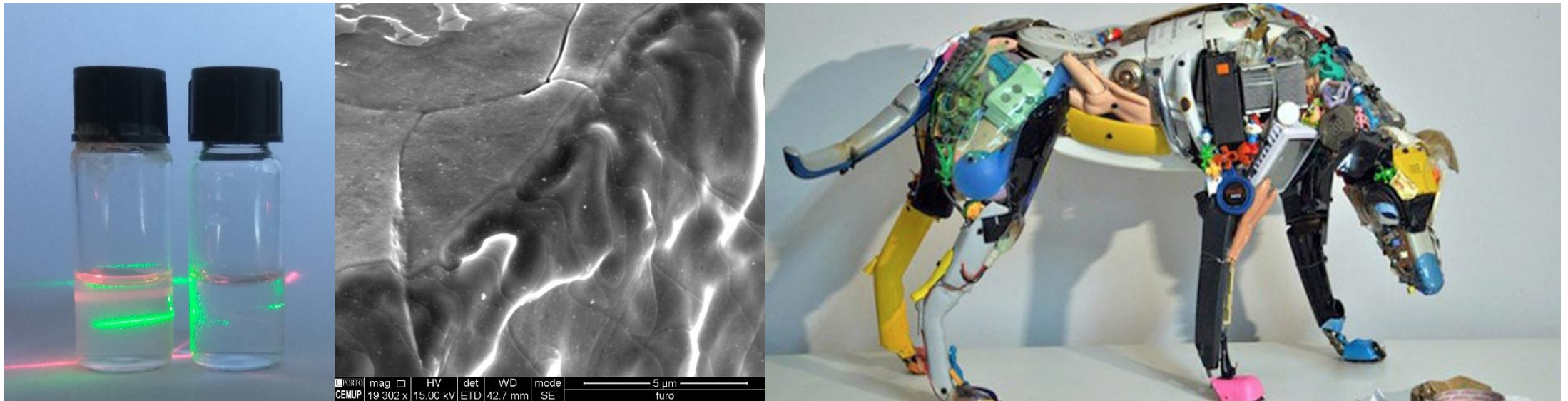
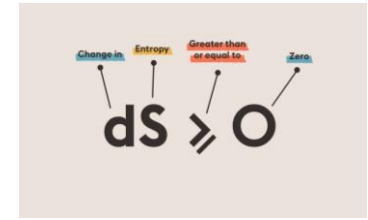


# Physical Chemistry

... iremos explorar, refletir, aprender ?..

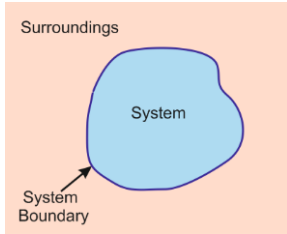
Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.





**Second Law of Thermodynamics** says that the amount of disorder in a thermodynamic system always increases.

The **Helmholtz** and **Gibbs** energies



$$dS_{\text{univ}} = dS_{\text{sys}} + dS_{\text{surr}} > 0$$

$$dS - \frac{dq}{T} \geq 0$$

**Clausius inequality**

$dS$  > Entropy change of the system

$dq$  > heat change of the system

**THERMODYNAMICS POTENTIALS**

Criteria of spontaneous

**Helmholtz** and **Gibbs** energies

Constant **volume**  
& **temperature**

$$dS - \frac{dU}{T} \geq 0$$

$$TdS \geq dU$$

$$dA = dU - TdS \leq 0$$

**Helmholtz**

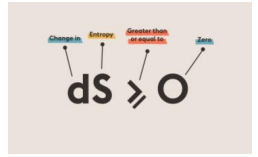
Constant **pressure**  
& **temperature**

