

Title

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Content

Introduction to solidification

- Technical importance of solidification
- General terms and basics in solidification
- The role of heat extraction
- Directional solidification
- Special solidification techniques
- Aim of computational materials science
- Dendritic solidification
- Eutectic solidification
- Peritectic solidification
- Monotectic solidification
- Course outline

Literature recommendations

A large part of this course is treated in [Kurz and Fisher, 1998] and [Porter et al., 2009]. A good german textbook is [Gottstein, 2007].

-  **Gottstein, G. (2007).**
Physikalische Grundlagen der Materialkunde.
Springer Verlag Berlin Heidelberg.
-  **Kurz, W. and Fisher, D. (1998).**
Fundamentals of solidification.
Trans Tech Publications Ltd, Switzerland Germany UK USA.
-  **Porter, D. A., Easterling, K. E., and Sherif, M. Y. (2009).**
Phase transformations in metals and alloys (third edition).
CRC Press, Taylor & Francis Group, Boca Raton, London, New York.

General problem definition

During processing of materials an inhomogeneous microstructure evolves, originating from the kinetics of the processes. This may lead to potentially weak points and eventually failure.

In this lecture, there is a focus on **metal solidification**. Here crystal nucleation, a necessary prerequisite to solidification, is a ubiquitous event. Glass, a metastable phase, is formed only at extremely high cooling rates.

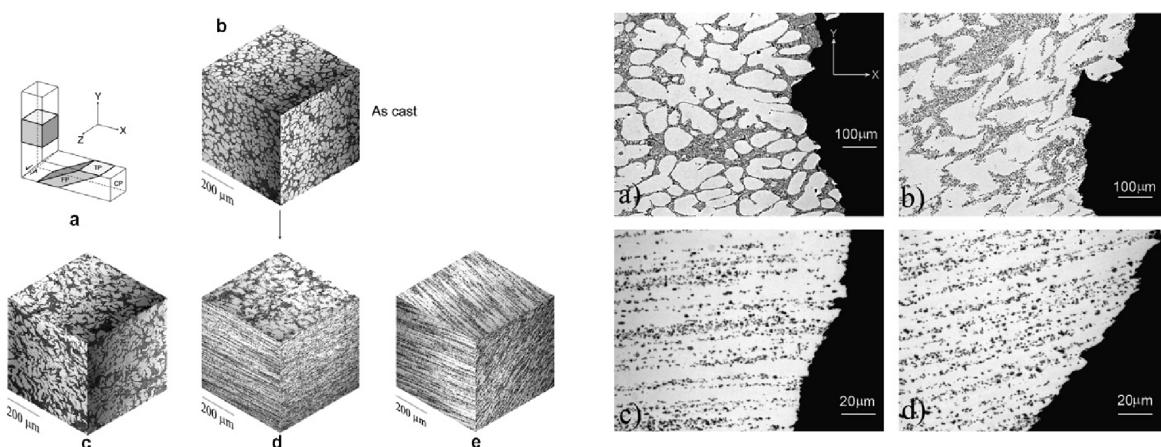
Modeling goal:

Understand microstructure evolution depending on different solidification conditions. → optimize processing parameters.

Effect of microstructure - example

Microstructure formed after casting may have severe effects on mechanical behaviour.

Example: Ingot casting of Al-7%Si alloy with subsequent ECAP processing (severe plastic deformation)



J.M. Garcia-Infanta et al., Scripta Mater. 58 (2008) 138.

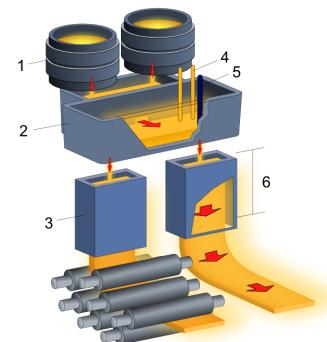
Technical importance of solidification

Solidification is one of the most important **forming processes** in materials science, involved in the production of almost all technical products. It is a very economic metal forming process (espec. for complex shaped pieces)



Solidification as a phase transition occurs during

- metal casting (ingot casting, continuous casting)
 - metal welding, soldering
 - polymer injection moulding
 - growth of silicon single or poly- crystals



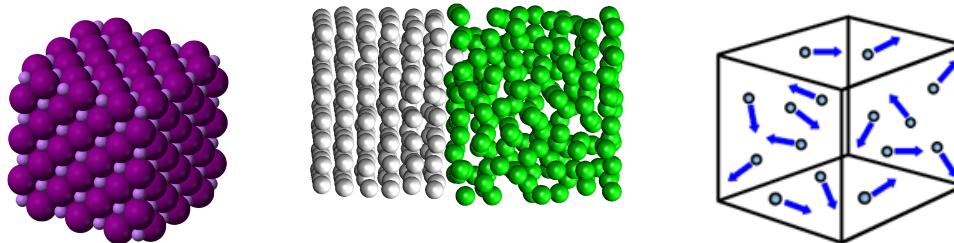
Technical solidification processes (incomplete)

Casting	continuous casting ingot casting investment casting precision casting die casting
Welding	arc-welding resistance welding laser/electron beam welding
Soldering/Brazing	
Rapid solidification	melt-spinning atomisation
Directional solidification	Bridgman Czochralski

Some general terms used in the course

Overview, most of the terms will be filled with 'live' during the following lectures.

- Phase: A phase is a homogeneous part in a possibly heterogeneous system (Gibbs¹). Here we have solid (**s**) and liquid (**l**). Can be related to the local atomic arrangement → construction of order parameters.

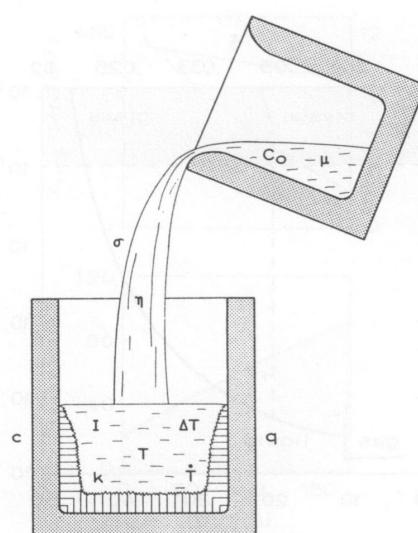


- Equilibrium: State of minimal free energy (G or F). Phases in contact do have enough time (locally) to reach this state.
 - Transition: may arise by changing a control parameter (temperature, pressure ...), during which latent heat is released/absorbed.

¹Josiah Willard Gibbs, 1839 - 1903, american physicist, chemist and mathematician

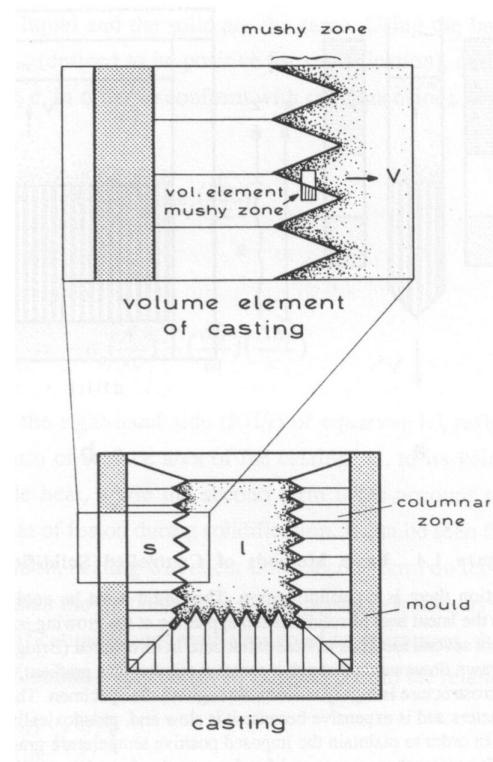
Solidification basics - casting

- Casting of a melt of composition C_0 and temperature T into the mold.
 - Cooling: A heat flux q depending on heat diffusivity k gives rise to undercooling ΔT of melt.
 - Then, due to the difference of chemical potentials μ between s - l crystallization starts, the speed of which is given by \dot{T} .
 - For the (macro) flow of melt the viscosity η and liquid-vapour surface tension σ may be important.



Solidified ingots - morphology

- Melt is usually cooled from the crucible wall
 - This results in growth, being fastest parallel to the temperature gradient G .
 - **Mushy zone:** the solid/liquid contact region, in which all growth determining kinetic processes take place → evolution of complicate interface structure.
 - Density changes give rise to shrinkage and porosity.

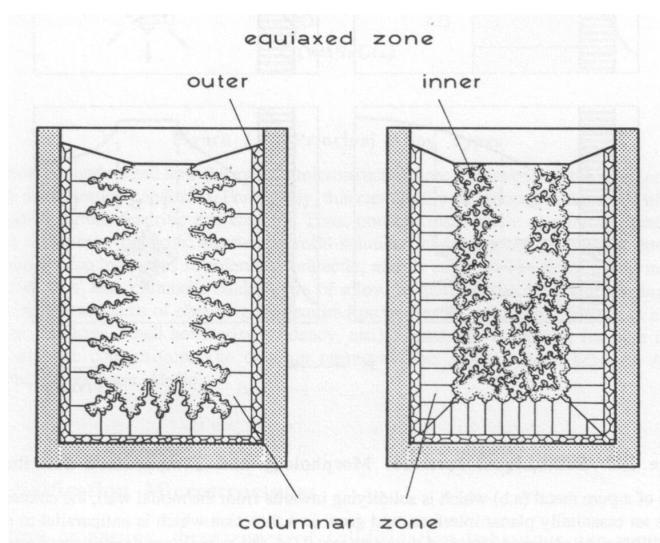


Solidified ingots - morphology II

Microstructure zones in cast ingot, schematic

Kurz and Fisher, Fig. 1.6

Aluminum ingot (5 cm)



The role of heat extraction

After casting the liquid metal, heat of different physical origin must be extracted:

- Heat related to the specific heat capacity of one phase: **enthalpy** decrease $\Delta H = \int_{T_1}^{T_2} CdT$
 - **Latent heat of fusion**, released in the phase transition: ΔH_f



Later, we will use the specific latent heat $\Delta h_f = \Delta H_f / V_m$ (V_m : molar volume) and specific heat capacity $c = C / V_m$.

Solidification stages

After casting, three different steps in the solidification can be observed in the cooling curve:

1. Cooling from pouring temperature, nucleation starts after falling below melting temperature T_m
 2. Reheating to T_m (recalescence) due to release of latent heat
 3. After complete transformation to solid, continued cooling sets on.

Figure: Quasi 1-D experiment, P. Thevoz et al., Metal Transact. 20 A (1989) 311

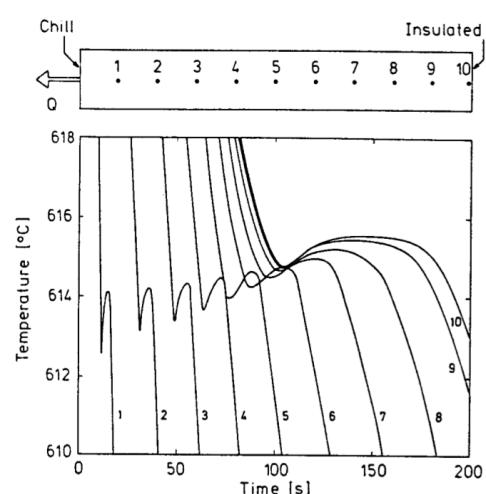


Fig. 5—Cooling curves for a 1-D casting of Al-7 pct Si ($T_{\text{liq}} = 618^\circ\text{C}$). The curves correspond to the locations indicated at the top of the figure. The difference between T_{liq} and the minimum of the cooling curve near the recalescence is defined as the maximum undercooling, ΔT_{max} .

Directional solidification - experiments

Experimental setup: Controlled solidification using optical microscopy with transparent binary analog substances.

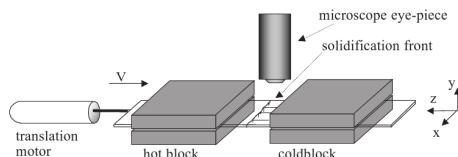
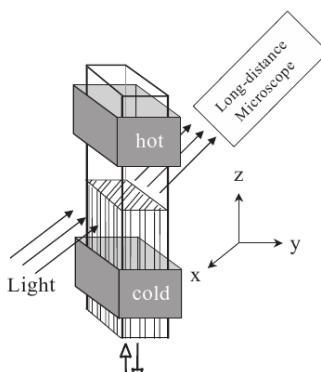


Fig. 4. Thin-sample directional-solidification setup.

2D:



3D:

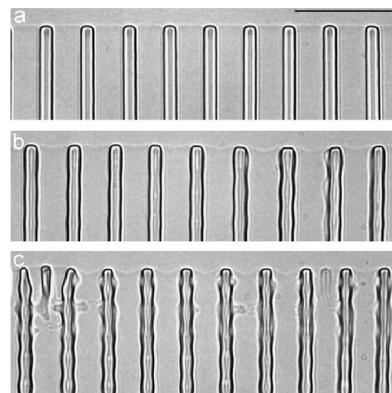


Fig. 9. Period-preserving oscillation ($1\lambda O$) patterns at different velocities. (a) $V = 0.053 \mu\text{m s}^{-1}$, $A \approx 1.5$. (b) $V = 0.090 \mu\text{m s}^{-1}$, $A \approx 2$. (c) $V = 0.18 \mu\text{m s}^{-1}$, $A \approx 2.7$. Lamella branching occurs through an unidentified 3D process. Scale bar: 50 μm .

Figure: Eutectic growth in SCN - DC, [Akamatsu et al., Journal of Crystal Growth 299 (2007) 418]

Directional solidification - principles

Steady heat extraction at pulling velocities v small enough to reach steady state.

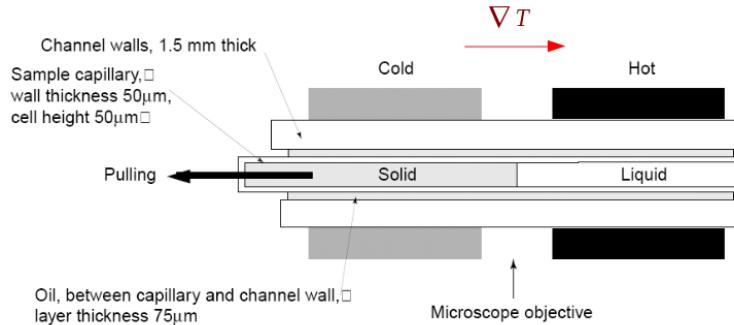
Growth rate ($= v$) and temperature gradient G can be separately controlled. If heat flux q_{ext} and temperature gradient are parallel:

$$\dot{T}_{s+z} = \frac{\partial T}{\partial z'} \cdot \frac{\partial z'}{\partial t} \Big|_{s+z} = G \cdot v \Big|_{s+z}$$

But: due to different heat conductivity in solid/liquid and release of latent heat:

$$G_{solid} \neq G_{liquid}$$

Experimental setup for alloys:



Directional solidification - technical applications

Production setup (schematic): Adjust (and move) temperature field by controlling current in electric coils.

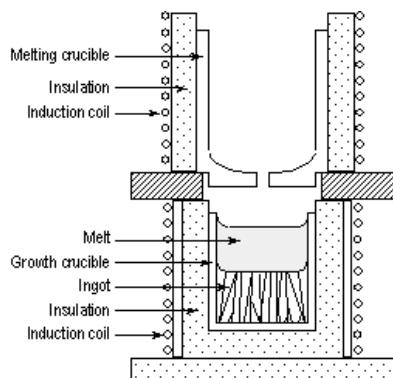


Figure: Al alloy - polycrystal [Tom Quested,
Microstructural kinetics group - Univ. of Cambridge.]

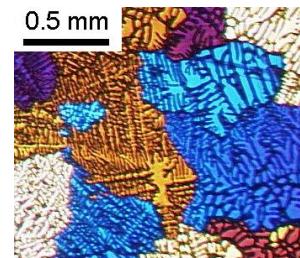


Figure: Solar grade silicon, directionally solidified using the Bridgeman method [B. Ryninen].



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Special solidification methods - metal matrix composites

Gas pressure infiltration of melt into fibre matrix to produce composite materials:

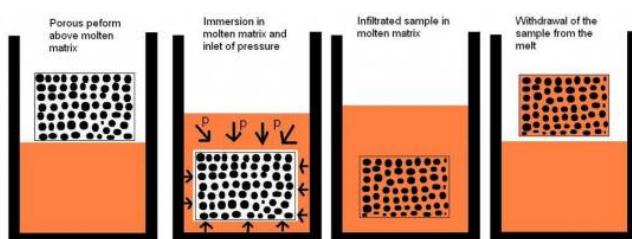


Figure: Steps of gas pressure infiltration: a) porous preform preheating; b) immersion of porous preform into the melt and inlet of pressurized gas; c) infiltrated sample in molten matrix and d) withdrawal of infiltrated sample from melt.

[Institute of materials & machine mechanics, Slovakian academy of sciences]

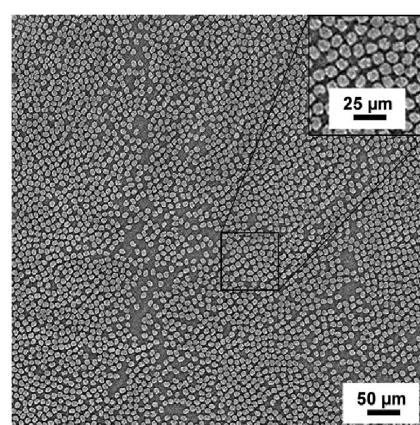


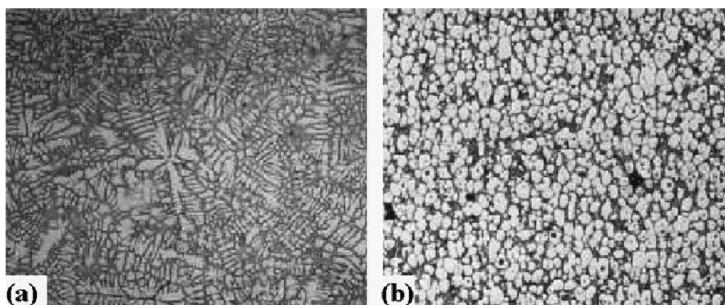
Figure: Pure Al matrix reinforced by unidirectional carbon fibres (65 vol %)

[G. Requena et al., Composites: Part A, 40 (2009) 152.]

