

Properties of the Gibbs energy

$$G = H - TS$$



$$dG = dH - TdS - SdT$$



$$dG = dU + pdV + Vdp - TdS - SdT$$



$$dG = TdS - pdV + pdV + Vdp - TdS - SdT$$



$$dG = Vdp - SdT \longrightarrow G = f(p, T)$$

$$H = U + pV$$



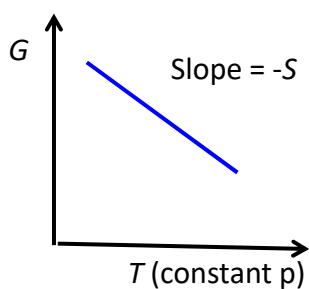
$$dH = dU + pdV + Vdp$$

$$dU = TdS - pdV$$

Properties of the Gibbs energy

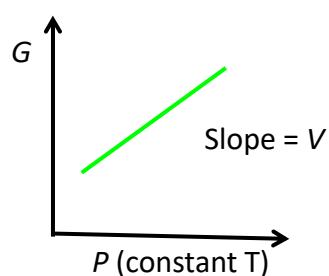
$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial T} \right)_p = -S$$



S is positive ($-S$ is negative) so
 G is **decreasing** with
 increasing T

$$\left(\frac{\partial G}{\partial p} \right)_T = V$$



V is positive so
 G is **increasing** with
 increasing p

Dependence of G on T

Using the same procedure
as for the dependence of
 G on p we get:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$



$$\int dG = -\int SdT$$

To go any further we need S as a function of T

Instead we start with: $G = H - TS$



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

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Dependence of G on T

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \rightarrow \int dG = -\int SdT$$

To go any further we need S as a function of T

$$-S = \frac{G - H}{T}$$



$$\frac{G}{T} = \frac{H}{T} - S$$



$$x = \frac{H}{T} - S$$

Let $x = \frac{G}{T}$



$$\left(\frac{\partial x}{\partial T}\right)_p = -\frac{H}{T^2}$$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$$

Gibbs-Helmholtz Equation

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$$

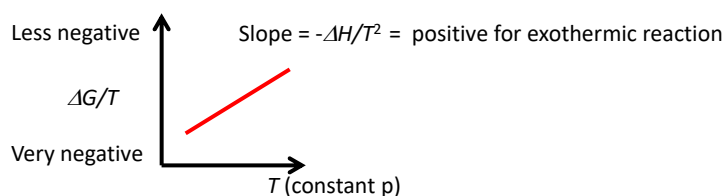
Dependence of G on T

$$\left(\frac{\partial \Delta G}{\partial T} \right)_p = -\Delta S \qquad \left(\frac{\partial (\Delta G / T)}{\partial T} \right)_p = -\frac{\Delta H}{T^2}$$

Gibbs-Helmholtz Equation

Changes in entropy or, more commonly, changes in enthalpy can be used to show how changes in the Gibbs energy vary with T

For a spontaneous ($\Delta G < 0$) exothermic reaction ($\Delta H < 0$) the change in Gibbs energy increases with increasing temperature.



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Dependence of G on p

It would be useful to determine the Gibbs energy at one pressure knowing its value at a different pressure.

$$dG = Vdp - SdT$$

We set $dT = 0$ and integrate:

$$\int_{G_i}^{G_f} dG = \int_{p_i}^{p_f} Vdp$$

$$\Delta G = \int_{p_i}^{p_f} Vdp$$

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} Vdp$$

Dependence of G on p

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$$

For gases V cannot be considered a constant with respect to pressure.

For a perfect gas:

$$\begin{aligned} G(p_f) &= G(p_i) + nRT \int_{p_i}^{p_f} \frac{dp}{p} \\ &= G(p_i) + nRT \ln \frac{p_f}{p_i} \end{aligned}$$

We can set p_i to equal the standard pressure, p^θ ($= 1$ bar).

Then the Gibbs energy at a pressure p is related to its standard Gibbs energy, G^θ

$$G(p_f) = G^\theta + nRT \ln \frac{p_f}{p^\theta}$$

Dependence of G on p

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$$

Liquids and Solids

Only slight changes of volume with pressure mean that we can effectively treat V as a constant.

$$G(p_f) = G(p_i) + V\Delta p$$

$$G(p_f) = G(p_i) + V(p_f - p_i)$$

Often $V \Delta p$ is very small and may be neglected i.e. G for solids and liquids under normal conditions is independent of p .