$$dS - \frac{dH}{T} \geq 0$$

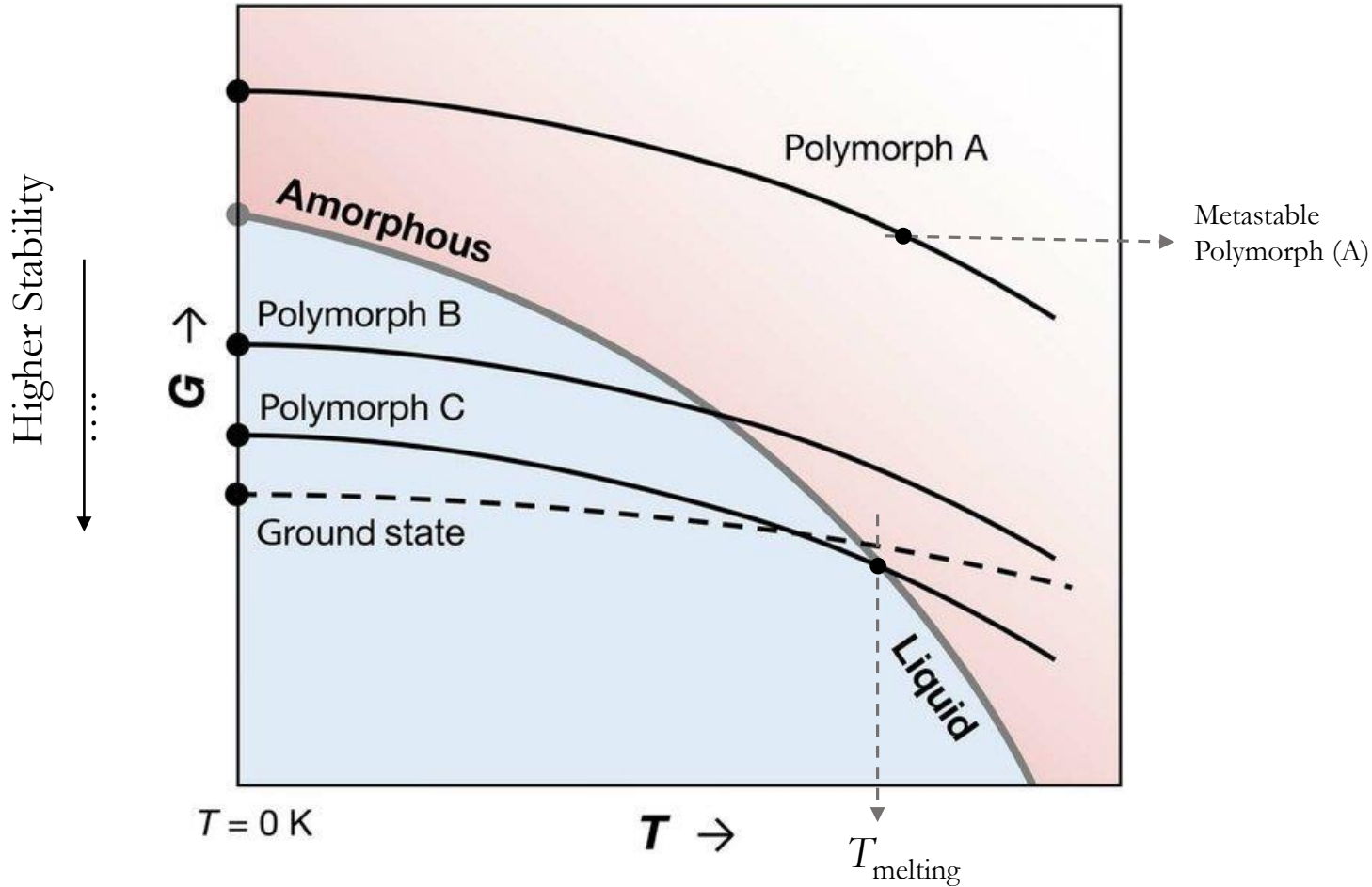
$$TdS \geq dH$$

$$dG = dH - TdS \leq 0$$

**Gibbs**



Gibbs energies vs (temperature)  
Solid system polymorphs



Gibbs Energy:  $G \equiv H - TS$

$$\Delta G = \Delta H - T\Delta S$$

$$dG = dH - TdS \leq 0$$

@ Constant **pressure**

**Lower Gibbs** energy

Means:

low thermodynamic potential  
High stability..