Special solidification methods - Thixocasting

Processing of metals (mostly Al, Cu, Mg) resulting in granular semi-solids with liquid vol. fractions of 30% - 60%.

Sample in solid state as cast (a) and semi-solid (b) a

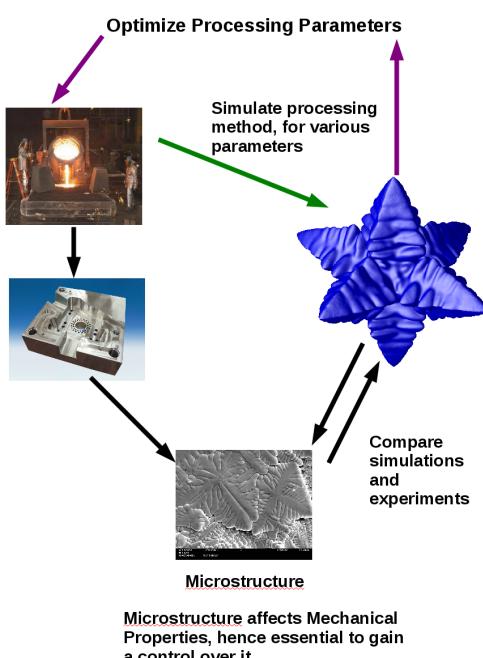


material with rheology like butter.

[H. V. Atkinson, Prog. Mat. Sci. 50 (2005) 341.]



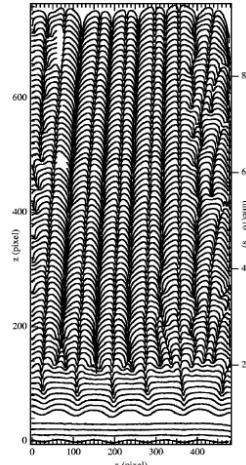
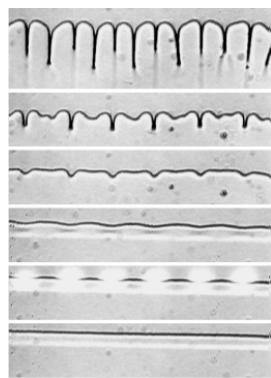
What is the aim of computational materials science?



- The macroscopic properties are a function of the microstructure
 - Dependence between the microstructure and the mechanical properties are generally determined experimentally
 - The dependence of the processing parameters and the microstructure →determined either experimentally or through mathematical modeling

Why is study of solidification important to physicists and engineers?

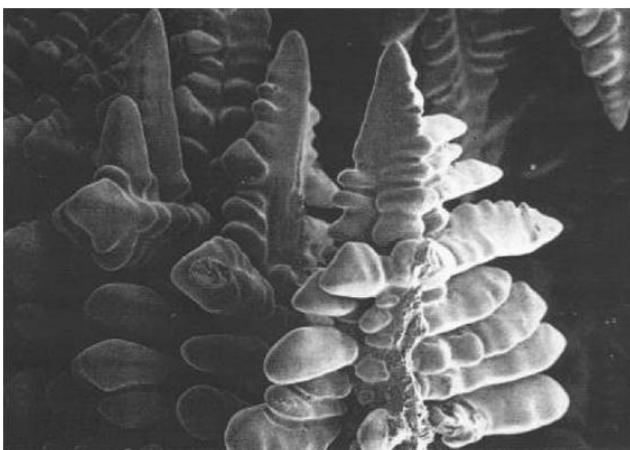
- Gain an understanding of the physics behind the pattern and microstructure formation
 - This would enable control of processing parameters
 - Hence, the microstructure and the corresponding mechanical properties



[W. Losert et al., Phys. Rev. E 58(6) (1998) 7492.]

Dendritic Solidification

Rather a ubiquitous type of front instability than a solidification mode



MOVIE

Succinonitrile-Aceton

[H. Esaka, J. Stramke and W. Kurz, Department of Materials, Swiss Federal Institute of Technology Lausanne, Switzerland]

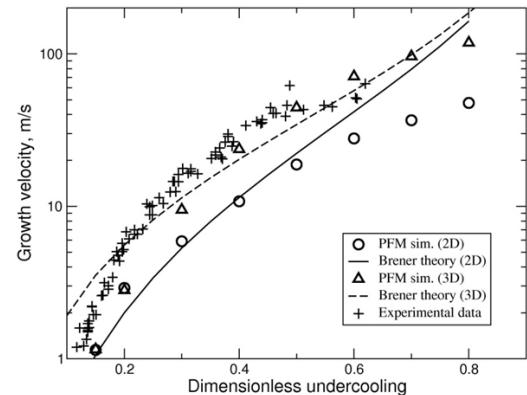
Co-Cr alloy

[Labo des Micro-Analyses des Surfaces, Besancon]

Dendritic Solidification - phase-field simulations

Solidification of pure Ni into undercooled melt ($\Delta T = 130K$, $\Delta T/\rho c_p = 0.3$)

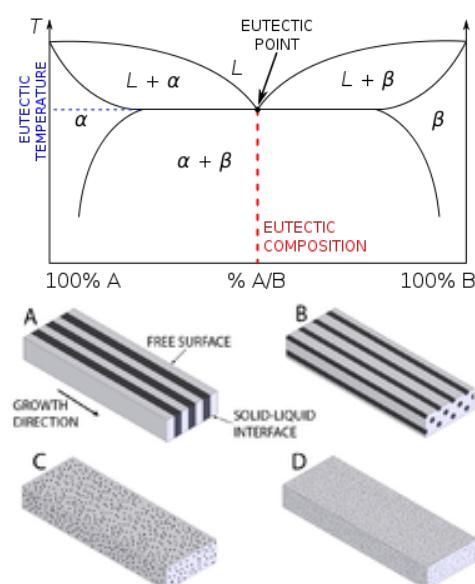
Parameter	Symbol	Dimension	Ni - Data
Melting temperature	T_M	K	1728
Latent heat	L	J/m ³	8.113×10^9
Specific heat	c_v	J/(m ³ K)	1.939×10^7
Thermal diffusivity	k	m ² /s	1.2×10^{-5}
Interfacial free energy	σ_0	J/m ²	0.326
Strength of interfacial energy	δ_c	—	0.018
Growth kinetics in <100> -crystallographic direction	μ_{100}	m/(sK)	0.52
Growth kinetics in <110> -crystallographic direction	μ_{110}	m/(sK)	0.40



with P. Galenko, D. Herlach, (DLR Köln), E. Brener, H. Müller-Krumbhaar (FZ Jülich)

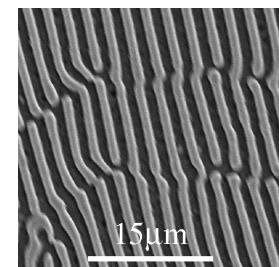
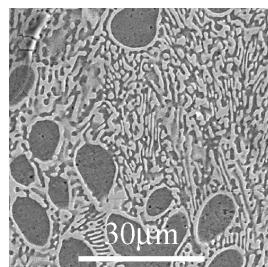
Eutectic Solidifications - Types and Instabilities

- What is eutectic growth/reaction;
 $L \longrightarrow S_1 + S_2$?
 - Below the eutectic temperature the liquid is unstable to decomposition to two solids
 - What is the volume fraction of the solid phases growing together?



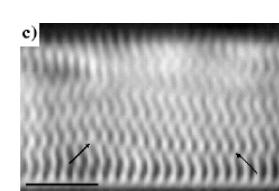
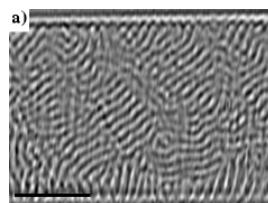
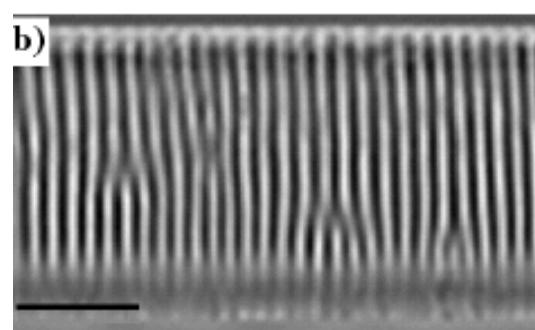
Eutectic Solidification - Length Scales

- What are the different length scales for diffusion?
 - Is there a physical basis for the choice of the length scale?
 - Mechanical properties → function of the length scale
 - Is it possible to determine this length scale as a function of the processing conditions?



Eutectic Solidification - Instabilities

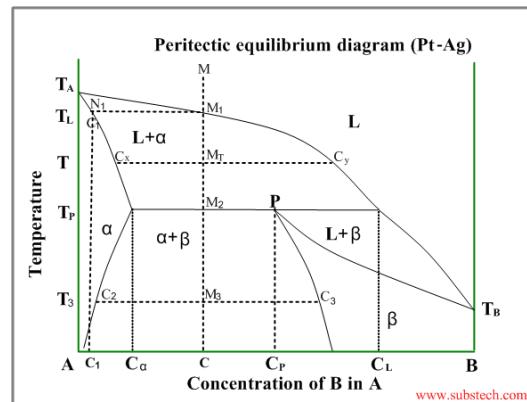
- Is it possible to get coupled growth over a whole range of length scales?
 - What makes coupled growth unstable?
 - What are the instabilities for large scale microstructure?
 - What are the instabilities for small scale microstructure?



Peritectic Solidification

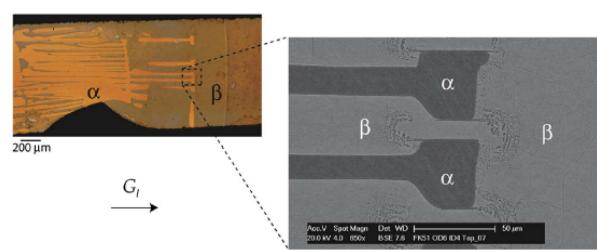
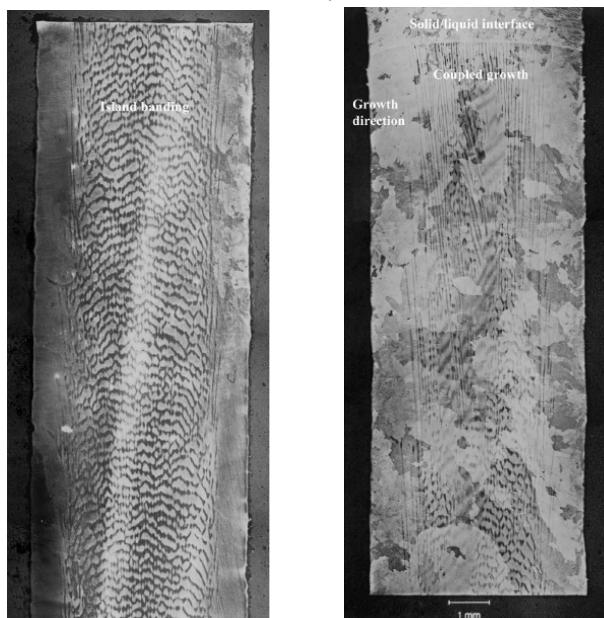
Reaction and Interesting Questions

- What is the peritectic reaction, $L + S_1 \longrightarrow S_2$?
 - Why is peritectic reaction important to study?
 - Steels ($Fe - C$)
 - Superalloys in NiAl system (Al_3Ni)
 - Nb
 - Perovskite ($YBaCuO$)

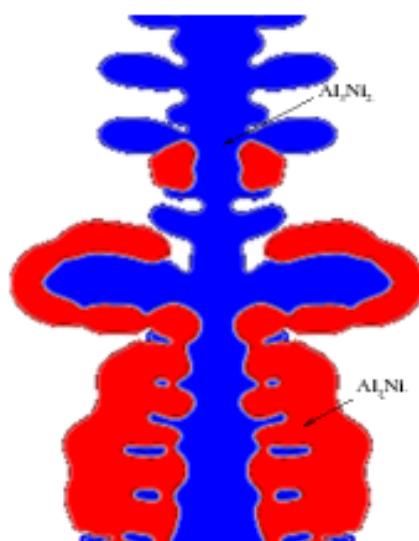
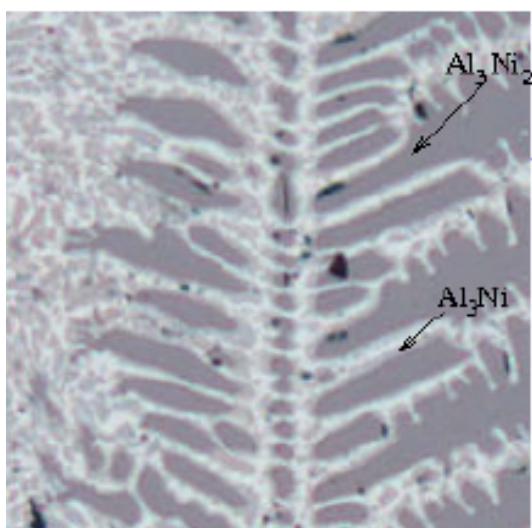


Peritectic Solidification - Microstructures I

Island structures, Banded structures and coupled growth:



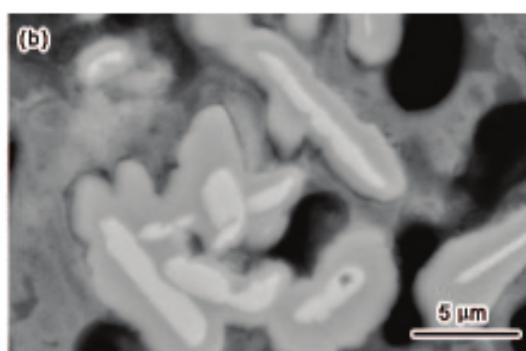
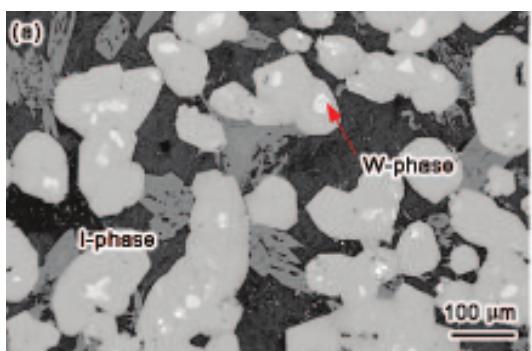
Peritectic Solidification - Microstructures II



[R. Siquieri et al., J. Phys. Cond. Mat. 21 (2009) 464112.]

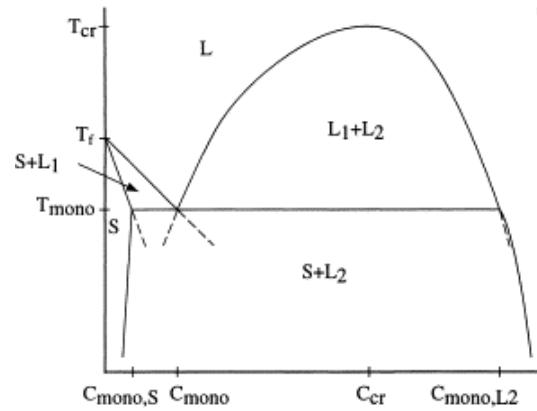
Peritectic Solidification - Interesting questions?

- Can two solid peritectic phases grow together?
 - How is it different from eutectic growth?
 - What are the patterns and instabilities in such microstructure?
 - What are the microstructures and the corresponding instabilities in 3D?



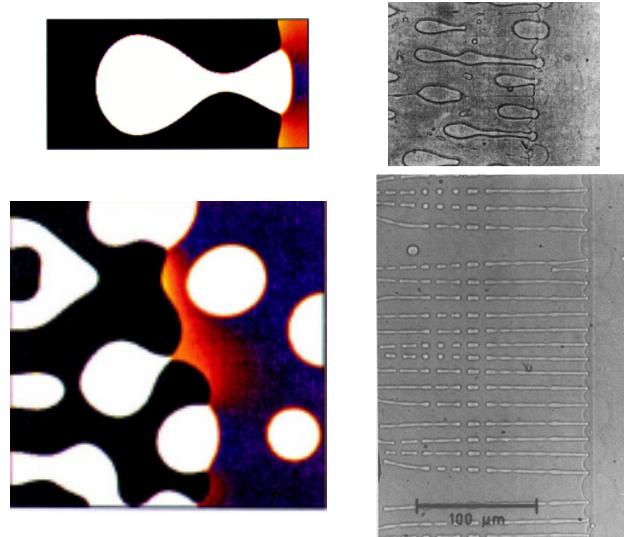
Monotectic Solidification - Challenges, microstructures

- What is the monotectic reaction, $L_1 \rightarrow L_2 + S$?
- Why is it interesting to learn about this reaction?
 - Lubrication phenomena (oil-oil mixtures)
 - Cu-Pb ($T_{mono} = 935^\circ$), Pb-Fe



Monotectic Solidification - Microstructures

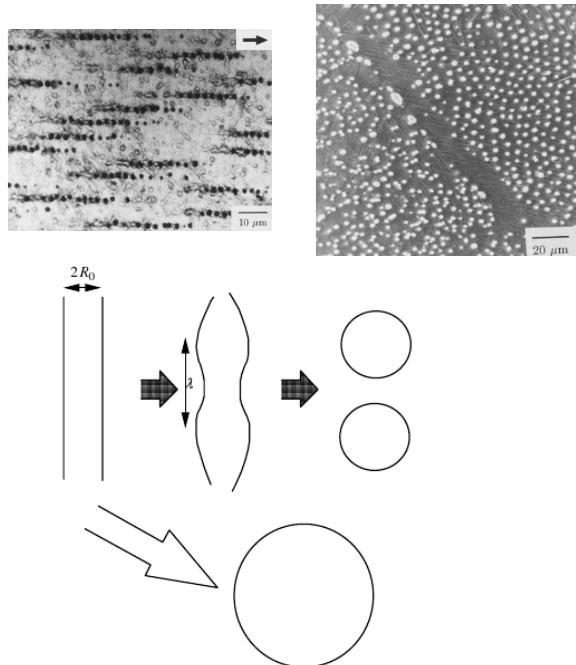
- What are the interesting microstructures?
- What are the physics behind the formation of each of these microstructures?