Variation of Gibbs Free Energy

- Fundamental equation of chemical thermodynamics

$$dG = -SdT + Vdp$$

where $\left(\frac{\partial G}{\partial T}\right)_p = -S$ and $\left(\frac{\partial G}{\partial p}\right)_T = V$

- Variation of G with T

$$\triangleright \left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T}$$

$$\triangleright \left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2} \quad \text{Gibbs-Helmholtz equation}$$

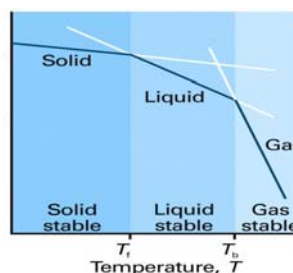
Variation of Gibbs Free Energy

- Variation of G with T

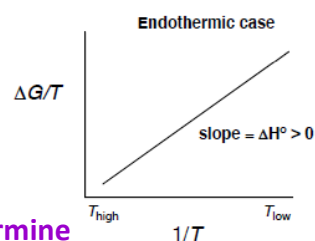
$$\triangleright \left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T}$$

$$\triangleright \left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2}$$

Gibbs-Helmholtz equation



$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$	$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_p = H$
$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$	$\left(\frac{\partial(\Delta G/T)}{\partial(1/T)}\right)_p = \Delta H$



If we know ΔH of a process, we can determine how $\Delta G/T$ varies with T .

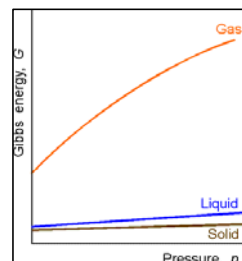
Variation of Gibbs Free Energy

- Variation of G with pressure p

$$dG = -SdT + Vdp$$

For an **isothermal** process, $\int_i^f dG = \int_i^f Vdp$

$$\therefore G(T, p_f) = G(T, p_i) + \int_i^f Vdp$$



For 1 mole of the substance, $G_m(T, p_f) = G_m(T, p_i) + \int_i^f V_m dp$

➤ In the condensed phase $G_m(T, p_f) = G_m(T, p_i) + (p_f - p_i)V_m$

➤ For an Ideal gas

$$G_m(T, p_f) = G_m(T, p_i) + RT \int_{p_i}^{p_f} \frac{dp}{p}$$

$$G_m(T, p_f) = G_m(T, p_i) + RT \ln \left(\frac{p_f}{p_i} \right)$$

Variation of Gibbs Free Energy

$$\left(\frac{\partial G}{\partial T} \right)_p = -S$$

$$\left(\frac{\partial G}{\partial p} \right)_T = V$$

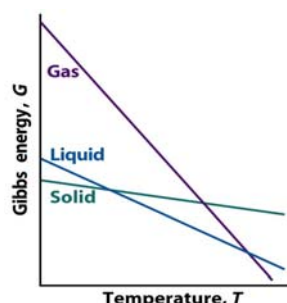
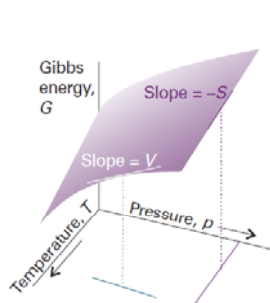


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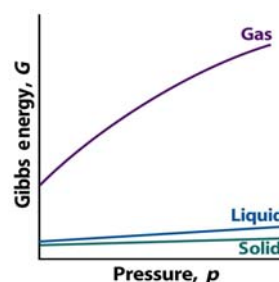


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Phase equilibria and chemical reaction equilibria

Limitations of the Fundamental Equation of Chemical Thermodynamics

$$dG = -SdT + Vdp$$

This equation is not applicable when

- system composition is changing due to **exchange of matter with surroundings** (open system)
- an **irreversible chemical reaction** takes place
- an **irreversible inter-phase transport of matter** takes place