## Gibbs energies of reaction !!



$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu \Delta_f G^\ominus - \sum_{\text{Reactants}} \nu \Delta_f G^\ominus$$

## Standard Gibbs energies of Formation

### Illustration 3.7 Calculating a standard Gibbs energy of reaction

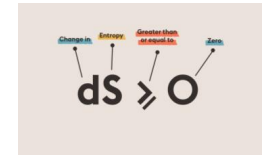
To calculate the standard Gibbs energy of the reaction  $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$  at 25°C, we write

$$\begin{aligned} \Delta_r G^\ominus &= \Delta_f G^\ominus(\text{CO}_2, \text{g}) - \left\{ \Delta_f G^\ominus(\text{CO}, \text{g}) + \frac{1}{2} \Delta_f G^\ominus(\text{O}_2, \text{g}) \right\} \\ &= -394.4 \text{ kJ mol}^{-1} - \left\{ (-137.2) + \frac{1}{2}(0) \right\} \text{ kJ mol}^{-1} \\ &= -257.2 \text{ kJ mol}^{-1} \end{aligned}$$

### Synoptic Table 3.4\* Standard Gibbs energies of formation (at 298 K)

	$\Delta_f G^\ominus / (\text{kJ mol}^{-1})$
Diamond, C(s)	+2.9
Benzene, C <sub>6</sub> H <sub>6</sub> (l)	+124.3
Methane, CH <sub>4</sub> (g)	-50.7
Carbon dioxide, CO <sub>2</sub> (g)	-394.4
Water, H <sub>2</sub> O(l)	-237.1
Ammonia, NH <sub>3</sub> (g)	-16.5
Sodium chloride, NaCl(s)	-384.1

\* More values are given in the *Data section*.



$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu \Delta_f G^\ominus - \sum_{\text{Reactants}} \nu \Delta_f G^\ominus$$

**Standard Gibbs** energies of Formation of (H<sup>+</sup>, aq)

$$\Delta_f G^\ominus(\text{H}^+, \text{aq}) = 0$$

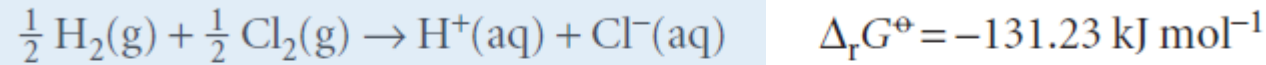
**Convention!**

**Standard Gibbs** energies of Formation of (H<sup>+</sup>, aq)

hydrogen ion, to have zero standard Gibbs energy of formation at all temperatures:

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu \Delta_f G^\ominus - \sum_{\text{Reactants}} \nu \Delta_f G^\ominus$$



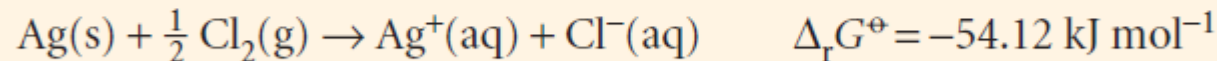
we can write

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{H}^+, \text{aq}) + \Delta_f G^\ominus(\text{Cl}^-, \text{aq}) = \Delta_f G^\ominus(\text{Cl}^-, \text{aq})$$

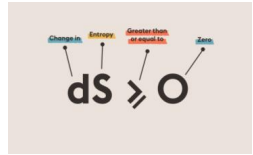
$$\Delta_f G^\ominus(\text{Cl}^-, \text{aq}) \text{ as } -131.23 \text{ kJ mol}^{-1}$$

### Illustration 3.8 *Calculating the standard Gibbs energy of formation of an ion*

With the value of  $\Delta_f G^\ominus(\text{Cl}^-, \text{aq})$  established, we can find the value of  $\Delta_f G^\ominus(\text{Ag}^+, \text{aq})$  from

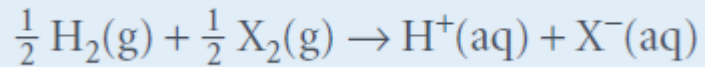


which leads to  $\Delta_f G^\ominus(\text{Ag}^+, \text{aq}) = +77.11 \text{ kJ mol}^{-1}$ .