Monotectic Solidification

What are the open questions?

- Is nucleation important?
 - How is the phenomena of fluid flow important?
 - No validated theory existing until now
 - What are the instabilities?
(Rayleigh)



Outline of the course

(Detailed sequence in handout)

1. Introduction to the process of solidification
 2. Thermodynamics and Transport Phenomena, necessary to understand the process
 3. Introduction to phase-field modeling
 4. Numerical Techniques
 5. Theoretical Analysis, of Dendritic, Eutectic and Peritectic Solidification
 6. Verification of theoretical concepts through modeling
 7. Outlook to the open questions and challenges

1 30.10.10

1.1 Lecture 2

Classification of materials (mat. sci.)

Materials can be classified into the following basic classes,

- metals
- ceramics
- polymers
- composites.

The aim of studying the materials science is in general to understand the functioning of the materials, their *properties*, the pathway to process materials and *optimize performance*, through an understanding of the correlation between the *structure* and the *performance*. In order to perform this task, it is essential to gain insights into the *thermodynamics* of materials, which enables us to qualify and predict the *equilibrium states* of a material given, a set of conditions.

Introduction to thermodynamics

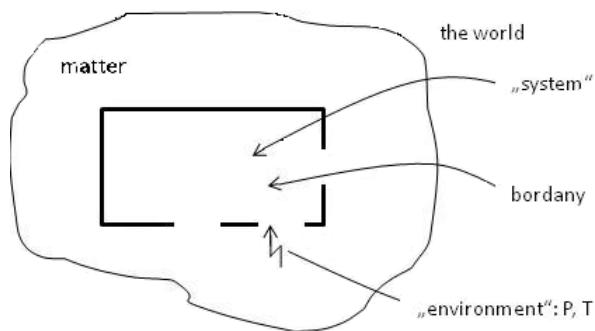


Figure 1.1: What is a *system*? The diagram illustrates the structure of the system in relation to the surroundings and the means of interaction.

microscopic state \leftrightarrow macroscopic state

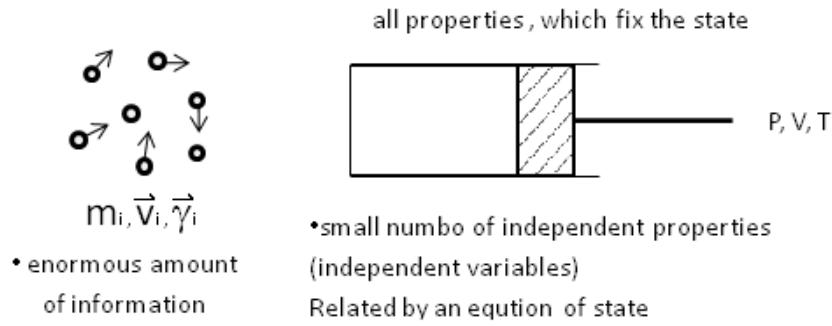


Figure 1.2: The *state* of the system can be completely defined at two levels. One is at the *microscopic level* called the *microscopic state*, which contains the information about the mass, velocity and position of the particles. The other is at the continuum scale, called the *macroscopic state* of the system, defined by variable, *pressure*, *volume* and *temperature*, where two variables are independent, and related to the third through a *state function*

An example of a 'simple system' consisting of 3 variables (2 indep.) can be for example where the volume, $V=V(P,T)$, which is a *state function* of the pressure and temperature of the system. A characteristic of a *state function* is that for any reversible process, the change of state describe by the state function depends *only* on the *end states*. This can be seen as follows: Process from 1 \rightarrow 2: volume change

$$\begin{aligned}\Delta V &= V_2 - V_1 \\ &= \underbrace{(V_a - V_1)}_{P=\text{const.} = P_1} + \underbrace{(V_2 - V_a)}_{T=\text{const.} = T_2}\end{aligned}$$

1 \rightarrow a \rightarrow 2

$$\Delta V = V_2 - V_1 = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T} \right)_{P_1} dT + \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P} \right)_{T_2} dP \quad (1)$$

1 \rightarrow b \rightarrow 2

$$\Delta V = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P} \right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T} \right)_{P_2} dT \quad (2)$$

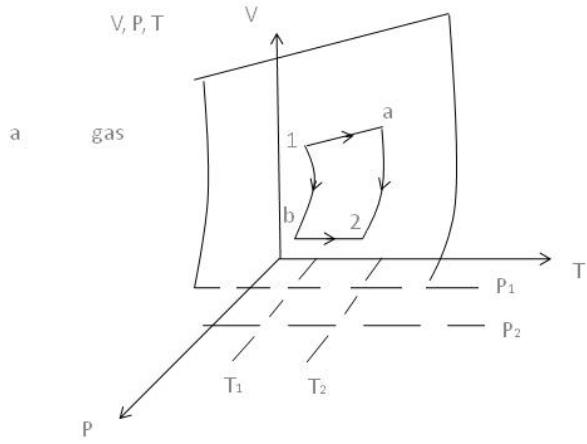


Figure 1.3: An exemplary process showing two reversible process from the start state (1) to end state (2), through the routes $1 \rightarrow a \rightarrow 2$ or $1 \rightarrow b \rightarrow 2$.

This means that $V=V(P,T)$ is a state function, as the integral does not depend on the integration path. The same result is found integrating the complete/total differential of V ,

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

between the limits P_2, T_2 and P_1, T_1 .

Equation of state for an ideal gas

- Robert Boyle (1660) $P \sim \frac{1}{V}$ ($T=\text{const}$)
- Alexandre-Ciser Charles (1787) $V \sim T$ ($P=\text{const}$)
- Joseph-Linis Gray-Lussac (1802)
- Coefficient of thermal expansion

$$\alpha = \frac{1}{V_o} \left(\frac{\partial V}{\partial T}\right)_P \approx \frac{1}{273} \quad \text{at } 0^\circ C$$

good for gases with low boiling points

model: ideal gas $\alpha = \frac{1}{273,15}$

$V(T=0 \text{ K}) = 0$ absolute Zero of Temp. Scale Combination of (Boyle) and (Charles) gives,

$$P_0 V_0 (T_1 P_0) = P V (T_1, P) \quad \text{and} \quad \frac{\overbrace{V_0(P_0, T_0)}^{V_0}}{T_0} = \frac{\overbrace{V(P_0, T)}^V}{T}$$

$$\Rightarrow \frac{PV}{T} = \frac{P_0 V_0}{T_0} = \text{const.} \quad (*)$$

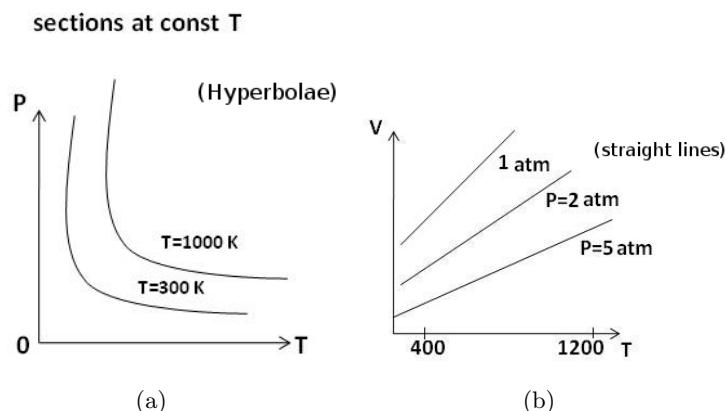


Figure 1.4: (a) Variation of the state function along given isotherms, (b) Variation of state function relation V and T at given isobars.

Extensive / intensive state variables

Intensive state variables are independent of the system size (P, T), extensive variables depend on size → can be transformed into intensive variables by division through mass (e.g. specific volume) or mole number (e.g. molar volume $V = \frac{V'}{n}$).

Phase diagrams, terms + examples A phase-diagram, shows the regions of stability of the different phases in a given systems. Complexity of the phase diagram depends on

no. of components (chemical compositions): chemical elements (Ni,Cu), stoichiometric compounds (H_2O), and general categorization can be given as follows:

- one-component (pure) system
- binary system
- ternary system
- quaternary system

One-comp. system (20 repr.)

A one component system is characterized by two independent variables, T, P. An exemplary phase diagram showing the stability regions of the phases solid, liquid and vapor is shown in figure [1.5](#).

within, $\begin{array}{l} AOB \rightarrow \text{liquid} \\ COA \rightarrow \text{s} \\ COB \rightarrow v \end{array} \right\}$ one-phase eq. (system:homogeneous)

on the line AO :two phases (s/l) coexist

→ two - phase eq. (system: heterogeneous)

→ pressure- temp. relation for eq. of sol/liq H_2O

CO: saturation vapor pressure of solid OB: saturation vapor pressure of liquid

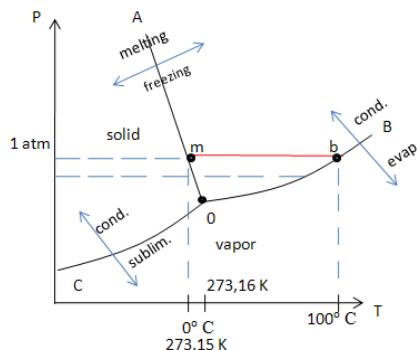


Figure 1.5: Phase diagram of the ice-water system.

ce-Water-Vapor

Two-component system → additional degree of freedom, composition

The complete diagram is three dimensional consisting of the variables, C,T,P,V. At const. pressure the diagram at (1 atm ~ 1 bar) can be drawn as follows,

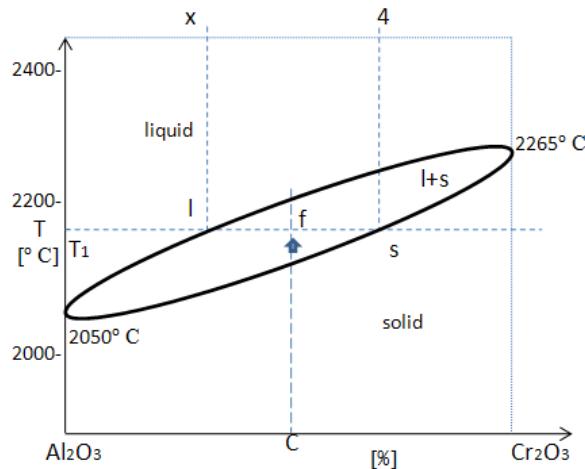


Figure 1.6: The phase diagram of a two component system.

example: system Al₂O₃-Cr₂O₃ (1 atm)

at $T < T_m$ (Al₂O₃) = 2050°C and

$T > T_m$ (Cr₂O₃) = 2265°C completely

miscible in all proportions ((Al₂O₃, Cr₂O₃ have similar crystalstructure and Al³⁺, Cr³⁺ similar size)

- single phase region, l,s
- two-phase region, l+s equil.

At any temperature and given composition, the relative fractions of two phases in equilibrium are derived through the well known *lever rule*. This can be written as follows. Let us say, that at the temperature T_1 , the equilibrium compositions of the solid and liquid are C_s and C_l respectively. Then, the fractions of solid and liquid must satisfy, the following mass balance relation:

$$C = C_s f_s + C_l f_l,$$

and since, there are only two phases in equilibrium, implies that $f_s + f_l = 1$. Using this the following relation for the solid and the liquid fractions can be derived,

$$f_s = \frac{(C - C_l)}{C_s - C_l}.$$

The first law of thermodynamics

The first law of thermodynamics is motivated from the basic concept of conservation of energy. The sum total change of the internal energy U which is the combination of the vibration, rotational and kinetic energies of the atoms, when a system goes undergoes a change of state equals the difference between the total amount of *heat* transferred to the body q and the *work* done *by* the body w . An expansive work is treated as work done *by* the body. Conversely, a compressive work is treated as work done *on* the body w . A differential change in the internal energy U can thus be written as,

$$dU = \delta q - \delta w.$$

Please note: the differential sign on the internal energy U , which the operator δ on the variables q and w . This signifies, a fundamental difference between a state function, whose change is independent of the path of integration, while, the quantities, q and w depend on the path of integration. This can be immediately be appreciated from figure, [Work](#) [1.7](#). For the three paths, a, b, c the change of state, U , is the same ($U_2 - U_1$). However, the work done, which is area under the curve is not.

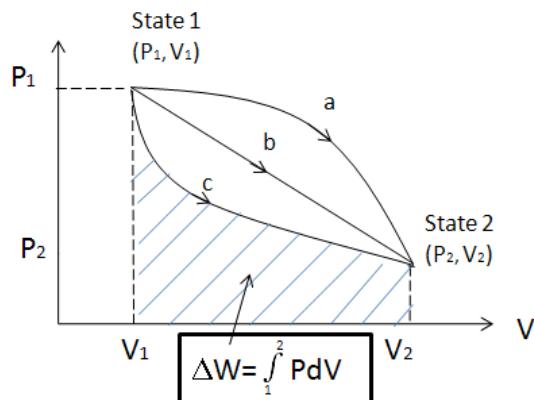


Figure 1.7: Three process paths taken by a fixed quantity of gas in moving from the state1 to the state2.

Work

For a cyclic process: $1 \rightarrow 2 \rightarrow 1$

$$\begin{aligned}\Delta U &= \int_1^2 dU + \int_2^1 dU \\ &= (U_2 - U_1) + (U_1 - U_2) = 0 = \oint dU\end{aligned}$$

For a simple one-component system, the internal energy is completely defined by two independent variables. If temperature and volume are chosen, then, the complete differential can be written as follows,

$\rightarrow \underbrace{\text{two independent state}}_{\text{variables}} \text{ variables } U = U(V, T)$

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

Examples of different processes:

- $T = \text{const.}$ - isothermal
- $P = \text{const.}$ - isobaric
- $V = \text{const.}$ - isochoric
- $(\Delta Q = 0$ - adiabatic)

* Constant - volume processes

$$\Delta W = \int P dV = 0 \quad dU = \delta Q_V, \quad \Rightarrow \Delta U = \Delta Q_V = \int_1^2 C_V dT$$

change of U = absorbed/rejected heat

* Constant - pressure processes

$$\Delta W = \int_1^2 P dV = P \int_1^2 dV = P(V_2 - V_1)$$

$$U_2 - U_1 = \Delta Q_P - P(V_2 - V_1)$$

$$\underbrace{(U_2 + PV_2)}_{\nwarrow \nearrow} - \underbrace{(U_1 + PV_1)}_{\nwarrow \nearrow} = \Delta Q_P$$

$\nwarrow \quad \nearrow$

all are state functions

In the above, all are state functions, hence, the resulting function is also a state function. We define new state function $H=U+PV$: which is called the *enthalpy* of the system.

