Phase transitions

Lectures in Physical Chemistry 4

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Phases

DEF a system is homogeneous, if
(1) it does not contain parts separated by macroscopic surfaces, and
(2) all intensive properties are identical in each point of the system

DEF a system is inhomogeneous, if it is not homogeneous

DEF a system is heterogeneous, if it contains phases

DEF phase: homogeneous part separated by macroscopic surfaces

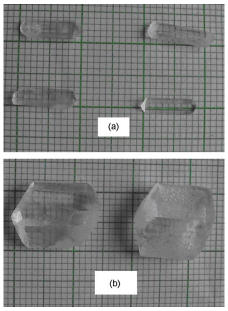
Examples for the phases of chemically pure species:

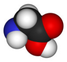
various physical states (solid, liquid, vapour)
allotropic forms (elements with different crystals): grey tin–white tin (Sn)
polimorfic forms (compounds with different crystals): calcite–aragonite ($CaCO_3$)

Phase equilibria

DEF phase equilibrium: equilibrium among the various phases of a pure species in a closed system.

melting equilibrium: solid–liquid equilibrium
evaporation equilibrium: liquid–vapour equilibrium
sublimation equilibrium: solid–vapour equilibrium



Allotropic transformations:
diamond–graphite (C), rhombic sulphur–monoclinic sulphur (S)
grey tin–white tin (Sn) [tin pest below 13.2 °C]
Polimorphic transformations:
calcite–aragonite ($CaCO_3$), glycin crystals ()

In equilibrium, the Gibbs free energy of the system is minimal at the given pressure and temperature (p, T, n constant)

In many cases it is not easy to check, therefore we will use another principle that is based on the molar Gibbs free energies.

equilibrium $\Leftrightarrow G_{m1} = G_{m2}$

two phases are in equilibrium (at p, T, n constant)

$\Rightarrow$ the molar Gibbs free energy of the species in the two phases are equal

otherwise the molecules of all species move to the phase having lower Gibbs free energy.

Proof (you do not have to know it on the test/exam):

phase 1: molar Gibbs free energy	G_{m1} ;	amount: n_1	„ice”
phase 2: molar Gibbs free energy	G_{m2} ;	amount: n_2	„water”

the total Gibbs free energy: $G = G_{m1}\ n_1 + G_{m2}\ n_2$
the change of G : $dG = G_{m1}\, dn_1 + G_{m2}\, dn_2$

if dn mole of phase 1 is converted to phase 2 (ice is melted)
$\Rightarrow dn_1 = -dn$ and $dn_2 = +dn$

the change of Gibbs free energy:
$dG = -G_{m1}\, dn + G_{m2}\, dn = dn\,(G_{m2} - G_{m1})$

dG negative (G decreases) if and only if $G_{m2} < G_{m1}$
If $G_{m2} = G_{m1}$ $\Rightarrow$ G does not change $\Rightarrow$ no phase transition

Clapeyron equation

There is equilibrium between two phases at pressure *p* and temperature *T*.
Small change of the state variables by d*p* and d*T* (see Lecture 3, p. 20)
⇒ new equilibrium ⇒ the molar Gibbs free energies will be equal again ⇒
the change of the molar Gibbs free energies is identical :

$dG_m = V_m dp - S_m dT$ and $dG_{m1} = dG_{m2}$

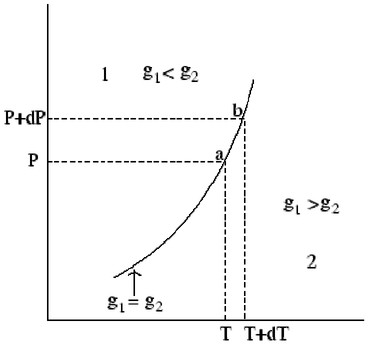
$\Rightarrow \quad V_{m1}dp - S_{m1}dT = V_{m2}dp - S_{m2}dT$

Rearranging this equation gives the
Clapeyron equation:

$$\frac{dp}{dT} = \frac{S_{m2} - S_{m1}}{V_{m2} - V_{m1}} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T\Delta V_m}$$

where $\Delta S_m = \Delta H_m / T$ and

ΔH_m molar enthalpy of phase change
(heat consumed or released at the phase change)

