![QF.DQB Química-Física — Faculdade de Ciências da Universidade do Porto]
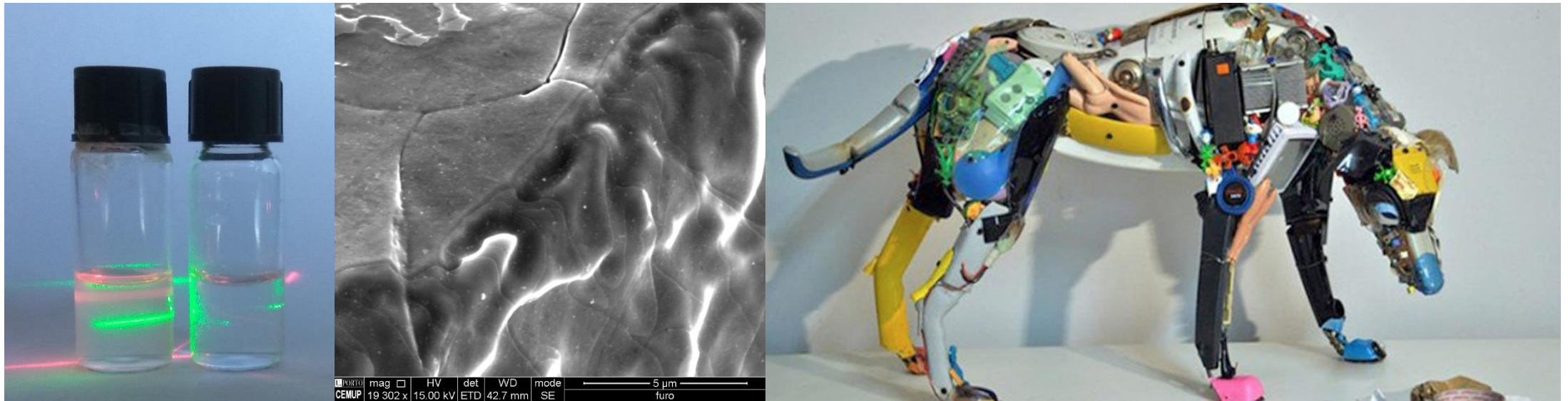
Physical Chemistry

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

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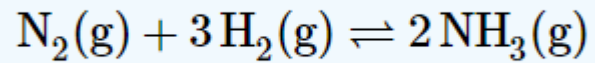
Third-law of thermodynamics

standard reaction entropy, $\Delta_r S^\ominus$

e.g. **Haber process** for the production of ammonia from nitrogen and hydrogen gas