At $P = \text{const.}$ $H_2 - H_1 = \Delta H = \Delta U + P\Delta V = \Delta Q_P = \int_1^2 C_P dT$

Heat capacity

The heat capacity, C , of a system is the ratio of the heat added to or withdrawn from the system to the resultant change in the temperature of the system. Thus,

$$C = \frac{\Delta Q}{\Delta T}; \text{ small changes } \Delta T : C = \frac{\delta Q}{dT}$$

This concept is however useful when there is no phase change. When a phase change occurs, the heat goes in the change of state while the temperature stay constant, which would result, in an infinite heat capacity by the above formula. Since, the state of a simple system is defined by two independent variables, the measurement of the heat capacity is completely defined, only when the variation of the other variables (pressure or volume) is defined. This leads to the following definitions of the heat capacities,

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V \Leftrightarrow dU = C_V dT \quad (\text{const. volume})$$

$$C_P = \left(\frac{\delta Q}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P \Leftrightarrow dH = C_P dT \quad (\text{const. pressure}).$$

C is extensive quantity, depending on system size (mass, volume, mole no.). One can make it intensive by dividing through respective number of moles. This gives us molar heat capacities,

$$c_P = \frac{C_P}{n}; \quad c_V = \frac{C_V}{n}.$$

For, $c_P > c_V$, as additional heat is required to provide work during expansion of the system,

$$\begin{aligned}
 c_p &= \left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad (1 \text{mole}) \\
 c_v &= \left(\frac{\partial U}{\partial T} \right)_V \\
 c_p - c_v &= \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \\
 \text{with } dU &= \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT \\
 \Rightarrow \left(\frac{\partial U}{\partial T} \right)_P &= \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial U}{\partial T} \right)_V
 \end{aligned}$$

$$\Rightarrow c_p - c_v = \underbrace{\left(\frac{\partial V}{\partial T} \right)_P}_{1} \left[P + \underbrace{\left(\frac{\partial U}{\partial V} \right)_T}_{2} \right]$$

To determine, the term $\frac{\partial U}{\partial V}_T$, Joule performed the experiment, as shown in figure [Joule's experiment](#) , which involved filling a copper vessel with a gas at some pressure and connecting this vessel via a stopcock to a similar but evacuated vessel. The two vessel system was immersed in a quantity of adiabatically contained water and the stopcock was opened, thus allowing free expansion of the gas into the evacuated vessel. After this expansion, Joule could not detect any change in temperature of the system, As the system, was adiabatically contained, and no work was performed and hence, from first law of thermodynamics, it follows that the total change in internal energy $\Delta U = 0$. From the total differential of U , one can then work out that, $\left(\frac{\partial U}{\partial V} \right)_T = 0$.

ideal gas:

This gives the following relation for gases:

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \Rightarrow C_P - C_V = P \left(\frac{\partial V}{\partial T} \right)_P .$$

In addition for 1 mole of ideal gas,: $PV=RT$ and hence $\underline{c_P - c_V = R}$

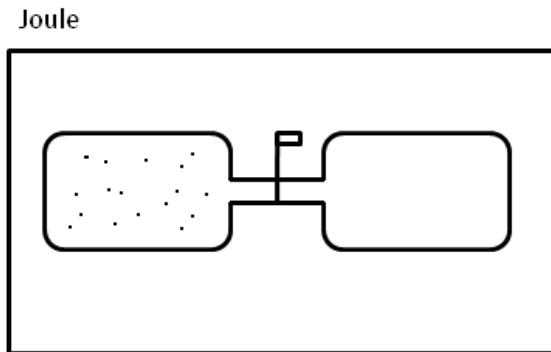


Figure 1.8: Joule's experiment

The term $P \left(\frac{\partial V}{\partial T} \right)_P$ represents work done in expanding gas against an constant external pressure P. The term $\left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$ represents the work done against *internal cohesive forces*.

$$\left(\frac{\partial U}{\partial V} \right)_T \approx 0 \text{ fo gases, but}$$

$$\left(\frac{\partial U}{\partial V} \right)_T \gg P \text{ for liquids, solids}$$

Reversible adiabatic process

$$\Delta W = \int_1^2 P dV \quad \text{only for reversible process}$$

$$\delta Q = 0 \Rightarrow dU = -\delta W$$

$$(1 \text{ mole}) = C_V dT \quad \delta W = P dV$$

$$C_V = \left(\frac{dU}{dT} \right)_V$$

$$C_V dT = -P dV = -\frac{RT}{V} dV$$

$$C_V \ln \frac{T_1}{T_2} = R \ln \frac{V_1}{V_2}$$

$$\left(\frac{T_2}{T_1}\right)^{C_V} = \left(\frac{V_1}{V_2}\right)^R \Leftrightarrow \boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}}$$

$$\left[\frac{C_P}{C_V} = \gamma; \quad C_P - C_V = R; \quad \frac{c_P}{c_V} - 1 = \frac{R}{C_V} = \gamma - 1 \right]$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{P_2 V_2}{P_1 V_1} \Rightarrow \boxed{\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^\gamma}$$

$$\Leftrightarrow P \cdot V^\gamma = \text{const} \text{ (adiabatic)}$$

Reversible isothermal process, ΔP , ΔV (ideal gas)

$$dU = \delta Q - \delta W$$

$$\text{isothermal} \quad dT = 0 \Rightarrow dU = 0 \Rightarrow \delta W = \delta Q = PdV = \frac{RT}{V} dV$$

$$1 \rightarrow 2 \quad \Delta W = \Delta Q = RT \ln \left(\frac{V_2}{V_1} \right) = RT \ln \left(\frac{P_1}{P_2} \right)$$

ΔP fixed $1 \rightarrow 2, 1 \rightarrow 3$

ΔW isothermal $> \Delta W_{\text{adiab}}$

\downarrow

$= \Delta Q$ isothermal (absorbed), $U = \text{const}$ $\Delta U = -\Delta W$

Second Law of Thermodynamics

In previous chapter, only extreme processes $\Delta W=0$ or $\Delta Q=0$ were studied. For $\Delta W \neq 0$ and $\Delta Q \neq 0$, is there a definite amount of work, which the system can do?

Here we need to,

→ identify two classes of processes - reversible and irreversible

→ introduce a state function, entropy S (gives the degree of irreversibility of a process)

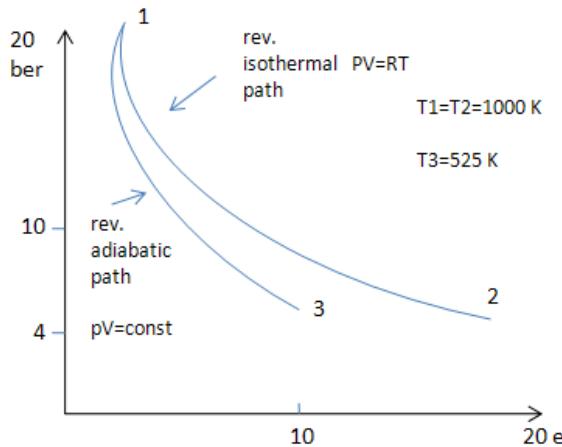


Figure 1.9: Description of a isothermal process $1 \rightarrow 2$ at $T=1000\text{K}$, while process $1 \rightarrow 3$ represents an adiabatic process.

Definition of Spontaneity

Spontaneous (=natural) processes Left to itself a system has two possibilities a) it stays in its initial state (=if it is in equilibrium; = state of rest) or
b) moves towards its equilibrium state, if it is away from equilibrium.

Hence, a process which involves, the movement of a system away from equilibrium towards its equilibrium state, is called a spontaneous process. Since, this process cannot be reversed without the application of an external agency, it is called an irreversible process, as it would require an irreversible change in the properties of the external agency.

Examples of two spontaneous processes,

1. Mixing of gases
2. Flow of heat down a temperature/conc. gradient

In both cases, the state of equilibrium is in (a) where the composition is uniform in the gas mixture, and in (b) the temperature of the system becomes uniform. A knowledge of the equilibrium allows us to decide, the direction of the spontaneous reaction given the initial state of the the system. During a spontaneous process, work is performed and as equilibrium is reached the ability to perform work is reduced and finally at equilibrium, the system is at rest. As work is performed, there is degradation of energy to heat and the ability to do work is lost.

Entropy and the quantification of irreversibility

There exist two distinct types of spontaneous processes,

- Conversion of work to heat (i.e degradation of mechanical energy to thermal energy)
- Flow of heat down a temperature gradient

If it is considered that during an irreversible process, the ability to do work is degraded, then it is possible to quantify the extent of degradation or the extent of irreversibility of the system. Consider the weight-heat reservoir system as shown in figure 1.10. The system consists of a weight-pulley arrangement which is coupled to a constant-temperature heat reservoir, and the system is at equilibrium when an upward force acting on the weight exactly balances the downward force, W , of the weight. If the upward force is removed then the equilibrium is upset and the weight spontaneously falls thus performing work which is converted by means of a suitable system of paddle wheels to heat which enters the constant temperature heat reservoir. Equilibrium is reattained when the upward force acting on the weight is replaced and the net effect of this process is that mechanical energy has been converted to thermal energy. Now three different experiments can be considered with this setup.

1. work performed by weight $\Delta W \rightarrow$ transformed to heat ΔQ entering reservoir at T_2
2. same amount of heat flows to a different reservoir at temperature T_1 where $T_1 < T_2$ which is in thermal contact
3. same as 1. , but now the main reservoir is at T_1 and heat flows into heat reservoir.

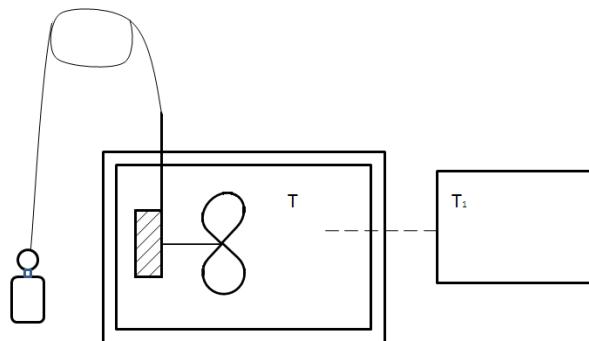


Figure 1.10: Weight-heat reservoir system

It can be perceived that process 3. is the sum of 1. and 2. And hence, process (3) should be more irreversible. Examining the processes closely, shows, that the amount

of heat Q and the temperature between which the heat flows, is important in finding a quantitative measure of irreversibility. Hence, we derive a term of the form $\frac{\Delta Q}{T}$, defined by the amount of heat ΔQ and (absol.)temperatures T_1, T_2 . With this definition we directly see that process (3) is more irreversible than (1) for $T_1 < T_2$. This degree of irreversibility we call as the increase of entropy S and define,

Entropy produced: $\Delta S = \frac{\Delta Q}{T}$.

If irreversibility is quantified, how do we visualize a reversible process?

A reversible process, is one where the degree of irreversibility is minimized. The ultimate minimization would occur when the concept of spontaneity is no longer applicable, which apparently implies that the system is only infinitesimally away from equilibrium such that the extent of degradation is as small as we please. This a reversible process, wherein, a system is taken from state A to state B, through string of states all at equilibrium. An illustration of a reversible process can be seen as follows.

Reversible process
 Consider a system as shown in [I.11](#). it consists of water in equilibrium with its vapor at given saturated pressure $P_{H_2O}(T)$, which is function of temperature T. Now the system is at rest where the P_{ext} exactly balances the saturated vapor pressure. Now consider, we reduce the external pressure by ΔP , which would then cause the gas to expand owing to mismatch of pressure, and the water would start to evaporate to restore equilibrium. Since, evaporation is an endothermic process, heat would be drawn in from the reservoir to maintain constant temperature T, by providing the required latent heat for the process. If after one mole of evaporation, the pressure is again increased to its original value, then the evaporation stops, and the work done by the system is $(P_{ext} - \Delta P)V$, where V is the molar volume of the gas. Conversely, when the pressure of the gas is now increased by an amount ΔP , this would cause the piston to fall rapidly, and the water-vapor would start to condense to restore equilibrium between the water- and water vapor. This is an exothermic process, which would need a transfer of heat to the reservoir to maintain the same temperature T. After one mole of gas has condensed, the external pressure is again increased to the saturation vapor pressure at the temperature T. This restores equilibrium and the total work done is $(P_{ext} + \Delta P)V$. In the total cyclic process, the total work done by the external agency is $2\delta PV$. Now a reversible process would be such, where this term is minimized. Or in other words, a system where the change in the external pressure is an infinitesimal δP , and the process is carried out slowly, such that the change in saturation is reduced and the heat flow keeps up wth the equilibrium.

It is thus seen that reversibility is approached when the evaporation or condensation processes are carried out in such a manner that the pressure exerted by the vapor is never more than infinitesimally different from its value at the saturation temperature T. It is also seen that as complete reversibility approached, the process becomes infinitely slow.

The whole process is summarized below:

example equilibrium: $P_{ext} = P_{H_2O}(T)$ and $T=T_{H_2O}=T_{vaporn}$

1. Pressure drop $P_{ext} - \Delta P$, work done

$$\Delta W = (P_{ext} - \Delta P)V \text{ (evaporation)}$$

2. Pressure increase $P_{ext} + \Delta P$

$$3. \Delta W = (P_{ext} + \Delta P)V \text{ (condensation)}$$

4. $\Delta W_{12} = 2\Delta P \cdot V$

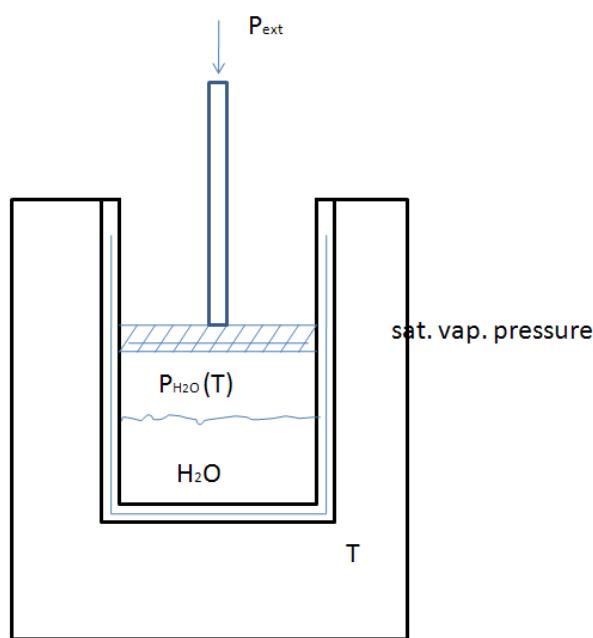


Figure 1.11: A hypothetical system of water in equilibrium with its vapor at saturated vapor pressure $P_{H_2O}(T)$, which is a function of temperature T . The system is kept in contact with a heat reservoir, and an external system to adjust the external pressure P_{ext} .

versibleprocess

Entropy and reversible heat Consider just the process of evaporation in the previous text. For a reversible process, the work done by the system is $P_{ext}V$. For any irreversible process, the work done by the system is $(P_{ext} - \Delta P)V$. It is clearly seen that maximum work W_{max} occurs during a reversible process.

1. Reversible process ($\Delta P \rightarrow \delta P$):

$$\begin{aligned}\Delta W_{max} &= P_{ext}V; \quad \Delta Q_{rev} = \Delta U + \Delta W_{max} \\ \Delta U &- \text{indep. of process} \\ \Delta W &= (P_{ext} - \Delta P)V; \quad \Delta Q = \Delta U + \Delta W \\ \text{difference} \Delta W_{max} - \Delta W &= \Delta Q_{rev} - \Delta Q \\ &\text{is degraded into heat within the irrev. process}\end{aligned}$$

Rev.: entropy change of heat reservoir: $\Delta S_{heat\ res.} = -\frac{\Delta Q_{rev}}{T}$

of H_2O / vapour: $\Delta S_{H_2O+vap.} = \frac{\Delta Q_{rev}}{T}$

$\Delta S_{total} = 0$

Irrev.: $\Delta Q < \Delta Q_{rev}$; $\Delta S_{heat\ res.} = -\frac{\Delta Q}{T}$

$\Delta S_{H_2O+vap.} = \frac{\Delta Q}{T} + \frac{\Delta Q_{rev} - \Delta Q}{T}$

$\Delta S_{total} = \frac{\Delta Q_{rev} - \Delta Q}{T} = \Delta S_{irrev} > 0$

for each possible process $\boxed{\Delta S_{H_2O+vap.} = \frac{\Delta Q}{T} + \Delta S_{irrev}}$

2. Condensation, reversible:

$$\left. \begin{array}{l} \Delta S_{H_2O+vap.} = -\frac{\Delta Q_{rev}}{T} \\ \Delta S_{heat+res.} = \frac{\Delta Q_{rev}}{T} \end{array} \right\} \Delta S_{total} = 0$$

irreversible

$$\left. \begin{array}{l} \Delta S_{H_2O+vap.} = -\underbrace{\frac{\Delta Q}{T}}_{leaving} + \underbrace{\frac{\Delta Q - \Delta Q_{rev}}{T}}_{heat\ created} \\ \Delta S_{H_2O+vap.} = -\frac{\Delta Q_{rev}}{T} \end{array} \right\} \Delta S_{total} = \frac{\Delta Q - \Delta Q_{rev}}{T} \quad \Delta Q > \Delta Q_{rev}, > 0$$

for each poss.: process $\boxed{\Delta S_{H_2O+vap.} = -\frac{\Delta Q}{T} + \Delta S_{irrev}}$

important $\Delta S = S_B - S_A = \frac{\Delta Q}{T} + \Delta S_{irr} = \frac{\Delta Q_{rev}}{T}$, indep. of the path/process.

