{\alpha}^{\alpha Fe}}$ Note that densities are						

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

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:

j	alloy		ferrite αFe		graphite C	
i	Fe	С	Fe	С	Fe	С
w_i^j / m%	95.70	4.30	99.98	0.02	0.00	100.00
<i>w^j /</i> m%	100.0		95.72		4.28	
x_i^j / at%	82.72	17.28	99.91	0.09	0.00	100.00
<i>x^j /</i> at%	100.0		82.80		17.20	
$ ho^{j}$ / kg/m 3	7119		7874		2260	
v^j / vol%	10	0.00	86.51		13.49	











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:

$$c_i = \frac{n_i}{V}, c_i^j = \frac{n_i^j}{V}$$

• Hence, *c* has a physical unit, e.g. the molar concentration $|c_i, c_i^j| = \frac{\text{mol}}{1}$





- 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.





Potential	Symbol	Interpretation
Internal energy	U = U(S, V)	Capacity to do work and release heat.
Helmholtz (free) energy	F = F(T, V)	Capacity to do mechanical and non- mechanical work.
Enthalpy	H = H(S, p)	Capacity to do non-mechanical work and release heat.
Gibbs (free) energy	G = G(T, p)	Capacity to do non-mechanical work.





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".

Symbol	Transformation	Differentials
U = U(S, V)	-	_
$F = F(\mathbf{T}, V)$	F = U - T S	$\mathrm{d}F = \mathrm{d}U - T \mathrm{d}S - S \mathrm{d}T$
$H = H(S, \mathbf{p})$	H = U + p V	$\mathrm{d}H = \mathrm{d}U + p \; \mathrm{d}V + V \; \mathrm{d}p$
G = G(T, p)	G = U - T S + p V	dG = dU - T dS - S dT + p dV + V dp





When the thermodynamic laws are applied: $\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W$ 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!

Symbol	Transformation	Differentials
U = U(S, V)	—	—
F = F(T, V)	F = U - T S	$\mathrm{d}F = 0 - p \mathrm{d}V - S \mathrm{d}T$
H = H(S, p)	H = U + p V	$\mathrm{d}H = 0 + T \mathrm{d}S + V \mathrm{d}p$
G = G(T,p)	G = U - T S + p V	dG = 0 - T dS - S dT $+T dS + V dp$





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

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

Symbol	Transformation	Differentials
U = U(S, V)	-	—
$F = F(\mathbf{T}, \mathbf{V})$	F = U - T S	$\mathrm{d}F = -p \; \mathrm{d}V - S \; \mathrm{d}T$
$H = H(\mathbf{S}, \mathbf{p})$	H = U + p V	$\mathrm{d}H = T \; \mathrm{d}S + V \; \mathrm{d}p$
G = G(T, p)	G = U - T S + p V	$\mathrm{d}G = -S \mathrm{d}T + V \mathrm{d}p$





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

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

Note that the partial differentials also become physically reasonable:

Differentials	Partial differentials
$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W = T \mathrm{d}S - p \mathrm{d}V$	$T = \frac{\partial U}{\partial S} _{V}, -p = \frac{\partial U}{\partial V} _{S}$
$\mathrm{d}F = -p \mathrm{d}V - S \mathrm{d}T$	$-p = \frac{\partial F}{\partial V} _{T}, -S = \frac{\partial F}{\partial T} _{V}$
$\mathrm{d}H = T \mathrm{d}S + V \mathrm{d}p$	$T = \frac{\partial H}{\partial S} _p, V = \frac{\partial H}{\partial p} _S$
$\mathrm{d}G = -\mathbf{S}\mathrm{d}T + \mathbf{V}\mathrm{d}p$	$-S = \frac{\partial G}{\partial T} _p, V = \frac{\partial G}{\partial p} _T$



Guggenheim Mnemonic





SUV-Fahrer tragen gerne pinke Hemden




Guggenheim Mnemonic





Guggenheim Mnemonic





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

$$\mathrm{d}U = T \,\mathrm{d}S - p \,\mathrm{d}V$$

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



Thermodynamic Potentials



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



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:

Potential	Transformation	Symbol		
Internal energy	—	$U = U(S, V, N_i, \varepsilon_{kl}, D_k, B_k, \dots)$		
Helmholtz (free) energy	F = U - T S	$F = F(T, V, N_i, \varepsilon_{kl}, D_k, B_k, \dots)$		
Enthalpy	H = U + p V	$H = H(S, p, N_i, \varepsilon_{kl}, D_k, B_k, \dots)$		
Gibbs (free) energy	G = U - T S + p V	$G = G(T, p, N_i, \varepsilon_{kl}, D_k, B_k, \dots)$		
Grand potential	$\Omega = U - T S - \sum_{i} \mu_i N_i$	$\Omega = \Omega(T, p, \mu_i, \varepsilon_{kl}, D_k, B_k, \dots)$		
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









Stability: Metastable





Stability: Metastable







Stability: Unstable







Thermodynamic Equilibrium



- For a simple thermodynamic system, following formalism for transitions of the system can be done based on the aforementioned statements:
 - $\bullet dU = dQ dW$

•
$$dH = d(U + pV) = dU + p dV + V dp = T dS - p dV + p dV + V dp$$

= $T dS + V dp$
at $p = \text{const.}$: $dH = T dS = dQ$ corr. to the heat involved

•
$$dF = d(U - TS) = dU - T dS - S dT = T dS - p dV - T dS - S dT$$

= $-p dV - S dT$
at $T = \text{const.}$: $dF = -p dV = -dW$ corr. to the work done on the system

•
$$dG = d(U - TS + pV) = V dp - S dT$$

at $T, p = \text{const.}$: $dG = 0$



Thermodynamic Equilibrium



- 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** ΔG^{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** ΔG^{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.