Developed by German chemist **Fritz Haber** in the early 20th century

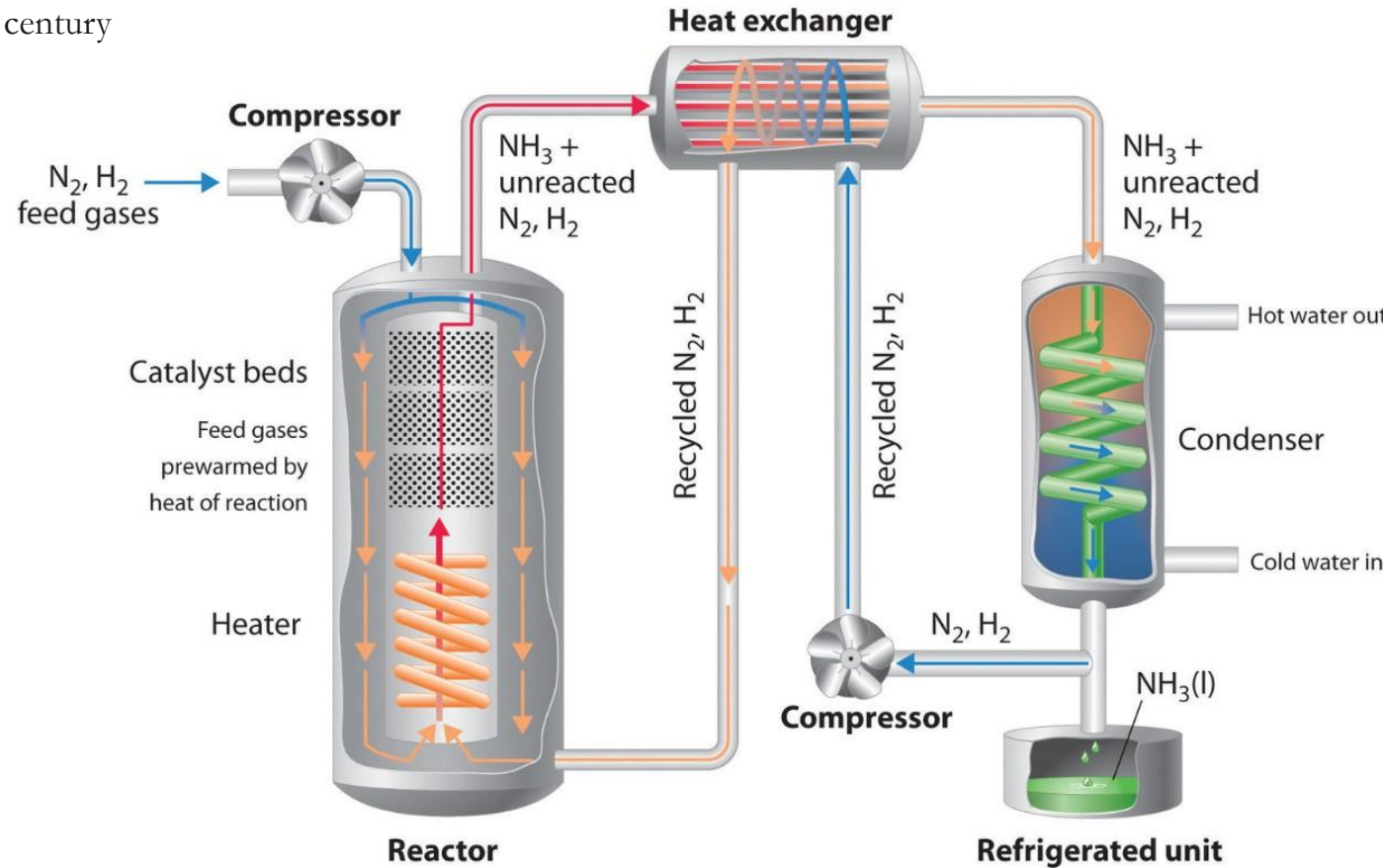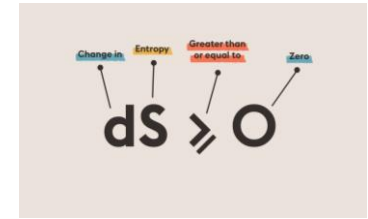$$\Delta_r S^\ominus = \sum_{Products} \nu S_m^\ominus - \sum_{Reactants} \nu S_m^\ominus$$