S is state function, only measurable for reversible process

Reversible isothermal compression, ideal gas (1 mole)

eq. path $(V_A, T) \rightarrow (V_B, T)$

isothermal comp $\Delta U = 0$; $\Delta W_{max} = \Delta Q_{rev}$

$$\Delta W = \int_{V_A}^{V_B} P dV = \int_{V_A}^{V_B} \frac{RT}{V} dV = RT \ln \frac{V_B}{V_A} < 0$$

$$\text{entropy change of gas } \Delta S_{gas} = \frac{\Delta Q_{rev}}{T} = R \ln \frac{V_B}{V_A} < 0$$

$$\Delta S_{heat\ res} = -\Delta S_{gas} = R \ln \frac{V_A}{V_B}$$

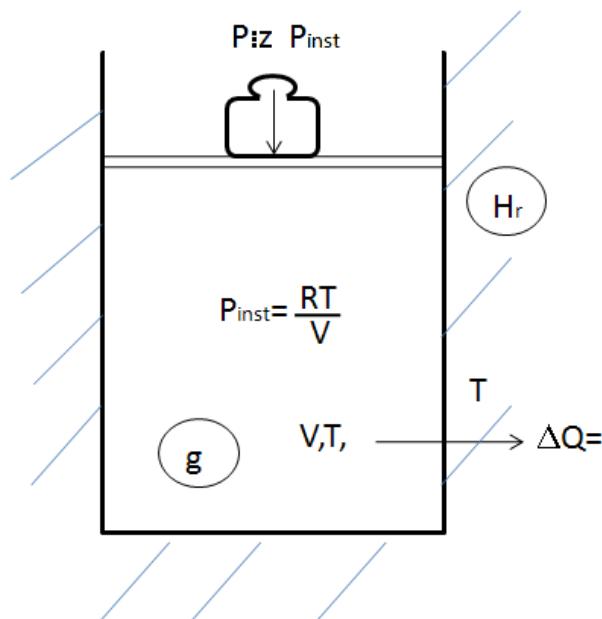


Figure 1.12

Reversible adiabatic expansion, ideal gas

eq. path $(P_A, T_A) \rightarrow (P_B, T_B)$, $\Delta Q=0$ if rev. proc. (quasistatic) and isolated (adiabatic)

$$\Delta S = 0, \text{ const. entropy } PV^\gamma = const \quad \gamma = \frac{C_P}{C_V} = \frac{5}{2}$$

$$\Delta W_{max} = \Delta U$$

Sudden increase of $P_A \rightarrow P_B$ from (P_A, T_A) : System leaves the P-V-T surface, entropy is produced, $T_B > T_{B,rev}$

$$\Delta W = \Delta U < \Delta W_{max}$$

Summary

1. Entropy S increases for irrev. process
2. $\Delta S_{rev} = 0$ (entropy is transferred from one part to another of the system)
3. S is a state function, $S = \frac{\Delta Q_{rev}}{T}$

Heat engines

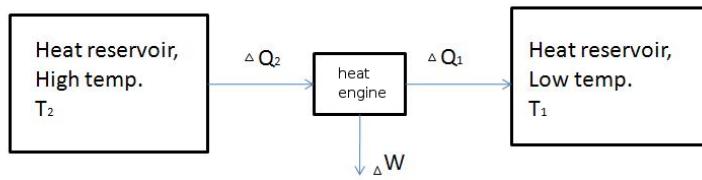


Figure 1.13

efficiency

$$\eta = \frac{\text{work obtained}}{\text{heat input}} = \frac{\Delta W}{\Delta Q_2}$$

Studied by Sadi Carnot (1824)

1. A → B isoth. expansion at T_2
2. B → C adiab exp. (rev.) $T_2 \rightarrow T_1$
3. C → D isoth. compression at T_1
4. D → A adiab. comp. $T_1 \rightarrow T_2$

One cycle: $\Delta W = \Delta W_1 + \Delta W_2 - \Delta W_3 - \Delta W_4$

$$\Delta Q = \Delta Q_2 - \Delta Q_1$$

$$\Delta U = 0 \Rightarrow \Delta Q = \Delta W = \Delta Q_2 - \Delta Q_1$$

$$\eta = \frac{\Delta W}{\Delta Q_2} = \frac{\Delta Q_2 - \Delta Q_1}{\Delta Q_2}$$

two heat engines 1 and 2, $\eta_2 > \eta_1$: reverse direction=heat pump

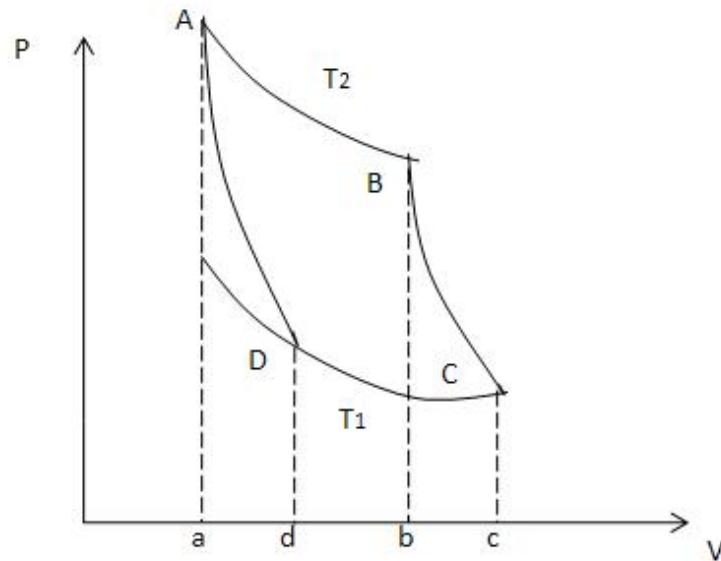


Figure 1.14

$$\left. \begin{array}{l} 2: \Delta W' = \Delta Q_2 - \Delta Q'_1 \\ 1: -\Delta W' = -\Delta Q_2 + \Delta Q_1 \end{array} \right\} \Delta W' - \Delta W = \Delta Q_1 - \Delta Q'_1 \quad \text{heat transferred directly to work other changes (Perp. mobile of 2nd kind)}$$

$$\left. \begin{array}{l} 2: \Delta W = \Delta Q'_2 - \Delta Q'_1 \\ 1: -\Delta W' = -\Delta Q_2 + \Delta Q_1 \end{array} \right\} \Delta Q_2 - \Delta Q'_2 = \underbrace{\Delta Q_1 - \Delta Q'_1}_{-(-\Delta Q_1 + \Delta Q'_1)} = \Delta Q \quad \text{heat flows from low temp. } T_1 \text{ to high temp. } T_2 \text{ without other changes}$$

2nd Law of Thermodynamics

There is no cyclic process to convert heat from reservoir directly into work without transferring heat to a cold reservoir

- To transfer heat from cold to hot reservoir, some amount of work is necessary.

(discuss.) All rev. Carnot cycles (T_2, T_1) have the same efficiency (the max.) and depend

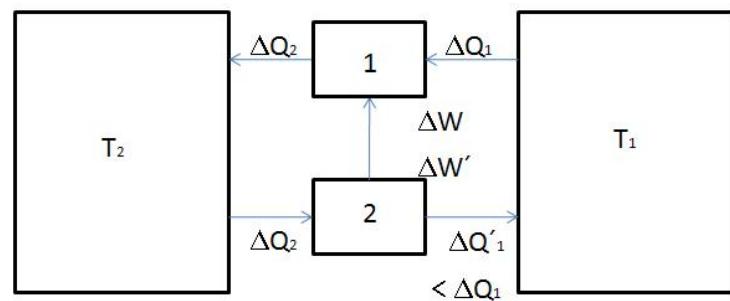


Figure 1.15

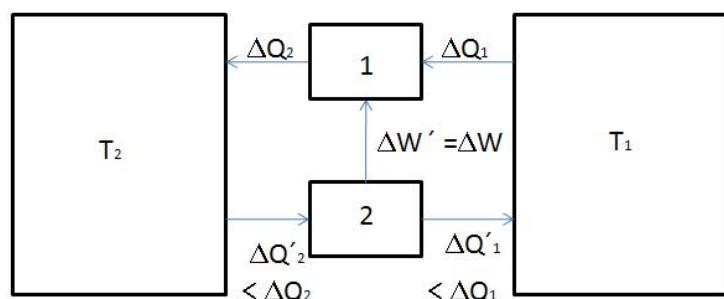


Figure 1.16

only on temperature

$$\begin{aligned}
 \eta &= 1 - \frac{\Delta Q_1}{\Delta Q_2} := 1 - f(T_1, T_2) \\
 \frac{\Delta Q_1}{\Delta Q_2} &= f(T_1, T_2) \quad \frac{\Delta Q_2}{\Delta Q_3} = f(T_2, T_3) \\
 \frac{\Delta Q_1}{\Delta Q_3} &= f(T_1, T_3) \\
 \Rightarrow \frac{\Delta Q_1}{\Delta Q_3} \cdot \frac{\Delta Q_3}{\Delta Q_2} &= \frac{\Delta Q_1}{\Delta Q_2} = \frac{f(T_1, T_3)}{f(T_2, T_3)} = f(T_1, T_2) \text{indep. of } \\
 T_3 &\Rightarrow f(T_1, T_3) = F(T_1)/F(T_3) \\
 \Rightarrow \frac{\Delta Q_1}{\Delta Q_2} &= \frac{F(T_1)}{F(T_2)} \stackrel{\text{Kelvin}}{:=} \frac{T_1}{T_2} \\
 &\qquad \text{efficiency} \\
 \eta &= \frac{\Delta Q_2 - \Delta Q_1}{\Delta Q_2} = \frac{T_2 - T_1}{T_2}
 \end{aligned}$$

defines an absolute temperature scale (indep. of warley substance)(Kelvin scale)
to ideal gas (eq. of state)

$$\begin{aligned}
 A \rightarrow B &\text{isoth. expansion} \quad \Delta U = 0; \quad \Delta Q_2 = \Delta W_1 = RT_2 \ln \frac{V_B}{V_A} \\
 B \rightarrow C &\text{adiab exp.} \quad \Delta Q = 0; \quad \Delta W_2 = -\Delta U = - \int_{T_2}^{T_1} C_V dT \\
 C \rightarrow D &\text{isoth. compression} \quad \Delta U = 0; \quad \Delta Q_1 = \Delta W_3 = RT_1 \ln \frac{V_D}{V_C} \\
 D \rightarrow A &\text{adiab. comp.} \quad \Delta Q = 0; \quad \Delta W_4 = - \int_{T_1}^{T_2} C_V dT
 \end{aligned}$$

total work done by gas:

$$\Delta W = \Delta W_1 + \Delta W_2 + \Delta W_3 + \Delta W_4 = RT_2 \ln \frac{V_B}{V_A} + RT_1 \ln \frac{V_D}{V_C}$$

total heat absorbed from hot reservoir

$$\Delta Q_2 = RT_2 \ln \frac{V_B}{V_A}$$

$$\text{within } \frac{V_B}{V_A} = \frac{V_C}{V_D} \quad (T \cdot V^{\gamma-1} = \text{const}) \Rightarrow \Delta W = R(T_2 - T_1) \ln \frac{V_B}{V_A}$$

this $\eta = \frac{\Delta W}{\Delta Q_2} = \frac{T_2 - T_1}{T_2}$

The second law of thermodynamics

Carnot process $\frac{\Delta Q_2 - \Delta Q_1}{\Delta Q_2} = \frac{T_2 - T_1}{T_2} \Leftrightarrow \frac{\Delta Q_1}{T_1} - \frac{\Delta Q_2}{T_2} = 0$

Any cyclic process can be broken down in a number of Carnot cycles for Zig-Zag path:
 $\sum \frac{\Delta Q}{T} = 0$

$\Delta Q > 0$ heat entering, $\Delta Q < 0$ heat leaving system

can be replaced in the limit by

$$\oint \underbrace{\frac{\delta Q}{T}}_{\substack{\text{total diff. of state} \\ \text{function}}} = 0$$

- the entropy S, defined by $dS = \frac{\delta Q_{rev}}{T}$ is a function of state

(eg loop ABA $\oint dS = 0 = \int_A^B dS + \int_B^A dS = (S_B - S_A) + (S_A - S_B) = 0$)

- For an adiabatically enclosed system, the entropy can never decrease

irreversible p. : $\Delta S > 0$

reversible p. : $\Delta S = 0$

Maximum work A → B $U_B - U_A = \Delta W - \Delta Q$

2nd Law limits the maximum amount of work extractable

$$\begin{aligned} dS &= \frac{\delta Q}{T} + dS_{irr}, \quad \delta Q = dU + \delta W \\ dS &= \frac{dU + \delta W}{T} + dS_{irr} \\ \delta W &= TdS - dU - TdS_{irr} \\ \delta W &\leq TdS - dU \end{aligned}$$

example: isothermal process, $\Delta W_{max} = T(S_B - S_A) - (U_B - U_A)$ if proc. is revers.

S is state function → ΔS it the same if expansion is used to create work or free expanded

Equilibrium= reached. when entropy reaches a maximum value

in an isolated system of constant int. energy U and volume V, eq. is attained at maximum entropy

example: reaction

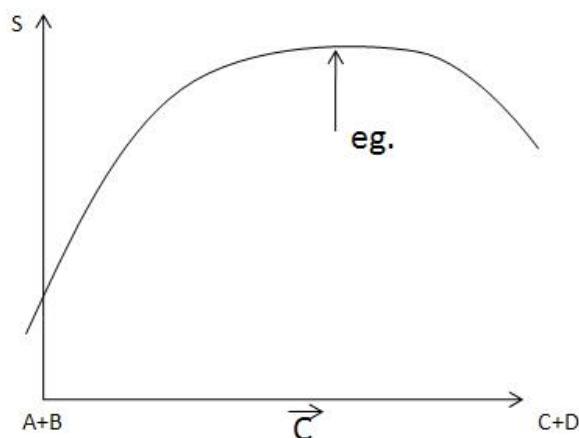
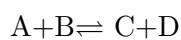


Figure 1.17

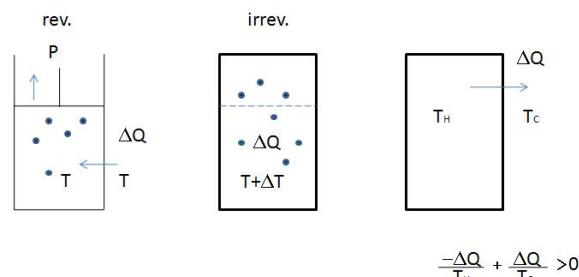


Figure 1.18

for closed system

$$\begin{aligned} dU &= \delta Q - \delta W; \delta W = PdV \\ dS &= \frac{\delta Q}{T} \\ \Rightarrow dU &= TdS - PdV (*) \\ U &= U(S, V) \text{ with } dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \end{aligned}$$

compare to (*)

$$\begin{aligned}
 T &= \left(\frac{\partial U}{\partial S}\right)_V \quad \text{temperature def.} \\
 P &= -\left(\frac{\partial U}{\partial V}\right)_S \quad \text{pressure def.} \\
 S &= S(U, V) \\
 dS &= \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV \stackrel{(*)}{=} \frac{dU}{T} + \frac{P dV}{T} \\
 \left(\frac{\partial S}{\partial V}\right)_U &= \frac{P}{T}
 \end{aligned}$$

Equilibrium occurs:

- in a system with fixed U and V, if entropy is maximized
- in a system with fixed S and V, if internal energy is minimized

Further development: S and V are inconvenient variables to be controlled in real world.

2 1.11.10

2.1 Lecture 3

Gibbs Free energy as a function of temperature and pressure.

Consider equilibrium between solid and liquid.

$$G_s = G_l$$

For infinitesimal changes: $dG_s = dG_l$

$$dG_s = -S_{(s)}dT + V_{(s)}dP$$

$$dG_l = -S_l dT + V_l dP$$

$$-S_{(s)}dT + V_{(s)}dP = -S_l dT + V_l dP$$

$$V_{(s)} - V_{(l)}dP = (S_{(s)} - S_{(l)})dT$$

$$\left(\frac{\partial P}{\partial T}\right)_{eq.} = \frac{\Delta S}{\Delta V} = \left(\frac{S_s - S_l}{V_s - V_l}\right)$$

$$\text{at eq.: } \Delta S = \frac{\Delta H_f}{T}$$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_{eq.} = \frac{\Delta H_f}{T \Delta V}} \quad \underline{\text{Clapeyron equation:}}$$

This gives the dependence of pressure on temperature (or the relation between the two) to maintain equilibrium.

Behavior of Gases, solutions, Phase-Diagrams:

P:-Pressure of Gas.

V:-Molar Volume.

R:-Gas constant.

T:-Absolute temperature

$$\left(\frac{pV}{RT} \rightarrow 1 \right)_{P \rightarrow 0} \quad \text{Real gases}$$

Mixture of Ideal Gases - (a model for solubility and mixing)

How do we treat a mixture of gases?

For a pure gas:- what is the relation of Gibbs free energy and pressure
closed system, $dI=0$ (Isothermal change from $P_1 \rightarrow P_2$)

$$dG = VdP$$

For 1 mole of “ideal” gas,

$$\begin{aligned} dG &= \frac{RT}{P} dP = RT d\ln P. \\ G(P_2, T) - G(P_1, T) &= RT \ln \frac{P_2}{P_1} \quad - (\text{I}) \\ G &= G^0 + RT \ln \frac{P}{P_0} \end{aligned}$$

$G^0 \rightarrow$ (Free energy of 1 mole, $P_0 = 1$ atm “Standard state”)

For a mixture:

Concept of “mole fraction”, “partial pressure”, “partial molar quantities”.

Mole fraction:

$$X_A = \frac{n_A}{n_A+n_B+n_C} \quad X_B = \frac{n_B}{n_A+n_B+n_C}; \quad X_C = \frac{n_C}{n_A+n_B+n_C}$$

$$X_A + X_B + X_C = 1 \quad (\text{representing composition})$$

Partial pressure: P_A :-Pressure exerted by component A, if it were alone present in a container,

$$\text{Total pressure } \boxed{P = p_A + p_B + p_C}$$

$$\begin{aligned} p_A &= \frac{n_A RT}{V'} \\ p_B &= \frac{n_B RT}{V'} \\ P = p_A + p_B &= \frac{(n_A + n_B)RT}{V'} \end{aligned}$$

Dalton's law of partial pressures $\boxed{p_A = X_A P}$

Partial molar quantities

Partial molar value of an extensive quantity Q, in a mixture i, j, k. (components)

$$\overline{Q}_i = \left(\frac{\partial Q'}{\partial n_i} \right)_{T,P,n_j,n_k} = \text{rate of change of } Q' \text{ with } n_i \text{ at } T, P, n_j, n_k = \text{const.}$$

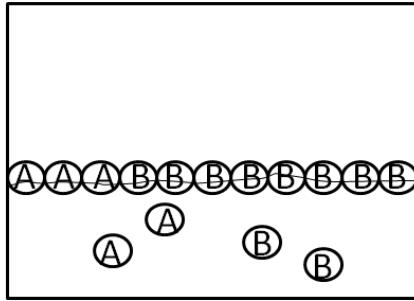
Q' : Value of Q for an arbitrary quantity system size of mixture for $Q \equiv G$.

$$\begin{aligned} \Omega &= U - TS - \mu N \\ d\Omega &= -SdT - PdV - Nd\mu \end{aligned}$$

$$\overline{G}_i = \left(\frac{\partial G'}{\partial n_i} \right)_{T,P,n_j,n_k} = \mu_i \text{ (chemical potential of the component in mixture)}$$

"Maxwell relations are also applicable for partial molar quantities" from fundamental rel.

$$\begin{aligned}
 \left(\frac{\partial G'}{\partial P} \right)_{T,comp} &= V' \\
 \left(\frac{\partial}{\partial n_i} \left(\frac{\partial G'}{\partial P} \right)_{T,comp} \right)_{T,P,n_j,n_k} &= \bar{V} \\
 = \left(\frac{\partial}{\partial P} \left(\frac{\partial G'}{\partial n_i} \right)_{T,P,n_j} \right)_{T,comp} &= \left(\frac{\partial \bar{G}_i}{\partial P} \right)_T
 \end{aligned}$$

Solutions**Figure 2.1**

$\gamma_{e(A)}$: rate of evaporation (A)

In pure A:

$$\sim e(-\frac{E_A^A}{KT})$$

$$(1) \gamma_{e(A)} = kp_A^0 := p_A^0 \text{ (saturated vap. pressure)}$$

In B: - $\gamma_{e(B)}$: - rate of evaporation (B)

$$\gamma_e(B) = k'p_B^0$$

In a mixture, the rate of evaporation of A is reduced by X_A (assumption: identical bond energies A-A, A-B, B-B and composition of surface like in bulk)

$$(2) \gamma_{e(A)} X_A = kp_A$$

$$\gamma_{e(B)} X_B = k'p_B$$

$$\boxed{p_A = X_A p_A^0 \quad p_B = X_B p_B^0} \quad \text{Raoult's Law}$$

Gibbs duhem Equation

How are partial molar quantities of components in a system related?