Thermodynamics of Open Systems

Limitations of the Fundamental Equation of Chemical Thermodynamics

$$dG = Vdp - SdT$$

Does not apply

- When composition is changing due to exchange of matter with surroundings (open system)
- Irreversible chemical reaction
- Irreversible inter-phase transport of matter

For one phase and multi-component system, in thermal and mechanical equilibrium but not in material equilibrium,

$$G = f(T, p, n_1, n_2, \dots),$$

$$dG = Vdp - SdT$$

For one phase and multi-component system, in thermal and mechanical equilibrium but not in material equilibrium,

$$G = f(T, p, n_1, n_2, \dots),$$

$$(T, p, n_1, n_2, \dots) \xrightarrow{\text{Irreversible}} (T+dT, p+dp, n_1+dn_1, n_2+dn_2, \dots)$$

$$dG = \left(\frac{\partial G}{\partial p} \right)_{T, n_i} dp + \left(\frac{\partial G}{\partial T} \right)_{p, n_i} dT + \left(\frac{\partial G}{\partial n_1} \right)_{T, p, n_j \neq n_1} dn_1 + \dots + \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j \neq n_i} dn_i$$

$$dG = Vdp - SdT + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j \neq n_i} dn_i$$

G is state function, dG is same if the process was reversible

Response of system to change in number of particles

- Internal energy for an open system $U = U(S, V, n_1, n_2, \dots, n_M)$

For an exact differential of the state function U ,

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \sum_{i=1}^M \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j \neq i}} dn_i$$

$$dU = T dS - p dV + \sum_{i=1}^M \mu_i dn_i$$

where chemical potential of the i -th component is defined as

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j \neq i}}$$

General Definition of Chemical Potential

- Chemical potential, μ_i is the rate of change of the thermodynamic potential with respect to change in number of particles, n_i of type i ($i=1, M$)

$$\begin{aligned} dU &= T dS - p dV + \sum_{i=1}^M \mu_i dn_i & \Rightarrow \mu_i &= \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j \neq i}} \\ dH &= T dS + V dp + \sum_{i=1}^M \mu_i dn_i & \Rightarrow \mu_i &= \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j \neq i}} \\ dA &= -S dT - p dV + \sum_{i=1}^M \mu_i dn_i & \Rightarrow \mu_i &= \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j \neq i}} \\ dG &= -S dT + V dp + \sum_{i=1}^M \mu_i dn_i & \Rightarrow \mu_i &= \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j \neq i}} \end{aligned}$$

Chemical Potential of a Pure Substance

- Let us consider n moles of a pure substance at a temperature T and pressure p
- By definition, the Gibbs free energy of this system is

$$G(T, p, n) = n G_m(T, p)$$

where G_m is the molar Gibbs free energy

- Chemical potential

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,p} = G_m$$

Chemical Potential of an Ideal Gas

For n moles of an ideal gas present at temperature T and pressure p

$$G = G^0 + nRT \ln \left(\frac{p}{p^0} \right)$$

$$\mu = \mu^0 + RT \ln \left(\frac{p}{p^0} \right)$$

Chemical Potential in a Mixture of M Ideal Gases

Assumption: The mixture behaves ideally at a temperature T and pressure p

x_i mole fraction of the i -th component ($i = 1, M$)

$p_i = x_i P$ partial pressure

The chemical potential of the i -component

$$\mu_i = \mu_i^0 + RT \ln \left(\frac{p_i}{p^0} \right) = \mu_i^0 + RT \ln \left(\frac{x_i p}{p^0} \right)$$

$$\mu_i = \mu_i^0 + RT \ln \left(\frac{p}{p^0} \right) + RT \ln x_i$$

$$\mu_i(T, p) = \mu_i^*(T, p) + RT \ln x_i$$

Chemical potential of i -th component in its pure phase

Property of Chemical Potential

At a given temperature T and pressure p ,

$$\mu_i(T, p) = \mu_i^*(T, p) + RT \ln x_i$$

Since $x_i < 1$,

$\mu_i(T, p)$ in the mixture $< \mu_i(T, p)$ in the pure phase

Property of Chemical Potential

$$dG = Vdp - SdT + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}} dn_i$$

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

$$\mu_i = f(T, p, n_1, n_2, \dots)$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p, T, n_{j \neq i}}$$

Applicable to single phase, multi component system at thermal and mechanical equilibrium but *not* material equilibrium.

$$dG_{p, T} = \sum_i \mu_i dn_i$$

$$dw_{\text{add, max}} = \sum_i \mu_i dn_i$$

For pure substance

$$\mu \text{ (Chemical Potential)} = G_m = G/n$$

Maximum additional work that can arise from changing the components of the system.