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

At 298.15 K : $\Delta_r S^0 = -\,\mathbf{198.3}$ J·K^{-1}·mol^{-1}

$\Delta_r H^0 = -\,92.0$ kJ·mol^{-1}

$\downarrow$

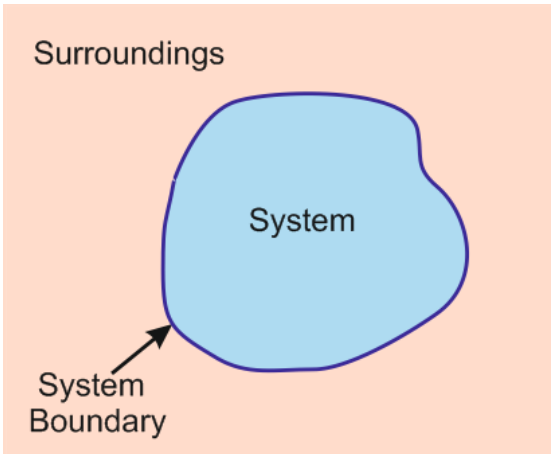$\Delta_{surr} S^0 = +\,308$ kJ·mol^{-1}

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

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

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

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

Clausius inequality

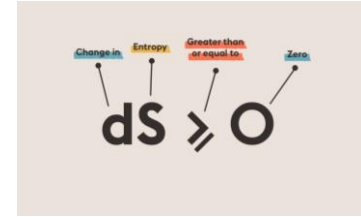dS > Entropy change of the system

dq > heat change of the system
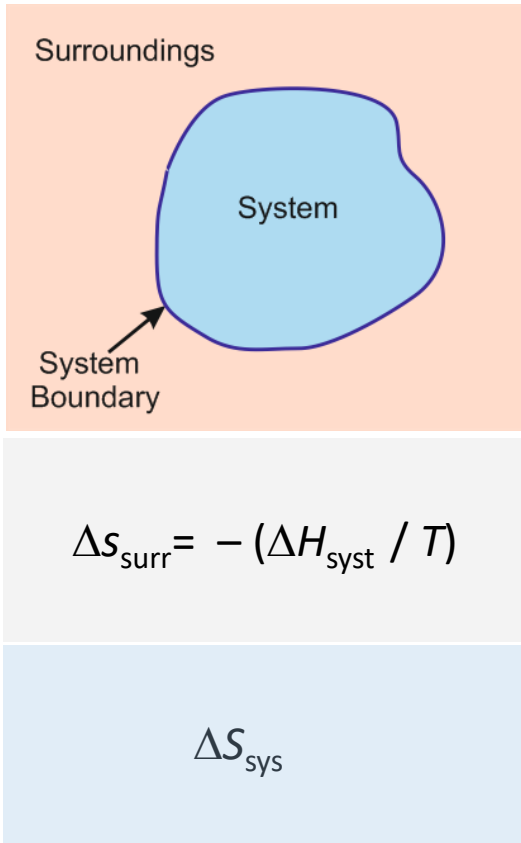

Constant **volume**	$dS - \dfrac{dU}{T} \geq 0$	$TdS \geq dU$
Constant **pressure**	$dS - \dfrac{dH}{T} \geq 0$	$TdS \geq dH$

Criteria of spontaneous

Spontaneous Physical and Chemical Processes !!?

$dS_{univ} = dS_{sys} + dS_{surr} \geq 0$

Surroundings

System

System Boundary

$\Delta s_{surr} = -(\Delta H_{syst} / T)$

ΔS_{sys}

Constant **pressure**

Gibbs Energy: $G \equiv H - TS$

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

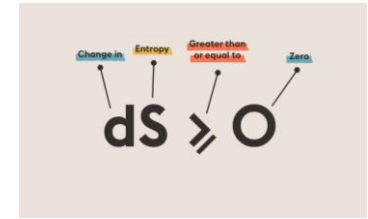$[-T]$ x $-T \Delta S_{univ} = \Delta H_{syst} - T \Delta S_{sys} < 0$

$\Delta S_{univ} > 0 \longrightarrow \Delta G < 0$
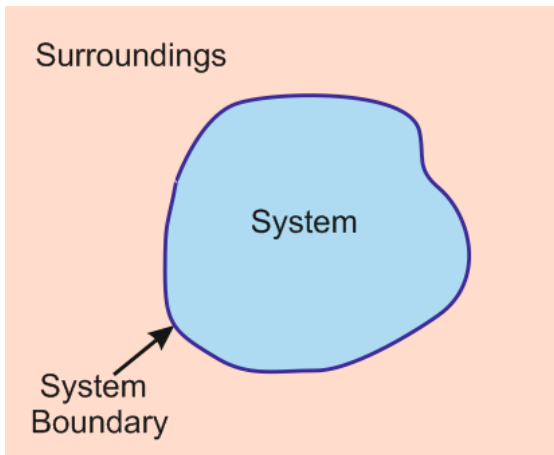
$\Delta S_{univ} = T \Delta S_{sys} - (\Delta H_{syst} / T) \geq 0$

Gibbs energy can be used as a criterion of spontaneously of a process occurring at constant pressure

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

Constant pressure

$\Delta G = -T \cdot \Delta S_{univ}$

Spontaneous Physical and Chemical Processes !!?