Let Q' be an extensive property

$$Q' = Q'(T, P, n_i, n_j, n_k \dots)$$

at const. T,P

$$dQ' = \left(\frac{\partial Q'}{\partial n_i} \right)_{T, n_j, n_k} dn_i + \left(\frac{\partial Q'}{\partial n_i} \right)_{T, n_j, n_k} dn_j + \left(\frac{\partial Q'}{\partial n_k} \right)_{T, n_i, n_j} dn_k \dots$$

$$dQ' = \bar{Q}_i dn_i + \bar{Q}_j dn_j + \bar{Q}_k dn_k \dots \quad (1)$$

also from definition:

$$Q' = \bar{Q}_i n_i + \bar{Q}_j n_j \dots$$

$$dQ' = (\bar{Q}_i dn_i + \bar{Q}_j dn_j + \dots) + d\bar{Q}_i n_i + d\bar{Q}_j n_j + \dots \quad (2)$$

(1) and (2) gives.

$$\boxed{\sum_i d\bar{Q}_i n_i = 0 ; \quad \text{or dividing by no. of moles of system} \Rightarrow \sum_i d\bar{Q}_i x_j = 0}$$

Binary solution(A,B) if $Q' \equiv G'$; T, P =const:

$$G' = n_A \bar{G}_A + n_B \bar{G}_B \quad G' : -\text{Gibbs energy}$$

$$(1) G \equiv X_A \bar{G}_A + X_B \bar{G}_B \quad G = \text{molar Gibbs energy}$$

$$\bar{G}_i = \text{Excess enthalpy}$$

Gibbs - Duhem:

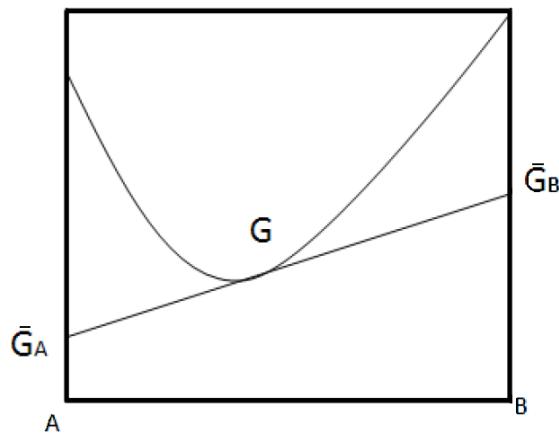


Figure 2.2

$$X_A \overline{dG}_A + X_B \overline{dG}_B = 0$$

$$dG = \overline{G}_A dX_A + \overline{G}_B dX_B$$

$$\frac{dG}{dX_A} = \overline{G}_A - \overline{G}_B$$

$$(2) \quad X_B \frac{dG}{dX_A} = X_B \overline{G}_A - X_B \overline{G}_B$$

$$(1) + (2) \quad G + X_B \frac{dG}{dX_A} = \overline{G}_A; \quad \overline{G}_B = G + X_A \frac{dG}{dX_B}$$

Properties of “Raoultion” “Ideal” Solutions

Some terminology

$$a_i(\text{activity of component i}) = \frac{f_i}{f_i^0}$$

When the vapor in equilibrium is ideal

$$a_i = \frac{p_i}{p_i^0} \dots (\text{II})$$

In addition if the component i exhibits Raoultion behavior $a_i = X_i$.

Change in Gibbs-free energy due to the formation of a solution: (A,B)

Deriving the free energy change in a mixture of gases (I)

$$\begin{aligned}\Delta\bar{G}_i &= G_{solution}^i - G_{(pure)}^i = RT \ln \frac{p_i}{p_i^0} \\ &= RT \ln a_i^0 \\ &= \bar{G}_i - G_i^0 = RT \ln a_i = RT \ln X_i\end{aligned}$$

Free energy before mixing:- $(n_A : A, n_B : B)$

$$n_A G_A^0 + n_B G_B^0$$

Free energy after mixing:-

$$n_A \bar{G}_A + n_B \bar{G}_B$$

Free energy change accompanying mixing:

$$\begin{aligned}\Delta G' &= n_A(\bar{G}_A - G_A^0) + n_B(\bar{G}_B - G_B^0). \\ &= n_A \Delta \bar{G}_A + n_B \Delta \bar{G}_B. \\ &= n_A RT \ln a_A + n_B RT \ln a_B. \\ &= \boxed{RT(n_A \ln a_A + n_B \ln a_B)}.\end{aligned}$$

For Ideal Solution

$$\Delta G' = RT(n_A \ln X_A + n_B \ln X_B).$$

for a mole

$$\boxed{\Delta G = RT(X_A \ln X_A + X_B \ln X_B)}.$$

Change in volume of an ideal Solution.

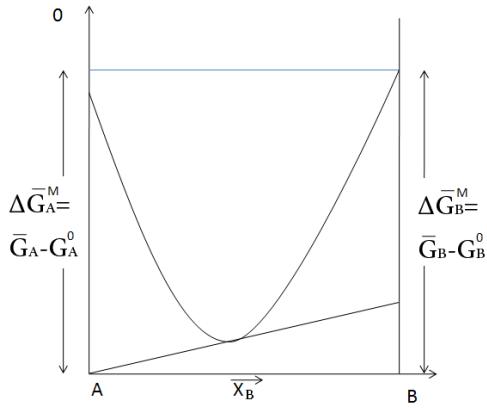


Figure 2.3

Using:-

$$\begin{aligned}
 \left(\frac{\partial G}{\partial P} \right)_{T,comp} &= V \\
 \left(\frac{\partial G_i}{\partial P} \right)_{T,C} &= \bar{V}_i; \quad \left(\frac{\partial G_i^0}{\partial P} \right)_{T,C} = V_i^0 \\
 \left(\frac{\partial (\bar{G}_i - G_i^0)}{\partial P} \right)_{T,C} &= \bar{V}_i - V_i^0 \\
 \left(\frac{\partial \Delta \bar{G}_i}{\partial P} \right)_{T,C} &= \bar{V}_i - V_i^0 \\
 \Delta \bar{G}_i &= RT \ln X_i \quad \therefore \quad \left(\frac{\partial \Delta \bar{G}_i}{\partial P} \right)_{T,C} = 0 \quad \text{or} \quad \bar{V}_i - V_i^0 = 0 \\
 \Rightarrow \Delta \bar{V}_i &= 0
 \end{aligned}$$

From this it follows:-

change of volume is zero in ideal mixing

$$\begin{aligned}
 \Rightarrow \Delta V' M &= n_A \Delta \bar{V}_A + n_B \Delta \bar{V}_B \\
 \Delta \bar{V}_A &= 0 \quad \text{and} \quad \Delta \bar{V}_B = 0
 \end{aligned}$$

Heat of formation of an ideal solution.

$$\begin{aligned}
 \left[\frac{\partial \bar{G}_i/T}{\partial T} \right]_{P,comp} &= -\frac{\bar{H}_i}{T^2}; \\
 \left[\frac{\partial \bar{G}_i^0/T}{\partial T} \right]_{P,comp} &= -\frac{\bar{H}_i^0}{T^2} \\
 -\frac{(\bar{H}_i - \bar{H}_i^0)}{T^2} &= -\frac{\Delta \bar{H}_i}{T^2} = \left[\frac{\partial (\bar{G}_i - \bar{G}_i^0)/T}{\partial T} \right] = \left[\frac{\partial \Delta \bar{G}^i/T}{\partial T} \right] \\
 \Rightarrow \frac{\partial (R \ln X_i)}{\partial T} &= \frac{\Delta H_i}{T^2} = 0 \\
 \Delta H' = n_A \bar{\Delta H}_A + n_B \bar{\Delta H}_B &= 0 \quad \Rightarrow \Delta \bar{H}_A \rightarrow 0 \quad \text{and} \quad \Delta \bar{H}_B \rightarrow 0.
 \end{aligned}$$

Entropy of formation

$$\begin{aligned}
 \left(\frac{\partial G}{\partial T} \right)_{P,comp} &= -S. \\
 \left(\frac{\partial \Delta G^M}{\partial T} \right)_{P,comp} &= -\Delta S^M = -R(X_A \ln X_A + X_B \ln X_B) \dots \quad \text{III}
 \end{aligned}$$

From the definition of configurational entropy.

$$\begin{aligned}
 \Delta S' &= k \ln \frac{(N_A + N_B)!}{N_A! N_B!} \\
 &= k[\ln(N_A + N_B)! - \ln N_A! - \ln N_B!]
 \end{aligned}$$

Apply stirlings's approximation

$$\begin{aligned}
 \Delta S' &= k[(N_A + N_B) \ln(N_A + N_B) - N_A - N_B \\
 &\quad - N_A \ln N_A + N_A - N_B \ln N_B + N_B] \\
 &= -k \left[N_A \ln \frac{(N_A)}{(N_A + N_B)} + N_B \ln \frac{(N_B)}{(N_A + N_B)} \right] \\
 \frac{N_A}{N_A + N_B} &= \frac{n_A}{n_A + n_B} = X_A. \\
 N_A : \frac{N_A}{N_0} & \text{ moles} = n_A; \quad N_B : \frac{N_B}{N_0} \quad \text{ moles} = n_B. \\
 &\downarrow \\
 &\text{Avogadro no} \\
 \Delta S' &= -k N_0 (n_A \ln X_A + n_B \ln X_B)
 \end{aligned}$$

$$1 \text{ mole: } \boxed{\Delta S = -R(X_A \ln X_A + X_B \ln X_B)} \cdots \text{IV}$$

$$\boxed{III \equiv IV} \quad !!!$$

The thermodynamic activity of a comp in solution

at temperature T: activity is the ratio of fugacity of a substance

$$a_i = \frac{f_i}{f_i^0} \quad \text{at T}$$

$$\text{for solution} \leftrightarrow \text{vapor} \quad f_i = P_i \quad \Rightarrow \quad a_i = \frac{P_i}{P_i^0}$$

$$\text{Raoultian behaviour} \quad a_i = X_i$$

$$\text{Henry behaviour} \quad a_i = k_i X_i$$

The Gibbs-Duhem equation

$$\begin{aligned} \left[\frac{\partial(G_i/T)}{\partial T} \right]_{P,comp} &= -\frac{\bar{H}_i}{T^2} \\ G &= H - TS \\ &= H + T \left(\frac{\partial G}{\partial T} \right)_P \\ \frac{G}{T} &= \frac{H}{T} + \left(\frac{\partial G}{\partial T} \right) \\ \frac{\partial(\frac{G}{T})}{\partial T} &= -\frac{H}{T^2} + \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P + \frac{\partial^2 G}{\partial T^2} \\ \frac{\partial^2 G}{\partial T^2} &= -\frac{\partial S}{\partial T} \\ S &= \frac{dH}{T} \\ \frac{\partial S}{\partial T} &= -\frac{1}{T} \frac{\partial H}{\partial T} \\ \frac{\partial(\frac{G}{T})}{\partial T} &= -\frac{H}{T^2} \end{aligned}$$

Gibbs-Helmoltz relation.

Gibbs-Phase Rule.

* N phases, K components

NK → degrees of freedom

(N-1)K → Equations of equilibrium

NK-(N-1)K=K

N → Equations of sum constraint

F=K-N

For Non, constant T,P F=K-N+2

$$\begin{aligned}
 & C_A G_A^\alpha + (1 - C_A) G_B^\alpha + RT(C_A \ln C_A + C_B \ln C_B) \\
 G = & C_A(G_A^\alpha + RT \ln C_A) + (1 - C_A)(G_B^\alpha + RT \ln(1 - C_A)). \\
 & \equiv C_A \overline{G_A}^\alpha + (1 - C_A) \overline{G_B}^\alpha
 \end{aligned}$$

$$\overline{G}_A^\alpha = G_A^\alpha + RT \ln C_A$$

$$G_B^A = G_B^\alpha + RT \ln C_B$$

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3.1 lecture 4

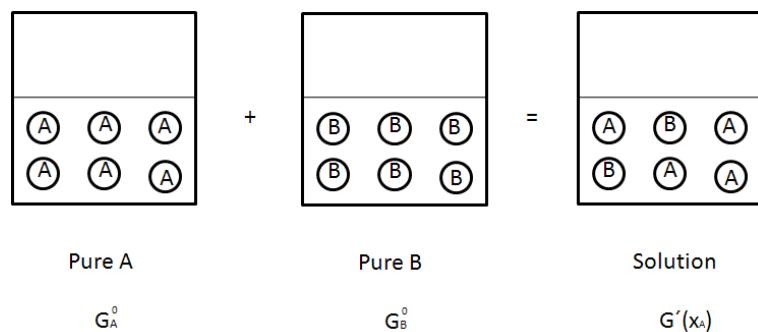


Figure 3.1

A solution is different from a mixture of pure A and pure B. Therefore for a composition of ' X_A ' in binary system A, B,

$$\begin{aligned}
 G_A^0 X_A + G_B^0 (1 - X_A) &\neq G'(X_A). \\
 G'(X_A) &= \bar{G}_A X_A + \bar{G}_B X_B. \\
 \Delta G(X_A) &= (\bar{G}_A - G_A^0) X_A + (\bar{G}_B - G_B^0) X_B. \\
 &= \Delta \bar{G}_A X_A + \Delta \bar{G}_B X_B.
 \end{aligned}$$

Where $\Delta \bar{G}_A$ is the partial molar Gibbs free energy change of the system for the component A.

For Ideal Solution ("Raoultian")

$$\Delta \bar{G}_A = RT \ln X_A; \quad \Delta \bar{G}_B = RT \ln X_B.$$

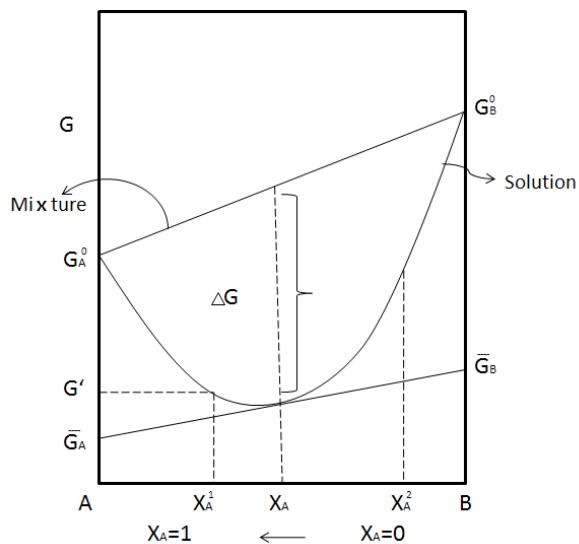


Figure 3.2

$$\Delta G^{MIX}(X_A) = X_A RT \ln X_A + X_B RT \ln X_B$$

Free energy change of entropy of mixing $\Delta S(X)$

$$\Delta S^{MIX} = -R(X_A \ln X_A + X_B \ln X_B)$$

Maximum randomness for "equal" mole fractions of components A, B. This holds also

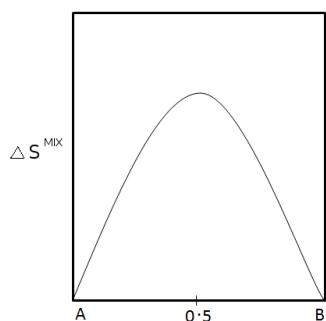


Figure 3.3

for more than 2 components (A, B, C, \dots) $\Rightarrow (X_A = X_B = X_C = \dots)$

To get the free energy of the system,

$$G = G_A^0 X_A + G_B^0 X_B + \Delta \bar{G}_A X_A + \Delta \bar{G}_B X_B.$$

Nobody can $\frac{(\text{calculate})}{\text{measure}}$ "absolute" 'G', but only change. So one would need a "reference" state. For the discussion, we fix the reference state as $T_0 = 298K$, P=1 atm. because most measurements are done at 1 atm.