Fundamental Equations of Thermodynamics or Gibbs Equations - Revisited

$$dU = TdS - pdV + \sum_{i=1}^n \mu_i dn_i \text{ where, } \mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}}$$

$$dH = TdS + Vdp + \sum_{i=1}^n \mu_i dn_i \text{ where, } \mu_i = \left(\frac{\partial H}{\partial n_i} \right)_{S, p, n_{j \neq i}}$$

$$dA = -SdT - pdV + \sum_{i=1}^n \mu_i dn_i \text{ where, } \mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_{j \neq i}}$$

$$dG = -SdT + Vdp + \sum_{i=1}^n \mu_i dn_i \text{ where, } \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}}$$

Applicable to single phase multi-component open system in thermal and mechanical equilibrium and pV work only.

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} = \left(\frac{\partial H}{\partial n_i} \right)_{S, p, n_{j \neq i}} = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_{j \neq i}} = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}}$$

Multi-phase Multi-Component System

$$dG^\alpha = V^\alpha dp - S^\alpha dT + \sum_i \mu_i^\alpha dn_i^\alpha$$

For one phase (α) system,
in thermal and mechanical
equilibrium pV work only

For multiple phases

$$dG = \sum_\alpha dG^\alpha = \sum_\alpha V^\alpha dp - \sum_\alpha S^\alpha dT + \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha$$

$$\mu_i^\alpha = \left(\frac{\partial G^\alpha}{\partial n_i^\alpha} \right)_{p, T, n_{j \neq i}^\alpha}$$

Since, S and V are extensive properties,

$$dG = Vdp - SdT + \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha$$

Thermal and mechanical
equilibrium. p - V work only

Material Equilibrium

$$dG = Vdp - SdT + \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha$$

For a liquid and vapour mixture of water and acetone,

$$dG = Vdp - SdT + \mu_w^v dn_w^v + \mu_{ac}^v dn_{ac}^v + \mu_w^l dn_w^l + \mu_{ac}^l dn_{ac}^l$$

$$dG_{p,T} = \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha$$

Thermal and mechanical equilibrium
and constant T and p . p - V work only

At complete equilibrium (thermal, mechanical, and material) at
constant T and p , pV work only, $dG = 0$.

$$\sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha = 0$$

Chemical Potential and Phase Equilibrium



$$dG^A = \mu_{i,A}(-dn_i) \text{ and } dG^B = \mu_{i,B}dn_i$$

$$dG = dG^A + dG^B = (\mu_{i,B} - \mu_{i,A})dn_i$$

Change taking place at constant T, p

If $\mu_{i,A} > \mu_{i,B}$, then $dG < 0$

If $\mu_{i,A} < \mu_{i,B}$, then $dG > 0$

If $\mu_{i,A} = \mu_{i,B}$, then $dG = 0$

• Spontaneous transport of i from phase A to phase B

• Spontaneous transport of i from phase B to phase A

• Phase Equilibrium

Substance i flows spontaneously from a phase with higher chemical potential to a phase with lower chemical potential

Spontaneous transfer of matter occurs from region of high to low μ

At equilibrium the chemical potential μ is the same everywhere

Gibbs-Duhem Equation

$$G_{p,T} = n_1\mu_1 + n_2\mu_2 + \cdots = \sum_i n_i\mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i$$

At constant p and T

At thermal and mechanical equilibrium.

$$\sum_i n_i d\mu_i = 0$$

Gibbs-Duhem Equation

For a binary mixture, $n_1 d\mu_1 + n_2 d\mu_2 = 0$

Hence, $d\mu_1 = -(n_2/n_1) d\mu_2$

If $n_2 > n_1$, a small change in μ_2 causes a large change in μ_1

Chemical potential of one component of a mixture cannot change independently of the chemical potentials of other components.