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

Constant **pressure**

$$\textbf{d}S_{\textbf{univ}} = dS_{sys} + dS_{surr} > 0$$
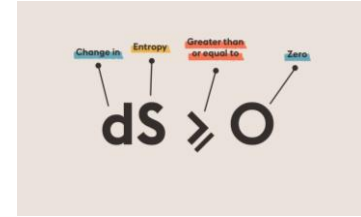
$$\Delta S_{surr} = - (\Delta H_{syst} / T)$$

$$\Delta S_{sys}$$

$$\Delta S_{univ} = T\,\Delta S_{sys} - (\Delta H_{syst} / T) \textbf{ >= 0}$$

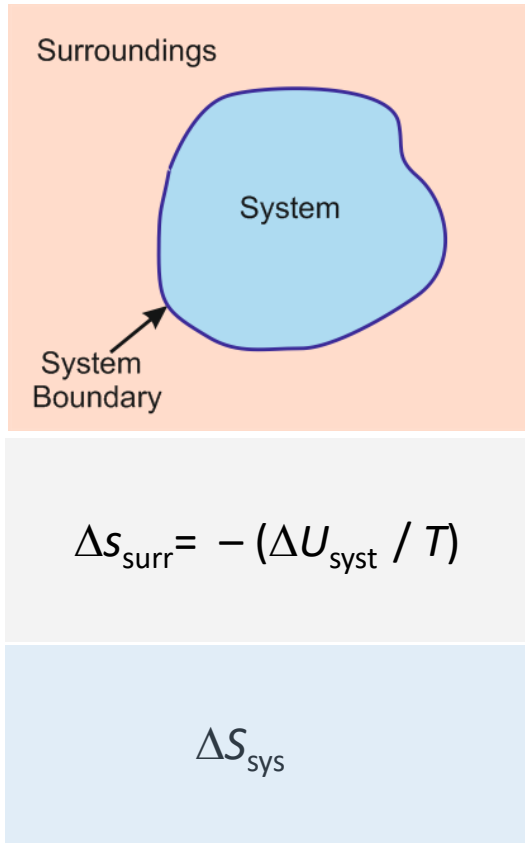$$[-T] \quad \times \quad -T\,\Delta S_{univ} = \Delta H_{syst} - T\,\Delta S_{sys} < 0$$

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

Gibbs Energy: *G ≡ H - TS*

Spontaneous Physical and Chemical Processes !!?

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

$dS_{univ} = dS_{sys} + dS_{surr} \geq 0$

$\Delta s_{surr} = -(\Delta U_{syst} / T)$

ΔS_{sys}

Constant **volume**

Helmholtz Energy: $A \equiv U - TS$

$$\Delta A = \Delta U - T\Delta S$$

$[-T] \times$ $-T \Delta S_{univ} = \Delta U_{syst} - T \Delta S_{sys} < 0$
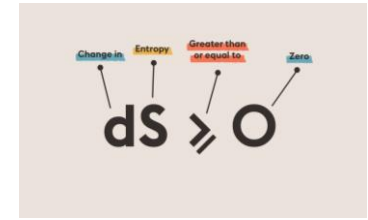
$\Delta S_{univ} > 0 \longrightarrow \Delta U < 0$

Constant pressure

$\Delta A = -T \cdot \Delta S_{univ}$

$\Delta S_{univ} = T \Delta S_{sys} - (\Delta U_{syst} / T) \geq 0$

Helmholtz energy can be used as a criterion of spontaneously of a process occurring at constant volume

Spontaneous Physical and Chemical Processes !!?