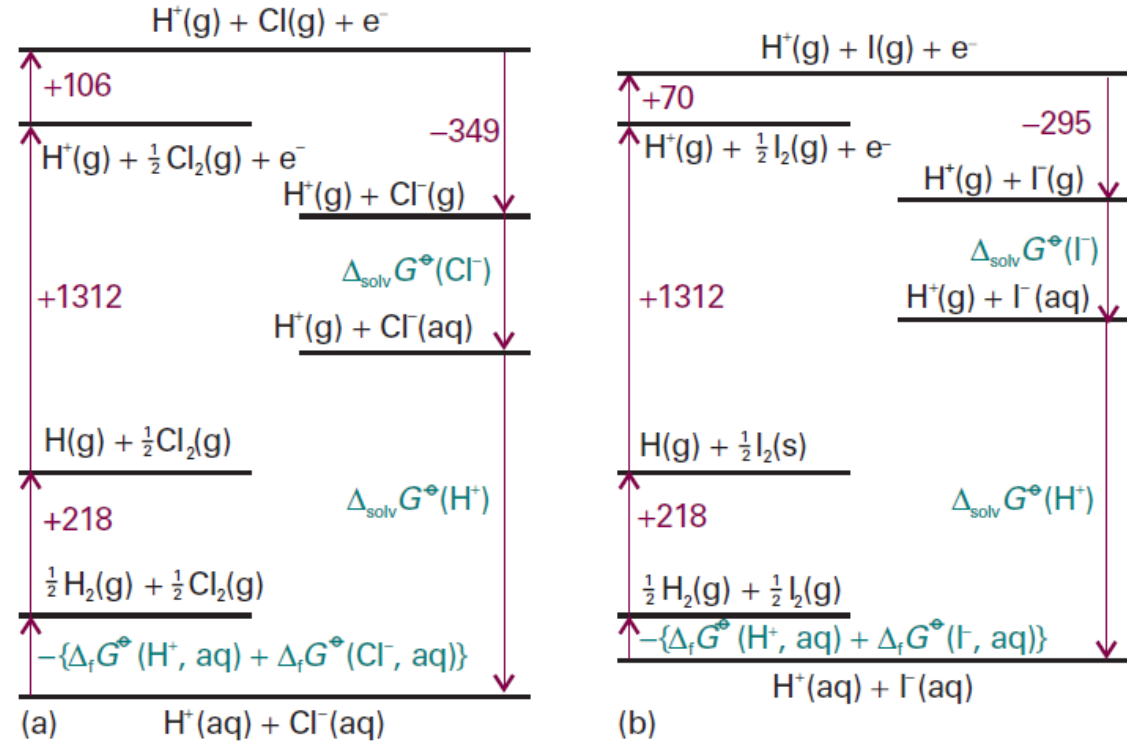
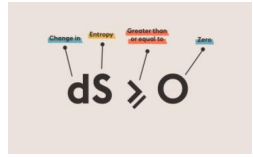


$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu \Delta_f G^\ominus - \sum_{\text{Reactants}} \nu \Delta_f G^\ominus$$

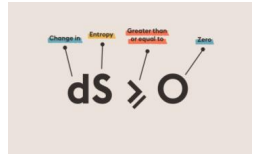


$$\Delta_f G^\ominus(\text{Cl}^-, \text{aq}) = 1272 \text{ kJ mol}^{-1} + \Delta_{\text{solv}} G^\ominus(\text{H}^+) + \Delta_{\text{solv}} G^\ominus(\text{Cl}^-)$$



**Fig. 3.17** The thermodynamic cycles for the discussion of the Gibbs energies of solvation (hydration) and formation of (a) chloride ions, (b) iodide ions in aqueous solution. The sum of the changes in Gibbs energies around the cycle sum to zero because  $G$  is a state function.

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$



$G$  may change because  $H$ ,  $T$ , and  $S$  all change.