Phase Stability and Equilibrium

- Stability of phase of a pure substance as function of temperature and pressure
- Phase equilibrium as function of temperature and pressure

Chemical Potential and Phase Equilibrium

Chemical potential for a component in a mixture: $\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_j}$

μ (Chemical Potential) for pure substance = $G_m = G/n$

Chemical potential for substance in the phases that are in equilibrium

$$\mu_i^\alpha(p, T) = \mu_i^\beta(p, T)$$

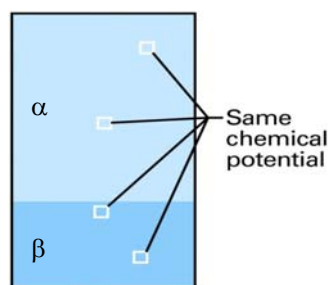


Figure 9.8
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At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.

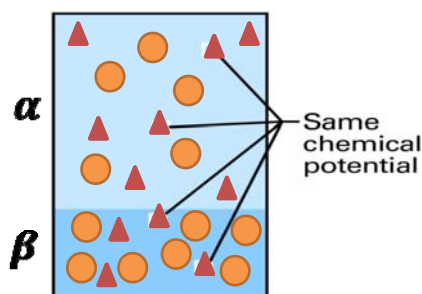
Chemical Potential and Phase Equilibrium

Chemical Potential of the *i*-th component in a mixture

$$\mu_i(T, p) = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}}$$

Chemical potential of the *i*-th component in a mixture in the phases that are in equilibrium

$$\mu_i^\alpha(T, p) = \mu_i^\beta(T, p)$$



At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases and how many components are present.

Phase Stability in a Pure Substance

$$dG = -SdT + Vdp$$

$$d\mu = -S_m dT + V_m dp$$

$$\mu = \mu(T, p)$$

Temperature dependence of phase stability

$$\left(\frac{\partial \mu}{\partial T} \right)_p = -S_m$$

$$S_m(\text{solid}) < S_m(\text{liquid}) \ll S_m(\text{gas})$$

At the melting point $T = T_f$

$$\mu_{\text{solid}} = \mu_{\text{liquid}}$$

At the boiling point $T = T_b$

$$\mu_{\text{liquid}} = \mu_{\text{gas}}$$

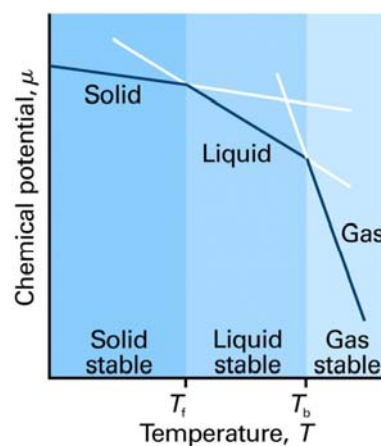
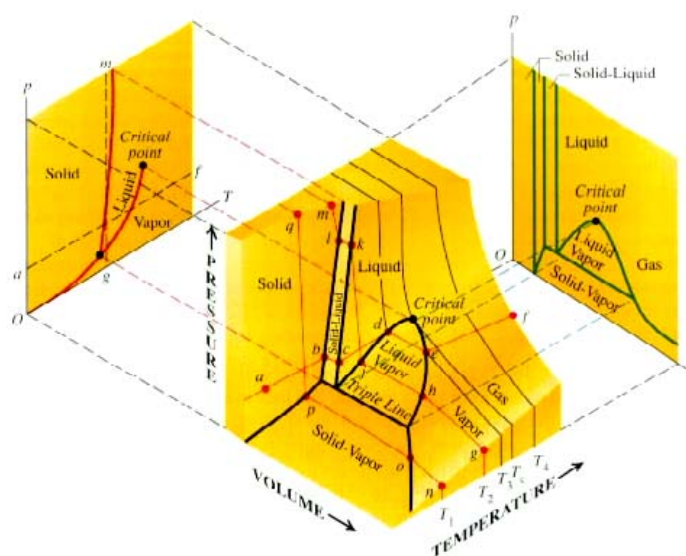