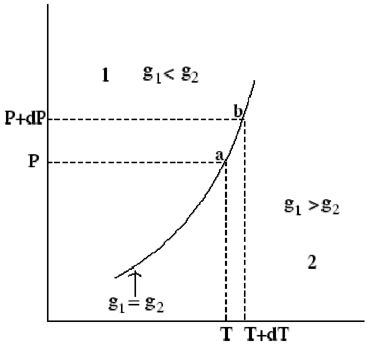


Clapeyron equation 2

$\Delta V_m = V_{m2} - V_{m1}$
$\Delta H_m = H_{m2} - H_{m1}$
$\Delta S_m = S_{m2} - S_{m1}$

the change of
extensive quantities
V, *H*, *S*
at phase change.

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T\Delta V_m}$$



Benoît Paul Émile Clapeyron
(1799 – 1864)
French engineer

Clapeyron equation 3

the integrated form of the Clapeyron equation:
if $\Delta H_m / \Delta V_m$ does not change with temperature

$$p_2 - p_1 = \frac{\Delta H_m}{\Delta V_m} \ln \frac{T_2}{T_1}.$$

The case of water:

Melting always requires heat: $\Delta H_m > 0$

<u>For water</u> the change of volume: $\Delta V_m < 0$

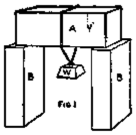
$\Rightarrow dp/dT < 0$

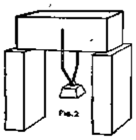
$\Rightarrow$ increasing pressure ($dp > 0$), the melting point decreases ($dT < 0$).

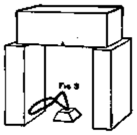
$$\frac{dp}{dT} = \frac{\Delta H_m}{T \Delta V_m}$$

Nice experiment:

Heavy weights on a thin wire:
the wire cuts the block of ice,
but ice is restored above the wire.
below the wire high pressure
the melting point of water lowered, the ice is melted
above the wire 1 atm pressure again, the melting point of water is 0 °C again, the water freezes.







Clausius–Clapeyron equation

Calculate the volume change at the evaporation of 1 mole water:
n= 1 mol water $\Rightarrow$ m= 18 g water
$\Rightarrow V_{liquid}$= 18 cm^3 $\Rightarrow V_{vapour}$ = 22000 cm^3
ΔV_m=22000-18 cm^3 = 21982 cm^3 ≈ 22000 cm^3 (ΔV_m= -0.08 %)

Two simplifying assumptions to the Clapeyron equation:

(1) the molar volume of the condensed phase (solid or liquid) is negligible compared to the molar volume of the vapour.
$\Delta V_m = V_{2m}$

(2) the molar volume of the vapour is calculated using the ideal gas law:

$$\Delta V_m \approx V_{2m} = RT/p$$

the <u>Clausius–Clapeyron equation is obtained</u>

$$\frac{1}{p}\frac{dp}{dT} = \frac{\Delta H_{vap}}{RT^2} \quad \text{rearranging:} \quad \frac{d \ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

R. J. E. Clausius
(1822 –1888)
German physicist

B. P. É. Clapeyron
(1799 – 1864)
French engineer

Boiling point

DEF boiling point: at this temperature the vapour pressure in the bubbles inside the liquid is equal to the external pressure.

DEF normal boiling point: boiling temperature at external pressure 1 atm (1 atm = 101325 Pa), (for water: 100.0 °C)

DEF standard boiling point: boiling temperature at external pressure 1 bar (1 bar = 100000 Pa), (for water: 99.6 °C)

DEF melting point: at this temperature the solid and the liquid phases are in equilibrium at a given pressure

DEF normal melting point: melting temperature at external pressure 1 atm

DEF standard melting point: melting temperature at external pressure 1 bar

DEF triple point:

1. melting temperature at its own vapour pressure
2. temperature and pressure, where the solid, liquid and vapour phases of a compound are in equilibrium

for water	273.16 K (+0.01 °C)	and 6.11×10^{-3} bar
for CO_2	216.8 K (-56.4 °C)	and 5.11 bar

Change of boiling point with pressure

If the molar evaporation enthalpy $\Delta H_{vap} > 0$ does not change with temperature, then the integrated form:

$$\ln\frac{p_2}{p_1} = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Application of the Clausius-Clapeyron equation:
the boiling point is known at one temperature and we should like to calculate it at another temperature.