$$dG = dH - d(TS) = dH - TdS - SdT$$

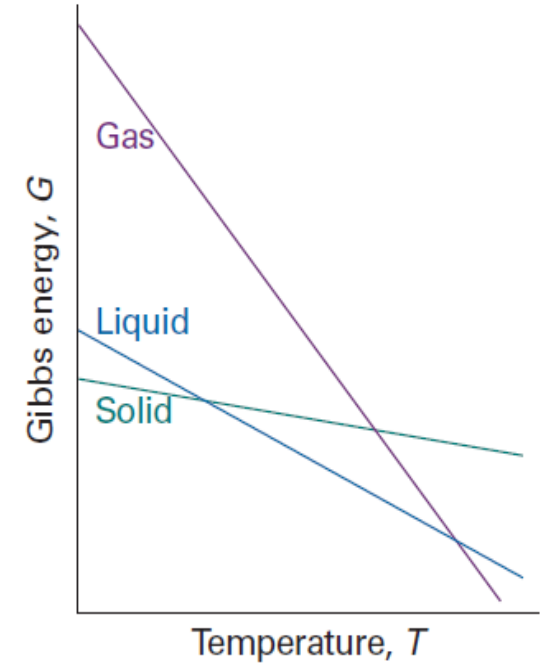
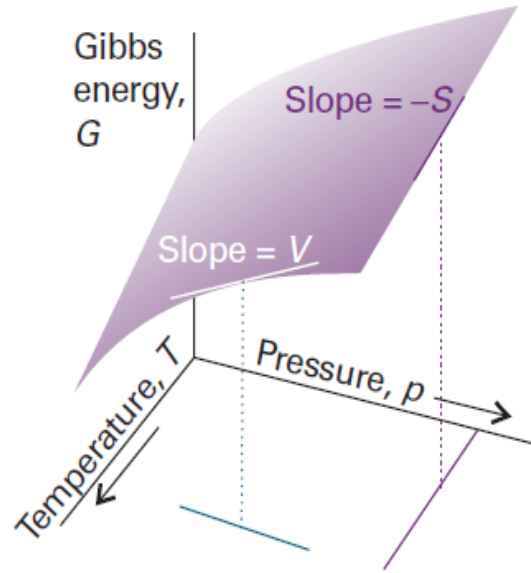
$$dH = dU + d(pV) = dU + pdV + Vdp$$

$$dU = TdS - pdV$$

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

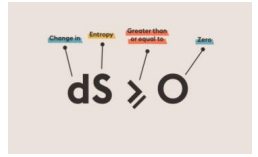
$$dG = Vdp - SdT$$

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

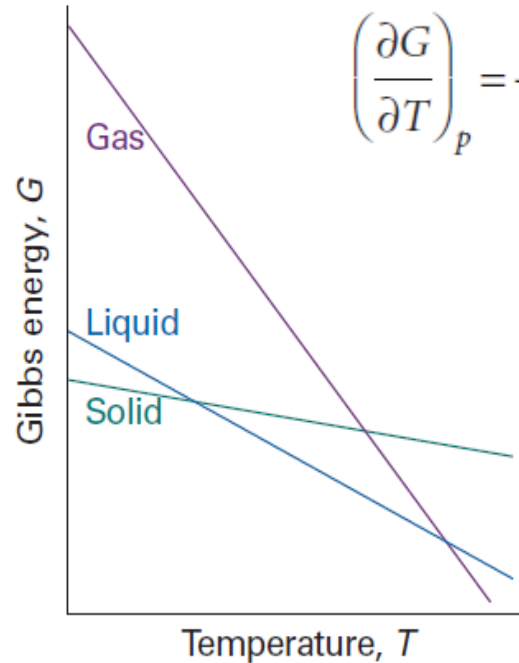
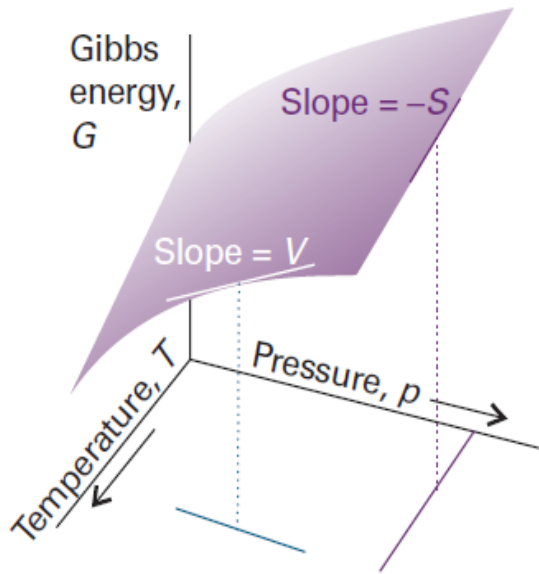




$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$



$G$  may change because  $H$ ,  $T$ , and  $S$  all change.

