

# 2106NSC

# Physical & Analytical Chemistry

# Thermodynamics 8

## Thermodynamic aspects of phase transitions

# Temperature dependence of phase stability

$$\left(\frac{\delta G_m}{\delta T}\right)_p = \left(\frac{\delta \mu}{\delta T}\right)_p = -S_m \quad \text{cf. Thermodynamics 4}$$

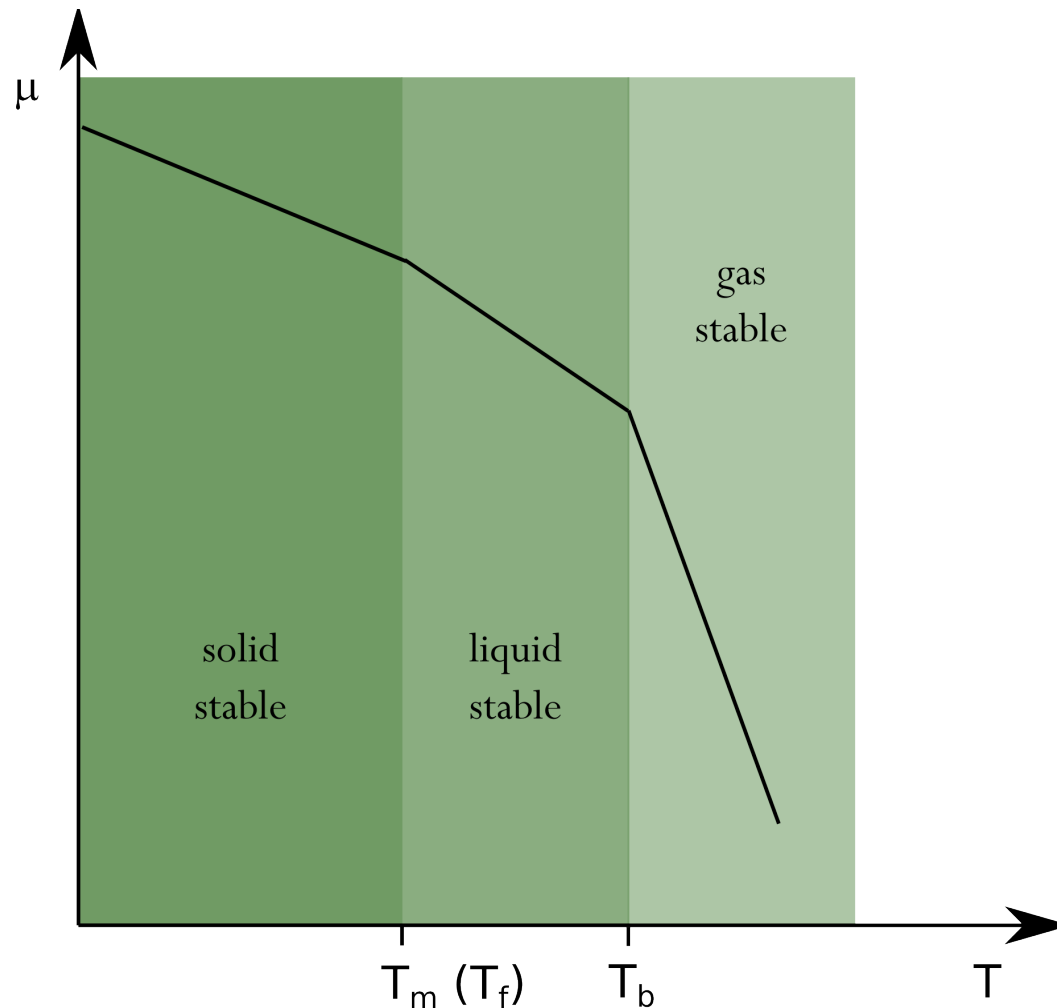
The molar entropy of a substance  $S_m$  is always positive.

Therefore, the change of the chemical potential  $\mu$  with increasing temperature at constant pressure is always negative.

The entropy is larger for gases than for liquids. Thus, the change in  $\mu$  is larger for gases than for liquids.

$S_m$  is generally larger for liquids than for solids.

# Temperature dependence of phase stability



The phase with the lowest chemical potential at a particular temperature is the most stable one (for that temperature).

The transition temperatures ( $T_m/T_f$  and  $T_b$ ) are the temperatures, at which the chemical potentials of the two interfacing phases are equal => equilibrium.