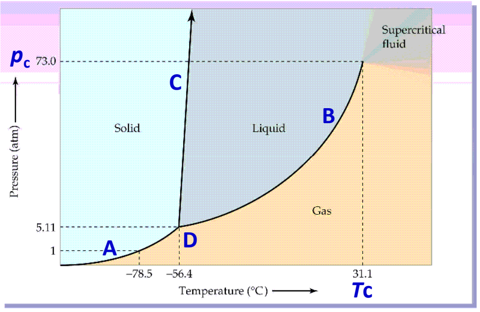
The evaporation enthalpy is always negative, therefore
- higher pressure – higher boiling point
- lower pressure – lower boiling point

distillation of a temperature sensitive compound at low temperature: pressure has to be decreased
⇒ vacuum distillation, rotary evaporator („rotavap”)

cooking at high temperature:
water has high boiling point at high pressure
⇒ pressure cooker

Phase diagram of CO_2

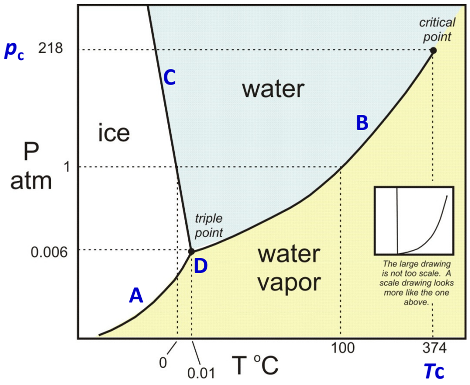
DEF Phase diagram of a substance shows the regions of temperature and pressure at which its phases are thermodynamically stable.



A: sublimation curve; **B**: tension curve; **C**: melting point curve; **D**: triple point; T_c: critical temperature; p_c: critical pressure.

p/atm	T/K	t/°C	comment
1.0	194.7	-78.5	atmospheric pressure
5.11	216.8	-56.3	triple point
67.0	298.15	25.0	room temperature
72.9	304.2	31.0	critical point

Phase diagram of H_2O

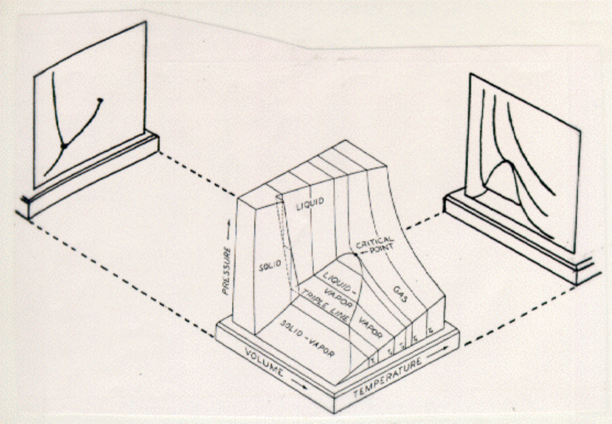


A: sublimation curve; **B**: tension curve; **C**: melting point curve; **D**: triple point; T_c: critical temperature; p_c: critical pressure.

p/atm	T/K	t/°C	comment
1.0	373.15	100.0	atmospheric pressure
0.006	273.16	0.01	triple point
0.032	298.15	25.0	room temperature
217.5	647.15	374.0	critical point

Phase diagram 3D

Phase diagram of the previous slides:
(T, p changes, V_m, n is fixed)



Phase diagram learned at the real gases:
(V_m, p changes T, n is fixed)

... and this is the 3D version
(V_m, T, p changes, n is fixed)

Gibbs' phase rule

DEF number of degrees of freedom F: the number of intensive properties that can be changed independently from each other without changing the number of phases (also called: variance of the system)

within the areas of the phases, p and T can be changed: $F = 2$

along curves A, B and C: $F = 1$ in triple point D: $F = 0$

Gibbs' phase rule: $\boldsymbol{F + P = C + 2}$

P	number of phases.
C	number of components

For pure compounds C = 1, therefore

degrees of freedom	$P = 3 - F$
within the areas of phases	$P = 1$
along curves A, B, and C	$P = 2$
in triple point D	$P = 3$

Josiah Willard Gibbs
(1839–1903)
USA physicist

The phase rule is applicable also for reactive systems.

THE END

of topic

phase transitions