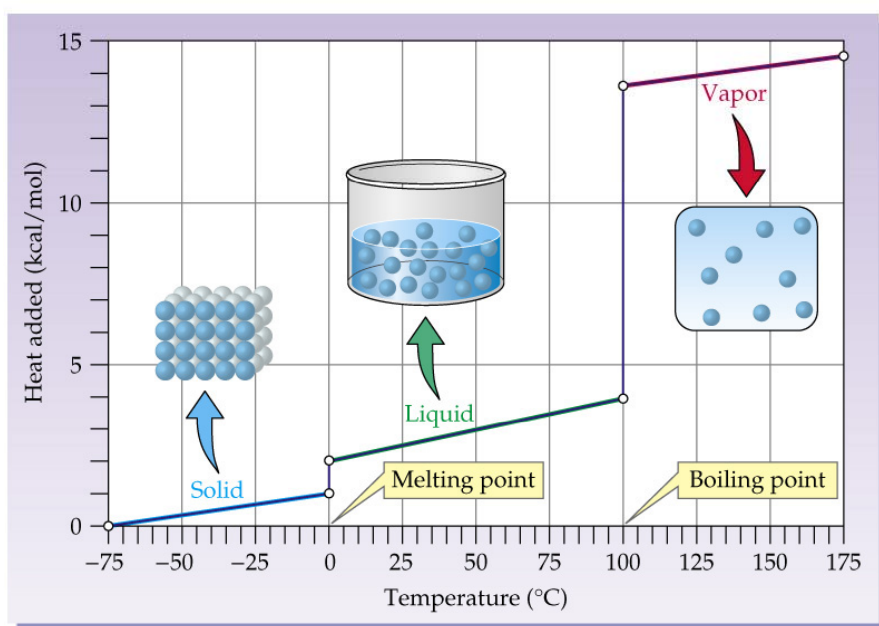
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Three Dimensional Phase Diagram



(courtesy F. Remer)

Heating Curve



Phase Stability in a Pure Substance

$$dG = -SdT + Vdp$$

$$d\mu = -S_m dT + V_m dp$$

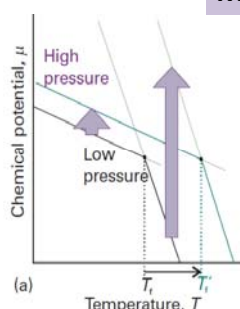
$$\mu = \mu(T, p)$$

Pressure dependence
of phase stability

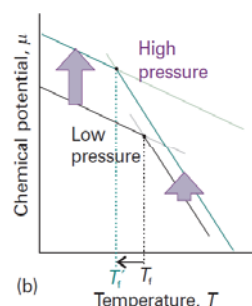
$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

$$V_m(\text{solid}) < V_m(\text{liquid}) \ll V_m(\text{gas})$$

Melting of solid



Melting point increases with pressure when $V_m(s) < V_m(l)$



Melting point decreases with pressure when $V_m(s) > V_m(l)$

Decrease in Melting Point of Ice on Increasing Pressure

Effect of pressure on the chemical potential of ice/water if the pressure is raised from 1.0 bar to 2.0 bar at 273 K.

$$\Delta\mu_T = V_m \Delta p = \frac{M}{\rho} \Delta p \quad M = 1.802 \times 10^{-2} \text{ kg mol}^{-1}$$

$$\Delta p = 1.0 \text{ bar} = 10^5 \text{ J m}^{-3}$$

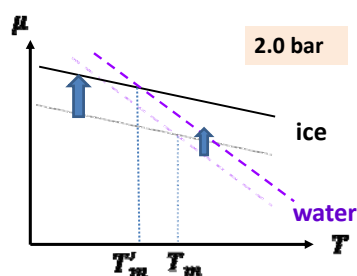
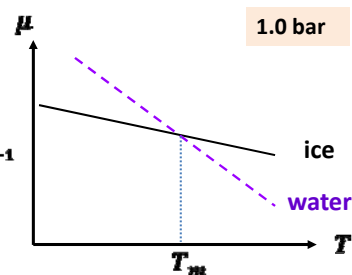
Ice
(density, $\rho_{\text{ice}} = 0.917 \times 10^3 \text{ kg m}^{-3}$)