# Pressure dependence of melting

$$\left(\frac{\delta G_m}{\delta p}\right)_T = \left(\frac{\delta \mu}{\delta p}\right)_T = V_m \quad \text{cf. Thermodynamics 4}$$

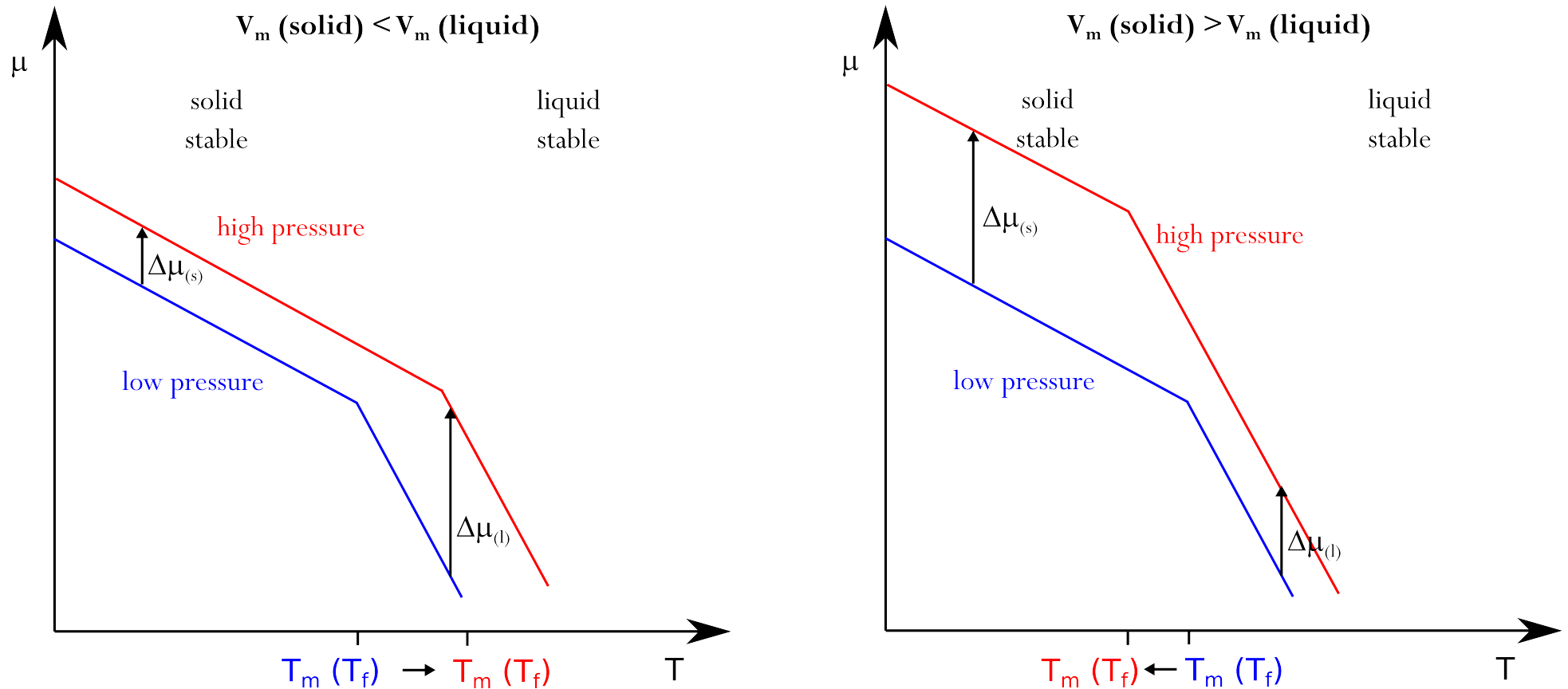
The molar volume  $V_m$  is always positive.

Therefore, the change of the chemical potential  $\mu$  with increasing pressure at constant temperature is always positive.

$V_m$  is generally larger for liquids than for solids (exception: water).

$T_f/T_m$  is generally larger at higher pressures (exception: water).

# Pressure dependence of melting



Left: If the molar volume  $V_m$  of the solid is smaller than that of the liquid, the chemical potential of the solid phase  $\mu_s$  increases less than the chemical potential of the liquid phase  $\mu_l$  when the pressure is increased. This results in an increase in the melting temperature  $T_m$ .

# Pressure dependence of vapour pressure

The vapour pressure rises with the pressure on the system:

$$p = p^* \cdot e^{\frac{V_m \cdot \Delta p}{R \cdot T}}$$

This equation can be obtained by using the fact that

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

and equating the change in differential of the chemical potential for the liquid and gas. We also assume an ideal gas.