Then at const P=1 atm.

$$\begin{aligned} \Delta G &= X_A \int_{T_0=298}^T dG_A^0 + X_B \int_{T_0=298}^T dG_B^0 + \Delta \bar{G}_A X_A + \Delta \bar{G}_B X_B. \\ G &= H - TS. \\ \Delta G^S &= \Delta H^S - T \Delta S^S \quad (\text{Free energy change}) \\ &= X_A \int_{T_0=298}^T Cp_A^S dT + X_B \int_{T_0=298}^T Cp_B^S dT - T \int_{T_0=298}^T \frac{Cp_A^S}{T} dT - \int_{T_0=298}^T \frac{Cp_B^S}{T} dT. \\ \Delta G^l &= \Delta H^l - T \Delta S^l. \\ &= X_A \int_{T_0=298}^{T_m} Cp_A^S dT + X_B \int_{T_0=298}^{T_m} Cp_B^S dT - T \int_{T_0=298}^{T_m} \frac{Cp_A^S}{T} dT - T \int_{T_0=298}^{T_m} \frac{Cp_B^S}{T} dT. \\ &\quad + (\Delta H_f^A - \frac{T \Delta H_f^A}{T_f}) X_A + (\Delta H_f^B - \frac{T \Delta H_f^B}{T_f}) X_B. \\ \Delta G^l &= X_A \int_{T_0=298}^T Cp_A^l dT + X_B \int_{T_0=298}^T Cp_B^l dT - TX_A \int_{T_0=298}^T \frac{Cp_A^l}{T} dT - TX_B \int_{T_0=298}^T \frac{Cp_B^l}{T} dT \\ &\quad + (\Delta H_f^A - \frac{T \Delta H_f^A}{T_f}) X_A + (\Delta H_f^B - \frac{T \Delta H_f^B}{T_f}) X_B \\ &= X \int_{T_m}^T C_V^l dT - T \int_{T_m}^T \frac{C_V^l}{T} \frac{dT}{d} + \Delta H_f - T \frac{\Delta H_f}{T_f}. \\ \Delta G^l &= X_A \int_{T_m}^T Cp_A^l dT + X_B \int_{T_m}^T Cp_B^l dT - X_A T \int_{T_m}^T Cp_A^l \frac{dT}{T} - X_B T \int_{T_m}^T Cp_B^l \frac{dT}{T} \\ &\quad + (\Delta H_f^A - \frac{T \Delta H_f^A}{T_f}) X_A + (\Delta H_f^B - \frac{T \Delta H_f^B}{T_f}) X_B. \\ \Delta G^S &= X_A \int_{T_m}^T Cp_A^S dT + X_B \int_{T_m}^T Cp_B^S dT - X_A T \int_{T_m}^T Cp_A^S \frac{dT}{T} - X_B T \int_{T_m}^T Cp_B^S \frac{dT}{T}. \\ &\quad \Delta G^l - \Delta G^S. \\ X_A \int_{T_m}^l \Delta Cp_A dt - X_A T \int \Delta Cp_A^l \frac{dT}{T} &\Rightarrow 0 \quad \text{for } \Delta Cp_A^{ls} = 0 \quad \text{for } \Delta Cp_B^{ls} = 0. \end{aligned}$$

$$X_B \int_{T_m}^l \Delta C p_B dT - X_B T \int \Delta C p_B^T \frac{dT}{T} \Rightarrow 0.$$

$$\Delta G^{l \rightarrow s} = \Delta H_f^A \left(\frac{T_f - T}{T_f} \right) X_A + \Delta H_f^B \frac{(T_f - T)}{T_f} X_B.$$

Taking liquid as reference.

$$\Delta G^S : \Delta H_f^A \frac{(T - T_f)}{T_f} X_A + \Delta H_f^B \frac{(T - T_f)}{T_f} X_B.$$

$$\Delta G^l = 0.$$

$$\Delta G^S = X_A \Delta H_f^A \frac{(T - T_f^A)}{T_f^A} + X_B \Delta H_f^B \frac{(T - T_f^B)}{T_f^B} + \overline{\Delta G}_A^S X_A + \overline{\Delta G}_B^S X_B.$$

$$\Delta G^l = \overline{\Delta G}_A^l X_A + \overline{\Delta G}_B^l X_B.$$

Points to note:

ΔH_f^A : - Latent heat of fusion. for $S \rightarrow L$ transition. In principle, the latent heat of transformation will then depend on the solid phase and the liquid phase.

\therefore We name $\Delta H_f \equiv L_A^\alpha \equiv \alpha \rightarrow L$ transformation for pure A.

What is the latent heat of transformation for an alloy of composition ' X_A '?

We can analogously derive as for the case of pure components at equilibrium;

$$\Delta G^{S-L} = 0.$$

$$\Delta H^{S-L} = T(\Delta S^S - \Delta S^L).$$

$$\Delta S^S = -\frac{\partial \Delta G^S}{\partial T}.$$

$$\Delta S^l = -\frac{\partial \Delta G^l}{\partial T}.$$

$$L^{S-L} = -\frac{1}{T} \left(\frac{\partial \Delta G^S}{\partial T} - \frac{\partial \Delta G^l}{\partial T} \right)_{X_A}.$$

How do we "geometrically" see the equilibrium between two phases in a binary system?

$$\overline{\Delta G}_A^S = \overline{\Delta G}_A^l$$

$$\overline{\Delta G}_B^S = \overline{\Delta G}_B^l$$

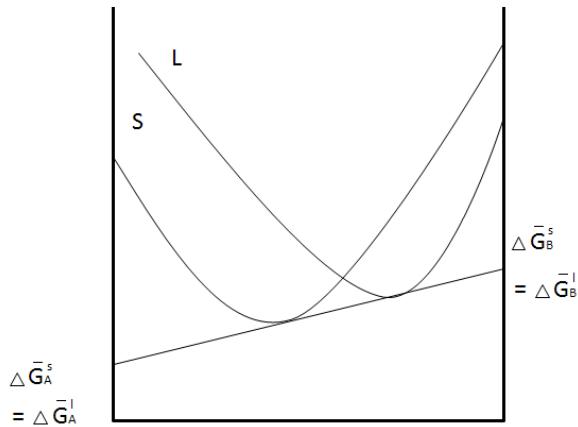


Figure 3.4

Thus, for a binary system (A,B) phase equilibrium between two phases (α, l) implies the partial molar Gibbs free energy of each component in each phase is equal.

≡ Equivalently, the compositions of the phases ' α ' and ' l ' at which these conditions hold correspond to the common tangent constructions.

For a system Ni-Cu:

Can we derive the phase-diagram?

$$\begin{aligned}\Delta G^\alpha &= X_A^\alpha L_A^\alpha \frac{(T - T_A^\alpha)}{T_A^\alpha} + X_B^\alpha L_B^\alpha \frac{(T - T_B^\alpha)}{T_B^\alpha} \\ &\quad + RT(X_A^\alpha \ln X_A^\alpha + X_B^\alpha \ln X_B^\alpha) \\ \Delta G^l &= RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l)\end{aligned}$$

At a Temperature 'T'

$$\begin{aligned}\Delta \bar{G}_A^\alpha &= \Delta \bar{G}_A^l \\ L_A^\alpha \frac{(T - T_A^\alpha)}{T_A^\alpha} + RT \ln X_A^\alpha &= RT \ln X_A^l \dots (1) \\ L_B^\alpha \frac{(T - T_B^\alpha)}{T_B^\alpha} + RT \ln X_B^\alpha &= RT \ln X_B^l \dots (2)\end{aligned}$$

For Ni-Cu:

$$L_{Ni}^\alpha = 2310 \text{ J/cm}^3 \quad L_{Cu}^\alpha = 1728 \text{ J/cm}^3. \\ R = 8.314 \text{ J/Kmol} \quad v = 7.42 \text{ cm}^3.$$

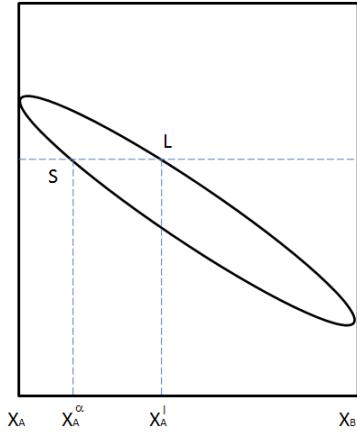


Figure 3.5

For phase-field purposes we always take free energy density so if we divide the free energy by the molar volume we get the free energy pure unit volume.

HHHH (1) and (2) become.

$$L_A^\alpha \frac{(T - T_A^\alpha)}{T_A^\alpha} + \frac{RT}{V_m} \ln X_A^\alpha = \frac{RT}{V_m} \ln X_A^l \\ L_B^\alpha \frac{(T - T_B^\alpha)}{T_B^\alpha} + \frac{RT}{V_m} \ln X_B^\alpha = \frac{RT}{V_m} \ln X_B^l$$

We can now non-dimensionalize our system by dividing throughout with $\frac{RT_A^\alpha}{V_m}$ and choosing T_A^α as reference temperature

$$\tilde{L}_A \frac{(\tilde{T} - \tilde{T}_A^\alpha)}{\tilde{T}_A^\alpha} + \tilde{T} \ln X_A^\alpha = \tilde{T} \ln X_A^l \\ \tilde{L}_B \frac{(\tilde{T} - \tilde{T}_B^\alpha)}{\tilde{T}_B^\alpha} + \tilde{T} \ln X_B^\alpha = \tilde{T} \ln X_B^l \\ \ln X_A^\alpha = \ln X_n^\alpha - \tilde{L}_A \frac{(\tilde{T} - \tilde{T}_A^\alpha)}{\tilde{T} \tilde{T}_A^\alpha}$$

$$= \ln X_A^\alpha - \tilde{L}_A \frac{(\tilde{T} - \tilde{T}_A^\alpha)}{\tilde{T}\tilde{T}_A^\alpha}.$$

Similarly;

$$\begin{aligned} \ln(1 - X_A^\alpha) &= \ln X_B^\alpha - \tilde{L}_B \frac{(\tilde{T} - \tilde{T}_B^\alpha)}{\tilde{T}\tilde{T}_B^\alpha} \\ \frac{X_A^\alpha}{(1 - X_A^\alpha)} &= \frac{\exp\left(\ln X_A^l - \frac{\tilde{L}_A(\tilde{T} - \tilde{T}_A^\alpha)}{\tilde{T}\tilde{T}_A^\alpha}\right)}{\exp\left(\ln X_B^l - \frac{\tilde{L}_B(\tilde{T} - \tilde{T}_B^\alpha)}{\tilde{T}\tilde{T}_B^\alpha}\right)} \end{aligned}$$

$$X_A^\alpha = \frac{\exp\left(\ln X_A^l - \frac{\tilde{L}_A(\tilde{T} - \tilde{T}_A^\alpha)}{\tilde{T}\tilde{T}_A^\alpha}\right)}{1 + \exp\left(\ln X_B^l - \frac{\tilde{L}_B(\tilde{T} - \tilde{T}_B^\alpha)}{\tilde{T}\tilde{T}_B^\alpha}\right)}$$

Equivalently the liquidus can be written as:

$$X_A^l = \frac{\exp\left(\ln X_A^\alpha + \frac{\tilde{L}_A(\tilde{T} - \tilde{T}_A^\alpha)}{\tilde{T}\tilde{T}_A^\alpha}\right)}{\left[1 + \exp\left(\ln X_B^\alpha + \frac{\tilde{L}_B(\tilde{T} - \tilde{T}_B^\alpha)}{\tilde{T}\tilde{T}_B^\alpha}\right)\right]}$$

Slopes of solidus and liquidus.

$$\begin{aligned} \text{I} - \quad \tilde{L}_A^\alpha \frac{(\tilde{T} - \tilde{T}_A^\alpha)}{\tilde{T}_A^\alpha} + \tilde{T} \ln X_A^\alpha &= \tilde{T} \ln X_A^l \\ \text{II} - \quad \tilde{L}_B^\alpha \frac{(\tilde{T} - \tilde{T}_B^\alpha)}{\tilde{T}_B^\alpha} + \tilde{T} \ln X_B^\alpha &= \tilde{T} \ln X_B^l \end{aligned}$$

$$\begin{aligned} X_A^\alpha + X_B^\alpha &= 1 \\ X_A^l + X_B^l &= 1 \end{aligned}$$

Variable $\tilde{T}, X_A^\alpha, X_B^\alpha, X_A^l, X_B^l$

There are four equations \Rightarrow Degree of freedom 5-4=1.

We choose X_B^l our independent variable.

Differentiate I

$$\frac{L_A^\alpha}{T^2} \left(\frac{\partial T}{\partial X_a^l} \right) + \frac{1}{X_A^\alpha} \frac{\partial X_A^\alpha}{\partial X_B^l} = \frac{-1}{X_A^l}$$

$$\text{III} \quad X_A^\alpha \frac{L_A^\alpha}{T^2} \cdot \left(\frac{\partial T}{\partial X_B^l} \right) + \frac{\partial X_A^\alpha}{\partial X_B^l} = -\frac{X_A^\alpha}{X_A^l}$$

Similarly for II

$$\text{IV} \quad X_B^\alpha \frac{L_B^\alpha}{T^2} \cdot \left(\frac{\partial T}{\partial X_A^l} \right) + \frac{\partial X_B^\alpha}{\partial X_A^l} = \frac{X_B^\alpha}{X_B^l}$$

Adding III and IV;

$$\begin{aligned} \frac{\partial X_A^\alpha}{\partial X_B^l} + \frac{\partial X_B^\alpha}{\partial X_A^l} &= 0 \\ \frac{1}{T^2} \frac{\partial T}{\partial X_A^l} (X_A^\alpha L_A^\alpha + X_B^\alpha L_B^\alpha) &= \frac{X_B^\alpha}{X_B^l} - \frac{X_A^\alpha}{X_A^l} \end{aligned}$$

$$\boxed{\frac{\partial T}{\partial X_B^l} = \frac{\frac{X_B^\alpha}{X_B^l} - \frac{X_A^\alpha}{X_A^l}}{\frac{1}{T^2} (X_A^\alpha L_A^\alpha + X_B^\alpha L_B^\alpha)}}$$

Similarly for solidus

$$\frac{\partial T}{\partial X_B^\alpha} = \frac{-(\frac{X_B^l}{X_B^\alpha} - \frac{X_A^l}{X_A^\alpha})}{\frac{1}{T^2} \{ X_A^l L_A^\alpha + X_B^l L_B^\alpha \}}$$

4 1.11.10

4.1 lecture 5

Phase-field Evolutions:

1. Van-der Waals: - 1893 (Density variations as a functions of ' h '

$h \rightarrow$ distance along gas-liquid interface.

Introduction of square gradient energy term).

2. Ginzburg-Landau: - 1920 (Free energy of a non-uniform system).

Cahn-Hilliard: - 1958 (Free energay of a non-uniform system).

3. Allen, Langer: - Frist phase-field formulations of dynamics

in phase transitions (solidification,Langer).

Free energy of a non-uniform system:

Postulate: - The free energy of a system dependent on an intensive property of the system depends on the local value and on its variation a cross a system (gradients).

f_0 : - Equilibrium energy of a uniform system at ' c '.

$f(c, \nabla c, \nabla^2 c \dots)$

Expanding ' f ' around ' f_0 ' as a Taylor series would allow us to write ' f ' as a function of compositions and its gradients. Sciens this ' f ' is a scalar, its value should be independent of the directions of the gradient: - hence only even powers of the gradient can occur in the expansion.

$$f(c, \nabla c, \nabla^2 c) = f_0(c) + k_1 \nabla^2 c + k_2 (\nabla c)^2 \dots$$

Integrating over a volume,

$$F = N_V \int_V f dV = N_V \int_V (f_0(c) + k_1 \nabla^2 c + k_2 (\nabla c)^2 \dots) dV.$$

N_V : - Number of molecules per unit volume.

$$\int_V k_1 \nabla^2 c dV = - \int_V \frac{\partial k_1}{\partial c} (\nabla c)^2 dV + \int_S k_1 (\nabla c \cdot \hat{n}) dS$$

One can always choose a surface such that the second integral goes to zero.

$$F = N_V \int_V f_o(c) + \left(k_2 - \frac{\partial k_1}{\partial c} \right) (\nabla c)^2 dV; \quad \left(k_2 - \frac{\partial k_1}{\partial c} \right) \Rightarrow k$$

$$F = N_v \int_v (f_o(c) + k(\nabla c)^2) dV$$

For convenience, and in cases where partial molar volumes of components are equal, one can write ' f'_0 ' also as a energy E/vol. such that,

$$F = \int_V (f'_o(c) + k'(\nabla c)^2) dV$$

' f'_0 ' and $k'(\nabla c)^2$ are quantities per unit vol. of the system.

What is the interfacial energy with this definition of energies?

Interface energy of the system by definition is the difference per unit area of the actual free energy of the system with the interface and what the system would have, if it were continuos.

The "continuons" term is uniquely defined at equilibrium between the phases α and β .

$\therefore \sigma$ can be written as: -

$$\begin{aligned} F &= A \int_x [f'_o(c) + k'(\nabla c)^2 - (c\mu_B(e) + (1-c)\mu_A(e))] dx. \\ \sigma &= \int_x [f'_o(c) + k'(\nabla c)^2 - (c\mu_B(e) + (1-c)\mu_A(e))] dx. \\ f'_o(c) &= c\mu_A + (1-c)\mu_B. \\ \sigma &= \int_x \{\mu_B - \mu_B(e) + (1-c)(\mu_A - \mu_A(e)) + k'(\nabla c)^2\} dx. \\ \Delta f(c) &= c(\mu_B - \mu_B(e)) + (1-c)(\mu_A - \mu_A(e)). \\ \Delta f(c) &> 0. \end{aligned}$$

$$\sigma = \int_x \{ \Delta f(c) + k' \left(\frac{\partial c}{\partial x} \right)^2 \} dx.$$

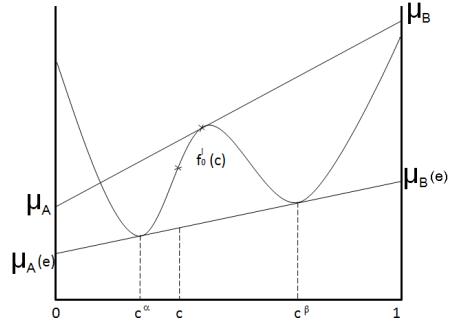


Figure 4.1

If one reduces $k'(\frac{\partial c}{\partial x})^2$ by making the interface broader it will be at the expense of incorporating more material at the interface, such that $\Delta f(c) \uparrow$ (goes up). On the other hand, reduction of material at the interface increases the gradient. A compromise between two terms gives an equilibrium interface.