- As seen on the slide before, the temperature dependence of G is of central interest in the following chapters in order to assess temperaturedepending phase transformations.
- The temperature dependence can be estimated by following temperature dependence of the enthalpy and entropy contribution:

G = H - T S





- 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:

$$H = H_0 + \int_0^T c_p(T) \, \mathrm{d}T$$





The heat capacity $c_p(T) = \frac{\partial H}{\partial T}|_p$ 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 $\Delta S^{tr} = \frac{Q^{tr}}{T^{tr}} = \frac{\Delta H^{tr}}{T^{tr}}$ and need to be added to *H*. In case of phase transformations, the integration must be performed stepwise for each phase.





- 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





The contribution by phonons is properly described by the Debye model

$$c_V \approx \frac{12\pi^4}{5} N k_{\rm B} \left(\frac{T}{\Theta_{\rm D}}\right)^3 \propto T^3 \text{ for } T < \Theta_{\rm D}$$

$$c_V = 3 N k_{\rm B} \text{ for } T \gg \Theta_{\rm D}$$

- The Debye model considers a linear dispersion relation of phonons $\omega \propto \mathbf{k}$ below $\omega_{\rm D}$ 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 $\omega_{\rm D}$ 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).





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:

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

is observed.





- The contribution of electrons was one of the most challenging subjects of solid state physics in the early 20th 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 $\frac{3}{2}k_{\rm B}$ 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:

 $c_V \propto T$













The experimental determination of *c* is usually performed for p = 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:

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

• γ is the Grüneisen parameter

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

• β 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, $c_p > c_V$.







G. K. White and S. J. Collocott: Heat Capacity of Reference Materials: Cu and W, Journal of Physical and Chemical Reference Data 13 (1984) 1251







P. D. Desai: Thermodynamic Properties of Iron and Silicon, Journal of Physical and Chemical Reference Data 15 (1986) 967







P. D. Desai: Thermodynamic Properties of Iron and Silicon, Journal of Physical and Chemical Reference Data 15 (1986) 967













The entropy *S* is similarly found by integration with:

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

• And similar to *H*, entropy changes due to transformations ΔS^{tr} need to be added to *S*.





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

$$\begin{split} G(T) &= H(T) - T S(T) \\ &= H_0 + \int_0^T \sum_n A_n T^n \, \mathrm{d}T - T S_0 - T \int_0^T \sum_n \frac{A_n T^n}{T} \, \mathrm{d}T \\ &= H_0 - T S_0 + \sum_n \frac{A_n}{n+1} T^{n+1} - T \int_0^T \sum_n A_n T^{n-1} \, \mathrm{d}T \\ &= H_0 - T S_0 + \sum_n \frac{A_n}{n+1} T^{n+1} - T \sum_n \frac{A_n}{n} T^n \\ &= H_0 - T S_0 + \sum_n \frac{A_n}{n+1} T^{n+1} - \sum_n \frac{A_n}{n} T^{n+1} \\ &= H_0 - T S_0 + \sum_n \frac{A_n}{n+1} T^{n+1} - \sum_n \frac{A_n}{n} T^{n+1} \\ &= H_0 - T S_0 - \sum_n \frac{A_n}{n(n+1)} T^{n+1} \end{split}$$











- 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 ω of a macro system in one and the same macro state: $S = k_{\rm B} \ln \omega$
- 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.



IAM Institute for Applied Materials

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 $\omega = 1$





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 $T_{\rm m}$ metals) up to 4.0 eV (high $T_{\rm m}$ 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

$$\Delta S^{\text{V,config}} = S^{\text{faulted}} - S^{\text{perfect}} = k_{\text{B}} \cdot \ln \frac{N!}{N^{\text{V}!} \cdot (N - N^{\text{V}})!} - k_{\text{B}} \cdot \ln 1$$
$$= k_{\text{B}} \cdot \left(\ln N! - \ln N^{\text{V}!} - \ln (N - N^{\text{V}})! \right)$$



Thermal Vacancies



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

Hence, G is:

$$\Delta G^{V} = N^{V} \Delta H^{V,F} - T \left(N_{V} \Delta S^{V,F} + \Delta S^{V,config} \right)$$

$$\text{with} \frac{d\Delta G^{V}}{dN^{V}}\Big|_{N^{V,0}} = 0 \text{ for thermodynamic equilibrium:} \frac{d\Delta G^{V}}{dN^{V}}\Big|_{N^{V,0}} = \Delta H^{V,F} - T \Delta S^{V,F} - T \frac{d\Delta S^{V,\text{config}}}{dN^{V}} \Delta H^{V,F} - T \Delta S^{V,F} + T \left(k_{B} \cdot \ln \frac{N^{V,0}}{N - N^{V,0}}\right) \approx \Delta H^{V,F} - T \Delta S^{V,F} + T \left(k_{B} \cdot \ln \frac{N^{V,0}}{N}\right) = 0$$



Thermal Vacancies



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

Metal	$\Delta H^{V,F}/eV$	$\Delta S^{V,F}/k_{ m B}$	$x^{V,0}/10^{-4}$ @ $T_{\rm m}$
Al	0.7	0.6	10
Cu	1.2	1.5	2
Au	1.0	1.1	7
Ag	1.1	_	2
Pb	0.5	0.7	2
Pt	1.5	1.3	—
Ni	1.7	_	—
Мо	3.0	_	—
W	4.0	2.3	1

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)

H. Mehrer: Diffusion in Solids, Berlin, Heidelberg: Springer-Verlag (2007)





Arrhenius Function







Arrhenius Function