**=> The vapour pressure will be less in an evacuated system than in one that contains ambient atmosphere.**

# Phase boundaries

Phase boundaries are  $p$ - $T$  lines where two phases  $\alpha$  and  $\beta$  coexist.

The boundaries are best discussed in terms of their slopes, i.e.  $(dp/dT)$ .

Due to co-existence of the two phases, there must be equilibrium and the changes in their chemical potentials must be equal:

$$d\mu_{\alpha}(p, T) = d\mu_{\beta}(p, T)$$

We know that  $d\mu = dG_m = V_m \cdot dp - S_m \cdot dT$  cf. **Thermodynamics 4**

Therefore:  $V_{m\alpha} \cdot dp - S_{m\alpha} \cdot dT = V_{m\beta} \cdot dp - S_{m\beta} \cdot dT$

$$(S_{m\beta} - S_{m\alpha}) \cdot dT = (V_{m\beta} - V_{m\alpha}) \cdot dp$$

$$\Delta S_{m,\text{trans}} / \Delta V_{m,\text{trans}} = dp / dT$$

**Clapeyron equation**



# Phase boundaries: solid – liquid

The Clapeyron equation for the fusion (melting) process:

$$\frac{d p}{d T} = \frac{\Delta S_{m, \text{fusion}}}{\Delta V_{m, \text{fusion}}} = \frac{\Delta H_{m, \text{fusion}}}{T_m \cdot \Delta V_{m, \text{fusion}}} \quad (\text{d}S = \text{d}H / T; \text{ cf. } \mathbf{\textit{Thermodynamics 3}})$$

$\Delta H_{m, \text{fusion}} = H_{m, \text{liquid}} - H_{m, \text{solid}}$  is generally positive

$\Delta V_{m, \text{fusion}} = V_{m, \text{liquid}} - V_{m, \text{solid}}$  is generally positive and rather small.

$\Rightarrow$   **$(dp/dT)$  is generally positive and large!**

# Phase boundaries: liquid – vapour

The Clapeyron equation for the vapourisation process:

$$\frac{d p}{d T} = \frac{\Delta S_{m, \text{vap}}}{\Delta V_{m, \text{vap}}} = \frac{\Delta H_{m, \text{vap}}}{T_b \cdot \Delta V_{m, \text{vap}}}$$

Note that we can not assume that  $\Delta V_m$  won't vary with  $T$ .

For an ideal gas, we can calculate the molar volume using the ideal gas equation:

$$V_m = R \cdot T / p$$

If we further assume that the volume of the liquid is negligible compared to the volume of the gas, then  $\Delta V_{\text{vap}} \approx V_m = R \cdot T / p$ :

$$\frac{d p}{d T} = \frac{\Delta H_{m, \text{vap}}}{T_m \cdot \Delta V_{m, \text{vap}}} = \frac{\Delta H_{m, \text{vap}}}{T \cdot (R \cdot T / p)}$$

$$\frac{d p}{p \cdot d T} = \frac{d(\ln p)}{d T} = \frac{\Delta H_{m, \text{vap}}}{R \cdot T^2} \quad \text{Clausius-Clapeyron equation}$$

# Phase boundaries: solid – vapour

The Clapeyron equation for the sublimation process:

$$\frac{d p}{d T} = \frac{\Delta S_{m, \text{subl}}}{\Delta V_{m, \text{subl}}} = \frac{\Delta H_{m, \text{subl}}}{T \cdot \Delta V_{m, \text{subl}}}$$

Again, we can not assume that  $\Delta V_m$  won't vary with  $T$ ; so we replace  $V_m$  with the expression from the ideal gas equation. We thus assume conditions of an ideal gas and negligible volume of the solid compared with the gas.

This yields:

$$\frac{d p}{d T} = \frac{\Delta H_{m, \text{subl}}}{T_m \cdot \Delta V_{m, \text{subl}}} = \frac{\Delta H_{m, \text{subl}}}{T \cdot (\text{R} \cdot T / p)}$$

$$\frac{d p}{p \cdot d T} = \frac{d(\ln p)}{d T} = \frac{\Delta H_{m, \text{subl}}}{\text{R} \cdot T^2}$$

# Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2<sup>nd</sup> Edition, Structural Chemistry Program, Griffith University.  
Sections III.4.1-III.4.9

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9<sup>th</sup> Edition, Oxford University Press.  
Sections 4.4 – 4.6 (pp. 143-152)