Concept of variational derivative/(Derivation of the Euler -Lagrange equation).

$$\begin{aligned} F &= \int f(c, \nabla c) dV \\ F(c + \delta c) &= \int \left(f + \frac{\partial f}{\partial c} \cdot \delta c + \frac{\partial^2 f}{\partial \nabla c} \cdot \delta \nabla c \right) dV \\ F &= \int \left(\frac{\partial f}{\partial c} \cdot \delta c + \frac{\partial f}{\partial \nabla c} \cdot \delta \nabla c \right) dV \end{aligned}$$

Weak apporoximation $\delta \nabla c = \nabla \delta c$

$$\begin{aligned} \delta F &= \int \left[\frac{\partial f}{\partial c} \cdot \delta c + \frac{\partial f}{\partial \nabla c} \cdot \nabla \delta c \right] dV \\ &= \int_V \frac{\partial f}{\partial c} \cdot \delta c dV + \int_S \left(\frac{\partial f}{\partial \nabla c} \cdot \hat{n} \right) dS \delta c - \int \nabla \cdot \frac{\partial f}{\partial \nabla c} \delta c dV \\ \delta F &= \int_V \frac{\partial f}{\partial c} \cdot \delta c dV - \int_S \nabla \cdot \frac{\partial f}{\partial \nabla c} \delta c dV \end{aligned}$$

The above is obtained by choosing a surface over which the surface integral goes to zero, this is always possible.

' δc ' is a delta function around ' c ' where we compute the variation. Using the property of ' δ ' function

$$\int_{-\infty}^{\infty} f(x)\delta(x - x_0)dx = f(x_0)\delta x$$

$$\delta F = \left\{ \left(\frac{\partial f}{\partial c} \right)_{c_0} - \left(\nabla \cdot \frac{\partial f}{\partial \nabla c} \right) \right\} \delta c.$$

$$\boxed{\frac{\delta F}{\delta c} = \frac{\partial f}{\partial c} - \nabla \cdot \frac{\partial f}{\partial \nabla c}}$$

$$\boxed{\frac{\delta F}{\delta c} = \left[\frac{\partial}{\partial c} - \nabla \cdot \frac{\partial}{\partial \nabla c} \right] f}$$

we name this operator : - $\frac{\delta}{\delta c} = \left\{ \frac{\partial}{\partial c} - \nabla \cdot \frac{\partial}{\partial \nabla c} \right\}.$

Using this operator on,

$$\sigma = \int_x \left[\Delta f(c) + k' \left(\frac{\partial c}{\partial x} \right)^2 \right] dx.$$

$$\frac{\partial \Delta f}{\partial c} = 2k' \frac{\partial^2 c}{\partial x^2}.$$

$$\int \frac{\partial \Delta f}{\partial c} \cdot \frac{dc}{dx} = \int 2k' \frac{\partial^2 c}{\partial x^2} \cdot \frac{dc}{dx}.$$

$$\Delta f = k' \left(\frac{\partial c}{\partial x} \right)^2 + const.$$

$$\text{At } x = \pm\infty \left(\frac{\partial c}{\partial x} \right)^2 = 0 \text{ and } \Delta f = 0.$$

Therefore: const=0

$$\begin{aligned}
\sigma_V \quad \Delta f &= k' \left(\frac{\partial c}{\partial x} \right)^2 : -\text{Equipartition of energy} \\
\therefore \sigma &= \int_x \Delta f(c) + k' \left(\frac{\partial c}{\partial x} \right)^2 dx. \\
&= 2 \int_x k' \left(\frac{\partial c}{\partial x} \right)^2 dx. \\
&= 2 \int_x k' \left(\frac{\partial c}{\partial x} \right) \cdot \frac{\partial c}{\partial x} dx \equiv 2 \int_x k' \sqrt{\Delta f / k'} dc.
\end{aligned}$$

$$\boxed{\sigma = 2 \int_x \sqrt{k' \Delta f} dc.}$$

$$\begin{aligned}
\text{Also } \frac{\Delta f}{k'} &= \left(\frac{dc}{dx} \right)^2 \\
\sqrt{\Delta f / k'} &= \frac{dc}{dx} \\
dx &= \frac{dc}{\sqrt{\Delta f / k'}} \\
\int_o^\lambda x &= \int_{c_\alpha}^{c_\beta} \frac{dc \cdot \sqrt{k'}}{\sqrt{\Delta f}}.
\end{aligned}$$

$$\boxed{\lambda = \int_{c_\alpha}^{c_\beta} \frac{\sqrt{k'} \cdot dc}{\sqrt{\Delta f}}.}$$

λ is the interface width.

We see - ' λ ' is inversely proportional to

$$\int_{c_\alpha}^{c_\beta} \frac{dc}{\sqrt{\Delta f(c)}}$$

5 1.11.10

5.1 lecture 6

In the Cahn-Hilliard approach, the surface energy ‘ σ ’ is fixed by the form of the free energy. While this is true for certain systems, in general the surface excess is a property independent of the free energy parameters. Hence one would like to set this property independent of the bulk system. The way to do this, is to choose two fields. 1) denoting the volume fraction of a phase and the second 2) the mole fraction of the components. Let us say the volume fraction corresponding to a phase is ϕ . Then in a two-phase system, the second phase has volume fractions $(1-\phi)$. This system can have minimum of two components. We denote A,B, with mole fractions c_A and c_B such that $c_A + c_B = 1$ in each phase and we can denote the ‘concentration’ field in the system as ‘c’.

Following the same principles to write the energy of the system as the Cahn-Hilliard equation, we can write,

$$F = \int [f(c, \phi) + k_\phi |\nabla \phi|^2] dx.$$

Points to note:

- 1) We have chosen the energy functional to be independent of the gradient in the concentration. This is true for small concentration gradients and corresponding small gradient energy coefficients for the concentration field.
- 2) $k\phi$, is the gradient energy coefficient for the gradients in the order parameter ‘ ϕ ’. This can be tuned to set the right surface energies.
- 3) $f(c, \phi)$ can be broken down into: -

$$f_b(c, \phi) + w(\phi).$$

where $w(\phi)$ denotes an equivalent term to $\Delta f(c)$ in the Cahn-Hilliard equation.

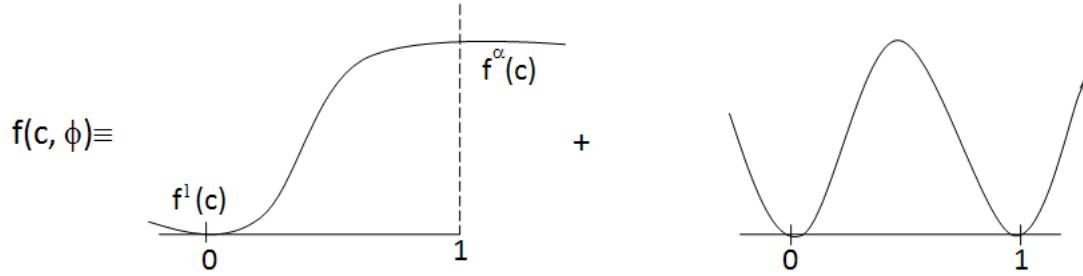


Figure 5.1

To define our surface energy we would need to define our energy of a uniform homogenous system; consisting of a mixture of two phases. This can be done similar to what we have encountered in the case of the Cahn-Hilliard equation.

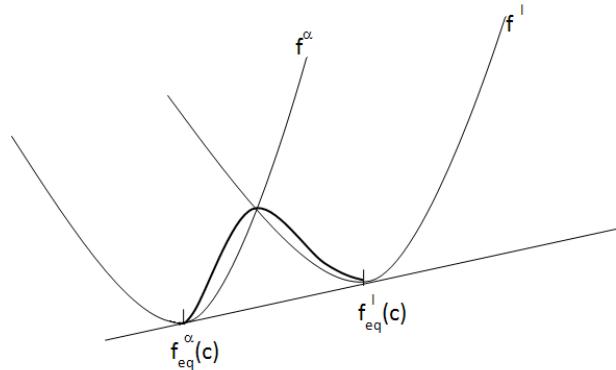


Figure 5.2

$$\therefore \Delta f(c, \phi) = f(c, \phi) - (f_{eq}^\alpha(c) + (1 - c)f_{eq}^l) + w(\phi).$$

Or alternatively in terms of the Grand Chemical potential or the partial molar Gibbs free energy of the system, we can write;

$$\Delta f(c, \phi) = f(c, \phi) - (\mu_A^{eq}c + \mu_B^{eq}(1 - c)) + w(\phi).$$

Then, the surface energy reduces to:

$$\sigma = \int_{-\infty}^{\infty} \{ [f(c, \phi) - (\mu_A^{eq}c + \mu_B^{eq}(1 - c))] + w(\phi) + k_\phi |\nabla \phi|^2 \} dx.$$

Notice, we have not lost the dependence of ‘ σ ’ on the free energy density of the phases. However, there exists now another tunable function $w(\phi)$ to get the surface energies that is representative of an interface.

The extremizer of the above function would be the Euler-Lagrange equations, we had for the Cahn-Hilliard equation.

$$\begin{aligned} \frac{\delta \sigma}{\delta \phi} &= \frac{\partial f(c, \phi)}{\partial \phi} + w'(\phi) - 2k_\phi \frac{d^2 \phi}{dx^2} = 0 \cdots (1) \\ \frac{\delta \sigma}{\delta c} &= \frac{\partial f}{\partial c} - (\mu_B - \mu_A) = 0. \\ \Rightarrow \frac{\partial f}{\partial c} &= (\mu_B - \mu_A) = \mu_{eq} \Rightarrow \text{chemical potential of the system.} \\ \frac{\partial f(\phi, c)}{\partial c} &= (\mu_B - \mu_A) \cdots (2). \end{aligned}$$

To integrate (ϕ) we need to write $(\frac{\partial f(c, \phi)}{\partial \phi})$ in terms of the total derivative of ‘ ϕ ’.

$$\begin{aligned} \frac{\partial f}{\partial \phi} &= \frac{df}{d\phi} - \frac{df}{dc} \cdot \frac{dc}{d\phi} \\ \text{From (2) the minimizing condition for } \frac{\partial f}{\partial c} &= (\mu_B - \mu_A) = \mu_{eq}. \\ \therefore \frac{\partial f}{\partial \phi} &= \frac{df}{d\phi} - \mu_{eq} \cdot \frac{dc}{d\phi} \Rightarrow \frac{d}{d\phi} (f - \mu c). \end{aligned}$$

Equation (1) becomes

$$\frac{d}{d\phi} (f - \mu c) + w'(\phi) - 2k_\phi \frac{d^2 \phi}{dx^2} = 0.$$

$$\frac{d}{d\phi} (f - \mu c) + w'(\phi) = 2k_\phi \frac{d^2 \phi}{dx^2}.$$

Multiplying $\left(\frac{d\phi}{dx} \right)$ on both sides.

$$2k_\phi \frac{d^2\phi}{dx^2} \frac{d\phi}{dx} = \frac{d}{d\phi}(f - \mu c) \cdot \frac{d\phi}{dx} + w'(\phi) \cdot \frac{d\phi}{dx}.$$

Integrate both sides.

$$k_\phi \left(\frac{d\phi}{dx} \right)^2 = (f - \mu c) - (f(0) - \mu c(0)) + w(\phi).$$

We denote $F(c, \phi) = (f - \mu c)$.

$$k_\phi \left(\frac{d\phi}{dx} \right)^2 = F(c, \phi) - F(c(0), 0) + w(\phi).$$

$$\left(\frac{d\phi}{dx} \right) = \frac{1}{\sqrt{k_\phi}} \sqrt{F(c, \phi) - F(c(0), 0) + w(\phi)}.$$

The surface energy ‘ σ ’ can then be derived using,

$$\begin{aligned} F(c, \phi) - F(c(0), 0) &= f(c, \phi) - (f(0) + \mu_{ep}c - \mu c(0)) \\ &= f(c, \phi) - (\mu_A^{eq}c + \mu_B^{eq}(1 - c)). \end{aligned}$$

$$\begin{aligned} \therefore \sigma &= 2 \int_{-\infty}^{\infty} k_\phi \left(\frac{d\phi}{dx} \right)^2 dx \equiv 2 \int_0^1 k_\phi \left(\frac{d\phi}{dx} \right) d\phi \\ &= 2 \int_0^1 k_\phi \cdot \frac{1}{\sqrt{k_\phi}} \sqrt{F(c, \phi) - F(c(0), 0) + w(\phi)} \cdot d\phi. \\ &= 2 \int_0^1 \sqrt{k_\phi} \sqrt{F(c, \phi) - F(c(0), 0) + w(\phi)} \cdot d\phi \cdots (3) \end{aligned}$$

The interface width can also be derived as;

$$\begin{aligned} \frac{d\phi}{dx} &= \frac{1}{\sqrt{k_\phi}} \sqrt{F(c, \phi) - F(c(0), 0) + w(\phi)}. \\ \int_0^1 \frac{\sqrt{k_\phi} d\phi}{\sqrt{F(c, \phi) - F(c(0), 0) + w(\phi)}} &= \lambda \cdots (4) \end{aligned}$$

Notice we can also use (2) to derive the equilibrium concentration profile.

$$\frac{\partial f}{\partial c}(\phi, c) = (\mu_B - \mu_A). \quad \text{Hence } c \text{ can be written as a function from ‘}\phi\text{’}.$$

In systems, where the free energy of the (phases) are closely related the term

$$F(c(\phi)) - F(c(0), 0)$$

is generally small, which implies equations (3) and (4) can be simplified to,

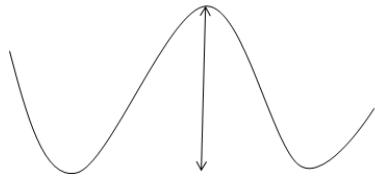


Figure 5.3

$$\begin{aligned}\sigma &= 2 \int_0^1 \sqrt{k_\phi} \sqrt{w(\phi)} \cdot d\phi \cdots (5) & \sigma \alpha \sqrt{k} \cdot \sqrt{w} \\ \lambda &= \int_0^1 \frac{\sqrt{k_\phi}}{\sqrt{w(\phi)}} \cdot d\phi \cdots (6) & \lambda \alpha \frac{\sqrt{k}}{\sqrt{w}} \\ && \sigma \lambda \alpha k_\phi \cdots (7) & k \alpha \sigma \lambda \\ && \sigma / \lambda \alpha w \cdots (8) & w \alpha \sigma / \lambda\end{aligned}$$

Therefore one can propose to write down F as;

$$F = \int_{\Omega} [f_b(c, \phi) + \sigma \lambda |\nabla \phi|^2 + \frac{\sigma}{\lambda} w(\phi)] d\Omega.$$

where $w(\phi)$ is dimensionless term.

We will use this formulation of the model throughout in our discussion.

Points to discuss:

1) what is the form of $w(\phi)$?

If we see (5) and (6) and use (7) and (8) we get;

$$\begin{aligned}\sigma &= 2 \sigma \int_0^1 \sqrt{w(\phi)} d\phi. \\ \therefore \text{we want } 2 \int_0^1 \sqrt{w(\phi)} d\phi &= 1.\end{aligned}$$

Possible constructions are;

$$w(\phi) = \frac{16}{\pi^2} \phi(1 - \phi) \quad (\text{Obstacle}) \quad \text{and} \quad 9\phi^2(1 - \phi)^2 \quad (\text{Double-well})$$

Integrate and verify the ansatz

Dynamics

We have two fields; c, ϕ in our system, while ' c ' is a conserved quantity, ' ϕ ' is non-conserved as we have transition from one phase to another.

The field ' c ' evolves through "gradient dynamics". This implies the driving force for flux is the gradient of a potential.

Conservation law for ' c ' can be writing down as

$$\frac{\partial c}{\partial t} = -\nabla \cdot J_e$$

From "irreversible thermodynamics" one can write down.

J_e ; as a result of a linear combination of driving forces in the system. the driving forces are the gradients of the intensive properties of the system.

$$J_e \alpha - L_0 \nabla(T) L_1 \nabla \left(\frac{\partial f}{\partial c} \right), \quad \frac{\partial f}{\partial c} \Rightarrow \text{chemical potential}$$

$$J_e \alpha - L_0 \nabla(T).$$

$$\therefore \boxed{\frac{\partial c}{\partial t} = \nabla \cdot \left(L_0 \nabla(T) + L_1 \nabla \left(\frac{\partial f}{\partial c} \right) \right) = \nabla \cdot \left(L_0 \nabla T + L_1 \nabla \left(\frac{\partial f}{\partial c} \right) \right)}$$

' L_0 ' represents the coupling between the temperature and concentration field. L_0, L_1 are mobility coefficients which denote velocity/(unit driviforce).

The system is uniform and stationary when there are no gradients in the system:

$$\nabla(T) = 0;$$

$$\nabla \left(\frac{\partial f}{\partial c} \right) = 0.$$

In general for a multi-component system;

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (L_{00} \nabla(T)) + \sum_j L_{ij} \nabla \left(\frac{\partial f}{\partial c_j} \right).$$

The field ‘ ϕ ’ has a dynamics based on a phenomenological minimization of energy,

$$\frac{\partial \phi}{\partial t} = -M \frac{\delta F}{\delta \phi}.$$