$$\Delta\mu_{\text{ice}} = +1.97 \text{ J mol}^{-1}$$

Water
(density, $\rho_{\text{water}} = 0.999 \times 10^3 \text{ kg m}^{-3}$)

$$\Delta\mu_{\text{water}} = +1.80 \text{ J mol}^{-1}$$

Water is more stable at $T = T_m$ at 2.0 bar



Phase Stability in a Pure Substance

Pressure dependence of phase stability

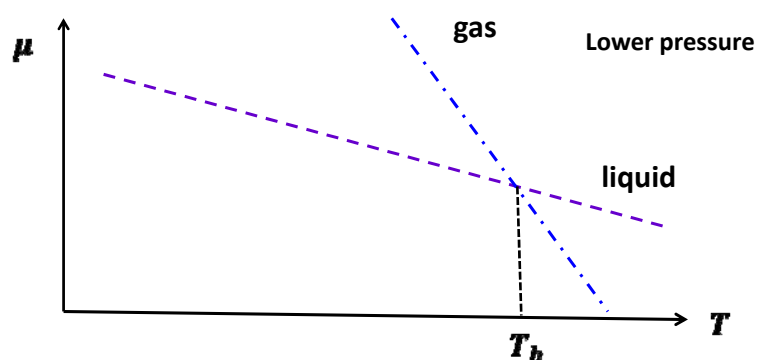
$$d\mu = -S_m dT + V_m dp$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

$$V_m(\text{solid}) < V_m(\text{liquid}) \ll V_m(\text{gas})$$

Vaporization:

$V_m(g) \gg V_m(l)$ resulting in a large decrease in T_b



Phase Stability in a Pure Substance

Pressure dependence of phase stability

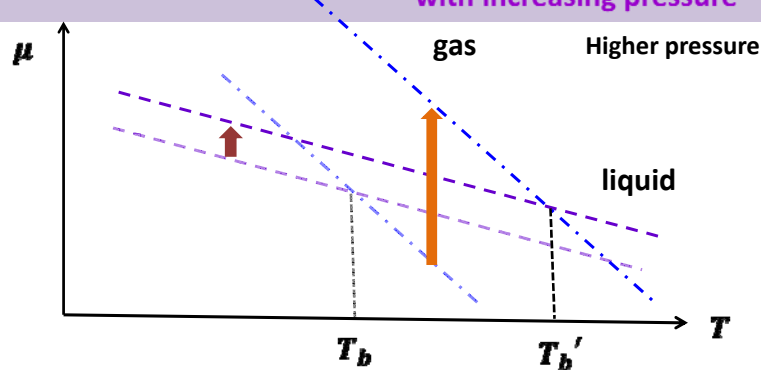
$$d\mu = -S_m dT + V_m dp$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

$$V_m(\text{solid}) < V_m(\text{liquid}) \ll V_m(\text{gas})$$

Vaporization:

$V_m(g) \gg V_m(l)$ resulting in a large increase in T_b with increasing pressure



Phase Stability in a Pure Substance

Pressure dependence of phase stability

$$d\mu = -S_m dT + V_m dp$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

$$V_m(\text{solid}) < V_m(\text{liquid}) \ll V_m(\text{gas})$$

Vaporization: $V_m(g) \gg V_m(l)$

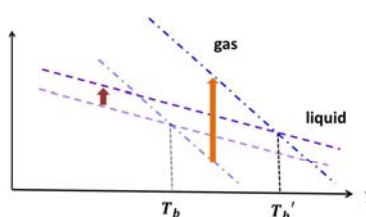
resulting in a large increase in T_b with increasing pressure

Liquid water (density, $\rho_{\text{water}} \approx 962 \text{ kg m}^{-3}$)

$$\Delta\mu_{\text{water}} = +1.87 \text{ J mol}^{-1}$$

Water vapor (density, $\rho_{\text{vap}} \approx 590 \text{ kg m}^{-3}$)

$$\Delta\mu_{\text{vapor}} = +3.05 \text{ J mol}^{-1}$$



At 373 K, 1.0 bar \rightarrow 2.0 bar

Liquid water remains as the more stable phase for higher pressure at 373 K

Application to Real World Problems

Melting point decreases with pressure when $V_m(s) > V_m(l)$

Ice and water



Skiing on ice surface

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