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

Constant **volume**

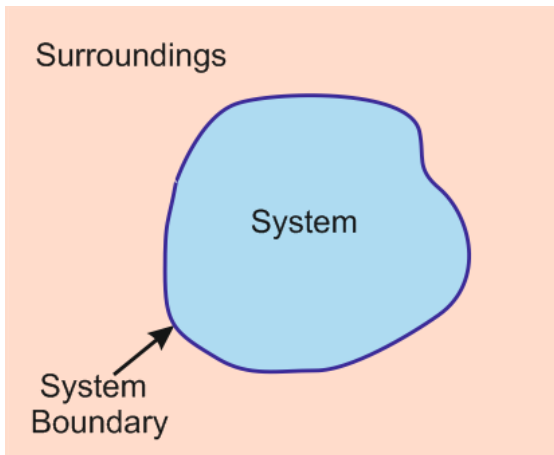$$dS_{univ} = dS_{sys} + dS_{surr} > 0$$

$$\Delta s_{surr} = -(\Delta U_{syst} \, / \, T)$$

$$\Delta S_{sys}$$

$$\Delta S_{univ} = T \, \Delta S_{sys} - (\Delta U_{syst} \, / \, T) >= 0$$

$[-T] \quad \times \qquad -T \, \Delta S_{univ} = \Delta U_{syst} - T \, \Delta S_{sys} < 0$

$$\Delta A = \Delta U - T\Delta S$$

Helmholtz Energy: $A \equiv U - TS$
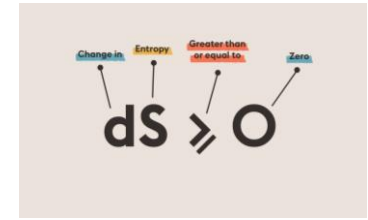
Spontaneous Physical and Chemical Processes !!?

Second Law of Thermodynamics
says that the amount of disorder in a thermodynamic system always increases.
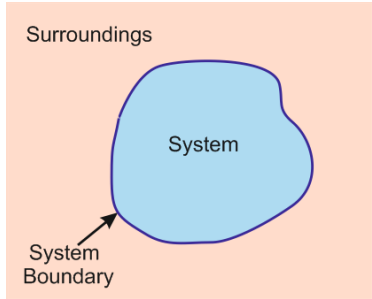
The **Helmholtz** and **Gibbs** energies

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

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

Clausius inequality

dS > Entropy change of the system

dq > heat change of the system

Criteria of spontaneous

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**

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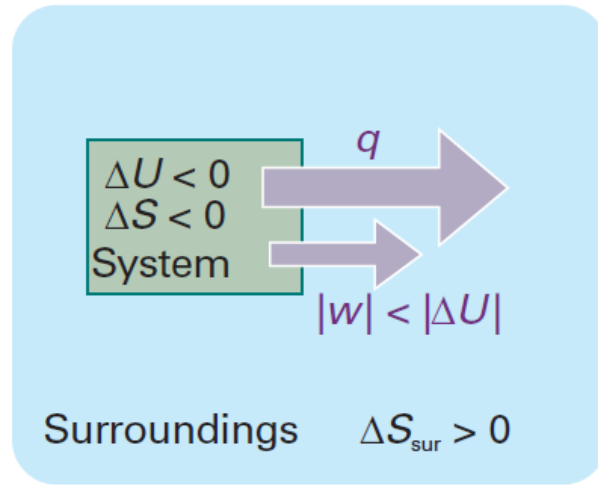
Clausius inequality