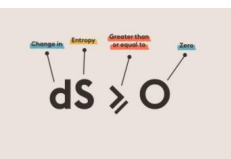


$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

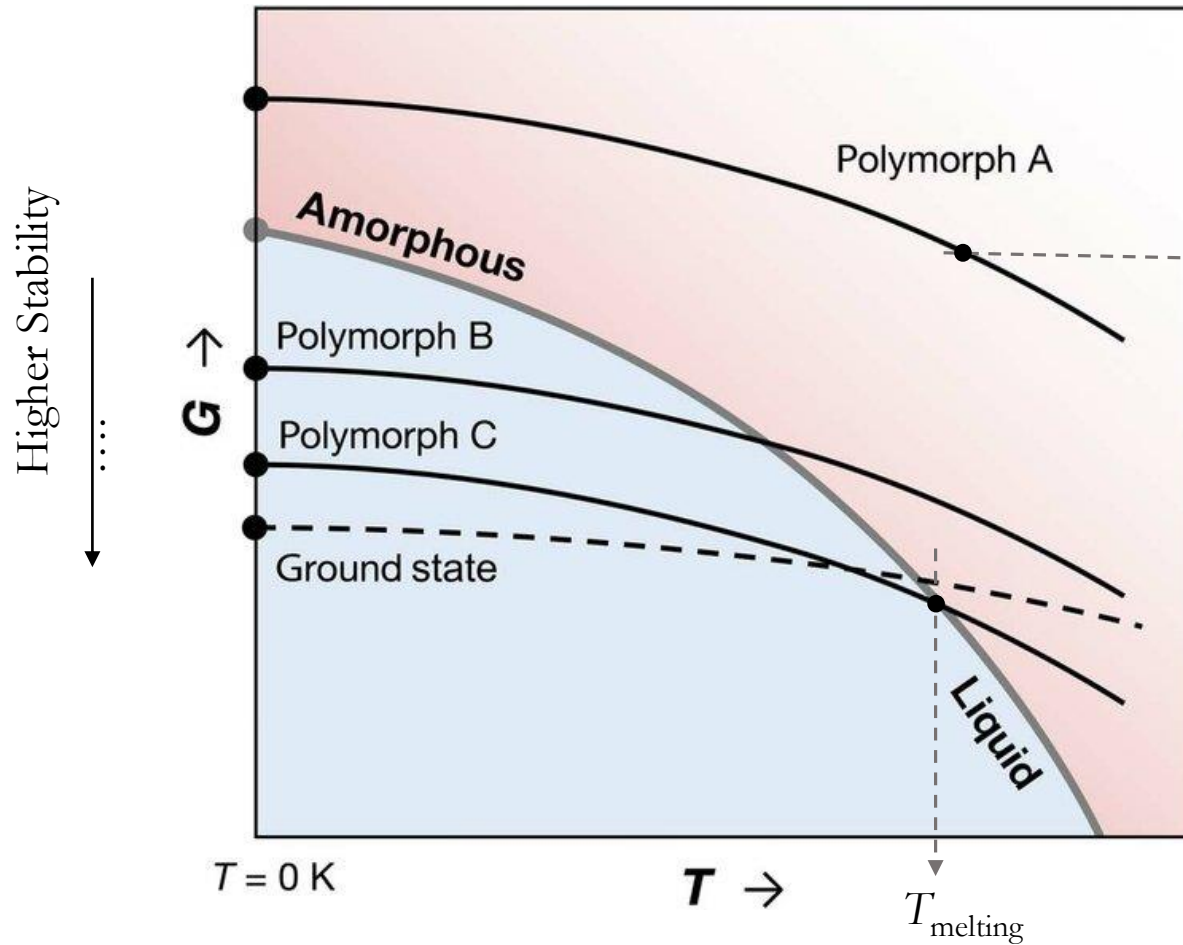
$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

Because  $S > 0$  for all substances,  
 $G$  always *decreases* when the **temperature is raised**

Because  $(\partial G/\partial T)_p$  becomes **more negative** as  $S$  increases,  
 $G$  decreases most sharply when the **entropy of the system is large**.



Gibbs energies vs (temperature) Solid system polymorphs



## Gibbs Energy: $G \equiv H - TS$

$$\Delta G = \Delta H - T\Delta S$$

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

$$dG = Vdp - SdT$$

@ Constant **pressure**

$$dG = dH - TdS \leq 0$$