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

dS ≥ O

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

dS$_{univ}$ = dS_{sys} + dS_{surr} > 0

dS > Entropy change of the system
dq > heat change of the system
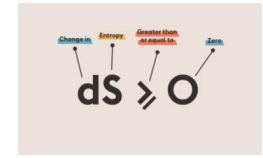
In the process depicted here, the entropy
of the system decreases, so that of the
surroundings must increase in order for the
process to be spontaneous, which means
that energy must pass from the system to
the surroundings as heat.
Therefore, **less work than ΔU can be obtained**.
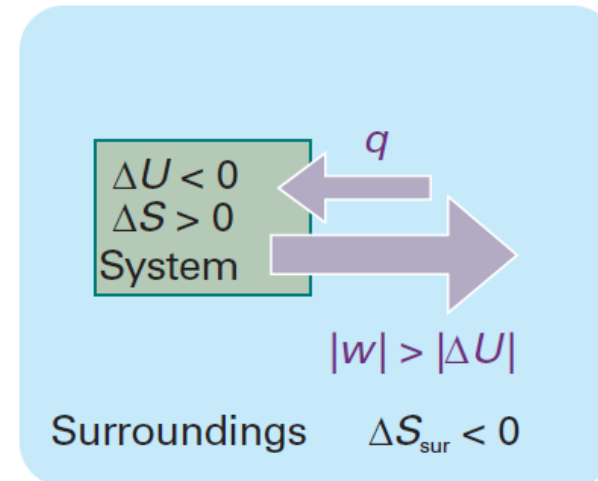
In this process, the entropy of the
system increases;
hence we can afford to lose some entropy of the
surroundings. That is, some of their energy may
be lost as heat to the system.
This energy can be returned to them as work.
Hence the **work done can exceed ΔU.**
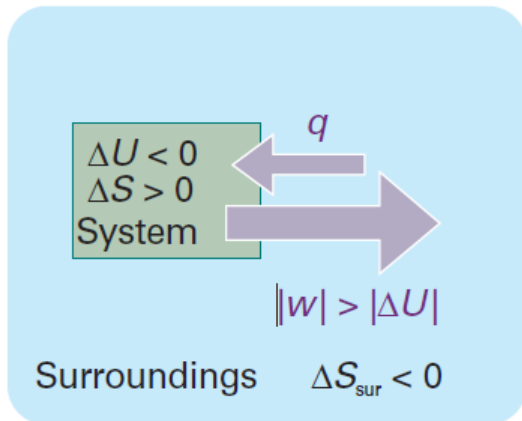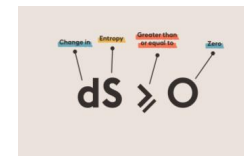
maximum work function

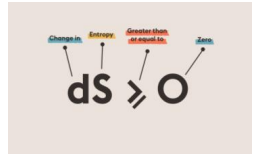*the change in the **Helmholtz function** is equal to the maximum work accompanying a process:*

$$dw_{max} = dA$$

When 1.000 mol $C_6H_{12}O_6$ (glucose) is oxidized to carbon dioxide and water at 25°C according to the equation $C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$, calorimetric measurements give $\Delta_r U^{\ominus} = -2808$ kJ mol^{-1} and $\Delta_r S = +182.4$ J K^{-1} mol^{-1} at 25°C. How much of this energy change can be extracted as (a) heat at constant pressure, (b) work?
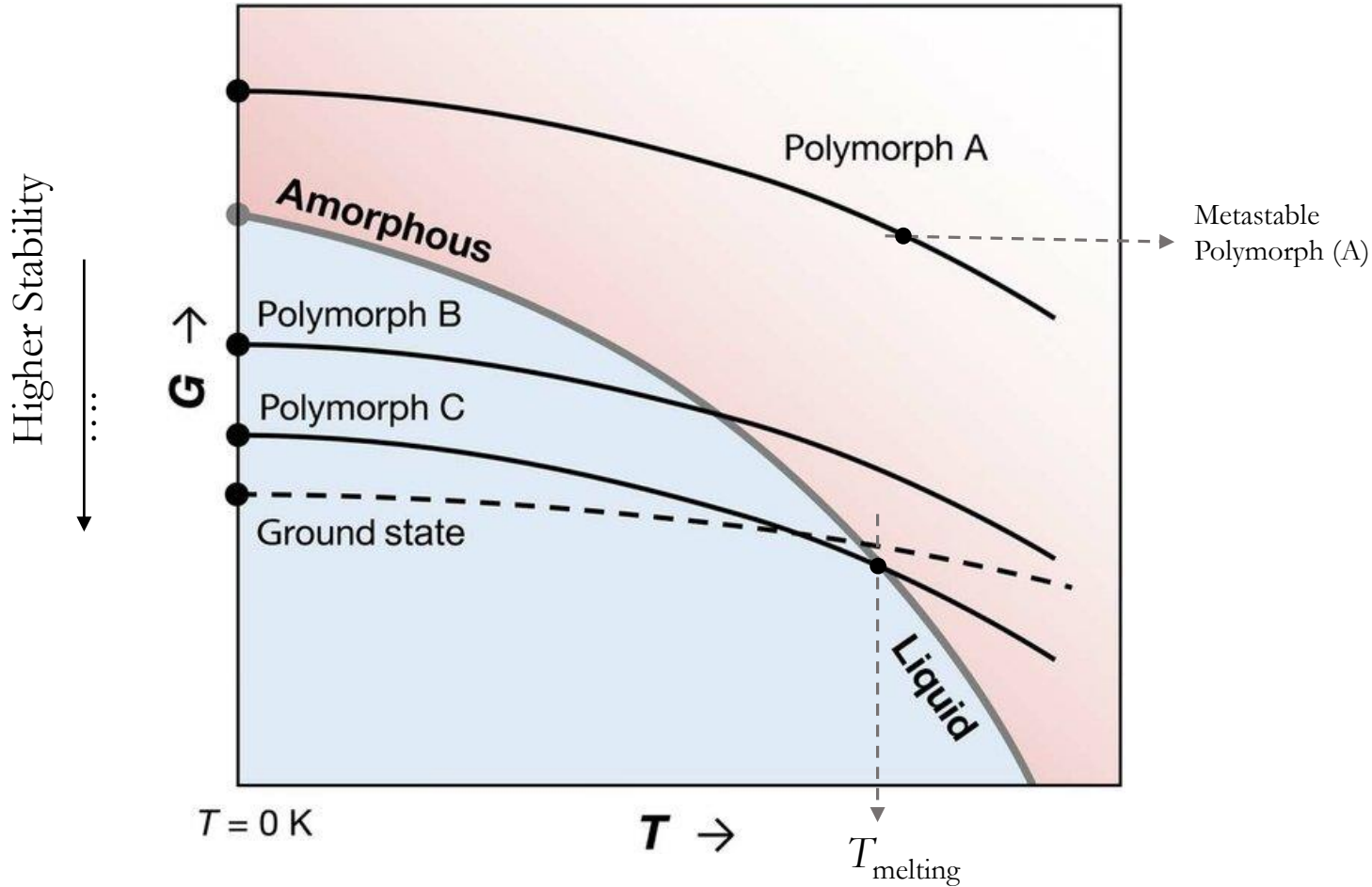
Answer (a) Because $\Delta v_g = 0$, we know that $\Delta_r H^{\ominus} = \Delta_r U^{\ominus} = -2808$ kJ mol^{-1}. Therefore, at constant pressure, the energy available as heat is 2808 kJ mol^{-1}. (b) Because $T = 298$ K, the value of $\Delta_r A^{\ominus}$ is

$$\Delta_r A^{\ominus} = \Delta_r U^{\ominus} - T\Delta_r S^{\ominus} = -2862 \text{ kJ mol}^{-1}$$

dq with the First Law, $dU = dq + dw$, and obtain

$$dU \leq TdS + dw$$

$$dw \geq dU - TdS$$

$$dw_{max} = dU - TdS$$

$$dw_{max} = dA$$

$$\Delta_r H = \Delta_r U + \Delta v_g RT.$$

Gibbs energies ..f (temperature)
Solid system polymorphs

Higher Stability

$G \uparrow$

Polymorph A

Amorphous

Polymorph B

Polymorph C

Ground state

Metastable
Polymorph (A)

Liquid

$T = 0$ K

$T \rightarrow$

T_{melting}

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..

$dS \geqslant O$