

Free Energies

CHEM 361A: Introduction to Physical Chemistry

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Lecture 8

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Learning Objective: Define the Gibbs Free Energy of single component systems and use it to draw phase diagrams.

References:

- Atkins and de Paula Focus 4A and 4B
- Chang Chapter 6

Spontaneity Revisited

Always quantifying both the entropy change for the system and surroundings to determine spontaneity is cumbersome. It is convenient to write ΔS_{Total} in terms of the system alone:

$$dS_{Total} = dS_{sys} + dS_{surr}$$

For a reversible process

$$dS_{Total} = dS_{sys} - \frac{dq_{rev}}{T}$$

- Constant Volume

$$dS_{Total} = dS_{sys} - \frac{dU}{T}$$

- Constant Pressure

$$dS_{Total} = dS_{sys} - \frac{dH}{T}$$

Gibbs and Helmholtz Free Energies

Multiply through by $-T$ and assume constant temperature

$$-TdS_{Total} = dU - TdS_{sys}$$

$$-TdS_{Total} = dH - TdS_{sys}$$

We can define new statefunctions

- Helmholtz Free Energy

$$A = U - TS$$

- Gibbs Free Energy

$$G = H - TS_{sys}$$

Small, isothermal changes in these new statefunctions

$$dA = dU - TdS_{sys} - \cancel{S_{sys}dT} \rightarrow 0$$

$$dA = -TdS_{Total}$$

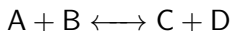
$$dG = dH - TdS_{sys} - \cancel{S_{sys}dT} \rightarrow 0$$

$$dG = -TdS_{Total}$$

So quantifying Helmholtz or Gibbs free energies quantifies if a process is spontaneous.

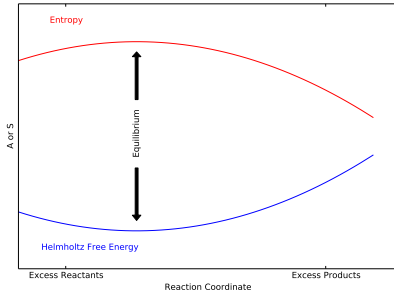
What ΔA Quantifies - Spontaneity

Consider the process (at constant volume and temperature)



Since

$$\Delta U - T\Delta S = \Delta A = -T\Delta S_{Total}$$



- $\Delta A > 0$ **reverse** process is spontaneous
- $\Delta A = 0$ system at equilibrium
- $\Delta A < 0$ **forward** process is spontaneous

What ΔA Quantifies - Total Work

To show the relationship between ΔA and w we will work with reversible processes. At constant temperature:

$$dA = dU - TdS$$

Then using the First Law of Thermodynamics ($dU = dw + dq$)

$$dA = dw + dq - TdS$$

and cancelling out like terms ($TdS = dq$):

$$dA = dw + \cancel{dq} - \cancel{dq}$$

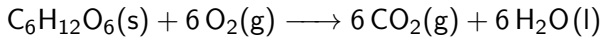
Since this relation holds for each infinitesimal step, then

$$\Delta A = w$$

So ΔA quantifies the total work of a process.

ΔA Example

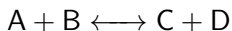
Consider the metabolism of glucose to water and carbon dioxide at 25°C:



The following changes are found from calorimetric measurements: $\Delta_r U = -2801.3 \text{ kJ mol}^{-1}$ and $\Delta_r S = 260.7 \text{ J K}^{-1} \text{ mol}^{-1}$. How much energy can be extracted as work?

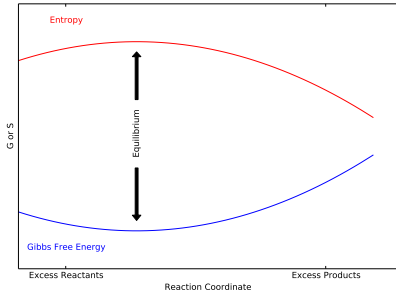
What ΔG Quantifies - Spontaneity

Consider the process (at constant pressure and temperature):



since

$$\Delta H - T\Delta S = \Delta G = -T\Delta S_{Total}$$



- $\Delta G > 0$ **reverse** process is spontaneous
- $\Delta G = 0$ system at equilibrium
- $\Delta G < 0$ **forward** process is spontaneous

What ΔG Quantifies - Non-expansion Work

To show the relationship between ΔG and w_{noexp} we will work with reversible processes. At constant temperature:

$$dG = dH - TdS$$

Additionally, assuming constant pressure we can use the definition of Enthalpy ($dH = dU + pdV$):

$$dG = dU + pdV - TdS$$

Then using the First Law of Thermodynamics ($dU = dw + dq$)

$$dG = dw + \cancel{dq} + pdV - \cancel{dq}$$

assuming that there is both expansion ($-pdV$) and non-expansion type work (dw_{noexp})

$$dG = dw_{noexp} - \cancel{pdV} + \cancel{pdV}$$

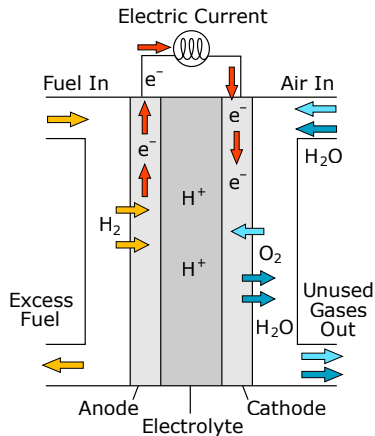
Since this relation holds for each infinitesimal step, then

$$\Delta G = w_{noexp}$$

Non-expansion Work

Recall that non-expansion work may include:

- Electrical Work in an electrochemical/biological cell
- Other kinds of mechanical work
 - Winding of a spring
 - Contraction of a muscle



An example of electrochemical work: a schematic of a fuel cell

Examples with Gibbs Free Energy

- 1 In a fuel cell, natural gases such as methane undergo the same redox reaction as in the combustion process to produce carbon dioxide and water to generate electricity. Calculate the maximum electrical work that can be obtained from 1 mole of methane at 25°C.

Standard Molar Gibbs Free Energy of Formation ($\Delta_f G^\ominus$)

- As for enthalpy, we cannot measure the absolute value of Gibbs energies.
- We assign a value of 0 to the $\Delta_f G^\ominus$ of an element in its most stable allotropic form at 1 bar and 298 K.

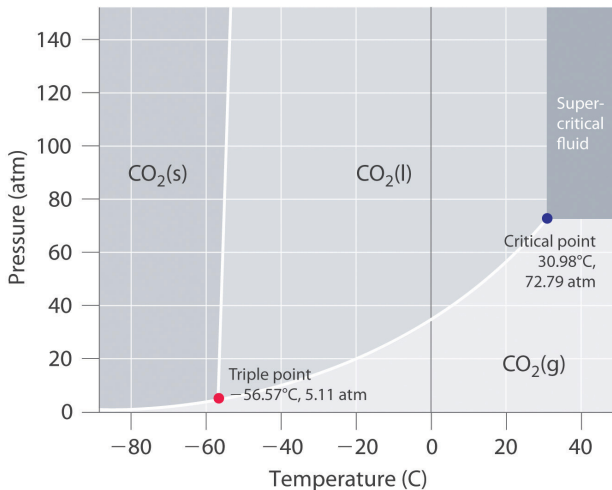
We can calculate $\Delta_f G^\ominus$ for each compound using

$$\Delta_f G^\ominus = \Delta_f H^\ominus - T\Delta S^\ominus$$

If the $\Delta_f G^\ominus$ is known for each component then

$$\Delta_r G^\ominus = \sum \nu \Delta_f G^\ominus (\text{products}) - \sum \nu \Delta_f G^\ominus (\text{reactants})$$

Phase Diagram of CO_2



Molar Gibbs Free Energy

When discussing if it is spontaneous for a given phase to form, it would be tempting to use the total Gibbs free energy. For example, for an ice cube floating in a large bath of water at 0°C :

$$G_{\text{solid}} < G_{\text{liquid}}$$

however, the water will not freeze since the solid and liquid phase are in equilibrium.

We must use a quantity that is independent of the total amount of the substance. This issue is solved by using the molar Gibbs Free Energy

$$\frac{G}{n} = G_m$$

We can still write for a ΔG

$$\Delta G = nG_m(2) - nG_m(1) = n(G_m(2) - G_m(1))$$

We can conclude that $\Delta G_m < 0$ still indicates a spontaneous process.

Change in Molar Gibbs Free Energy Example

Calculate the value of ΔG_m for the melting of ice at 0°C , -10°C , and 10°C . The molar enthalpy and entropy of fusion of water are 6.01 kJ mol^{-1} and $22.0 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, and are assumed to be temperature independent.

Variation of Gibbs Free Energy

Starting from the definition of Gibbs Free Energy

$$G = H - TS$$

Substituting in for the definition of Enthalpy and the first law
($H = w + q + PV$)

$$G = w + q + PV - TS$$

For an infinitesimal process

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

Assuming only expansion work and a reversible process

$$dG = \cancel{-pdV} + \cancel{TdS} + Vdp + \cancel{pdV} - \cancel{TdS} - SdT$$

so

$$dG = Vdp - SdT$$

Variation of Gibbs Free Energy with Pressure

Starting with

$$dG = Vdp - SdT$$

If it is an isothermal process ($\Delta T = 0$) and divide both sides by the number of moles, n , we get

$$dG_m = V_m dp$$

If we integrate

- V_m Constant

$$\int_{G_{m,i}}^{G_{m,f}} dG_m = V_m \int_{p_i}^{p_f} dp$$

$$\Delta G_m = V_m \Delta p$$

- V_m Varies (Ideal Gas Law)

$$\int_{G_{m,i}}^{G_{m,f}} dG_m = \int_{p_i}^{p_f} \frac{RT}{p} dp$$

$$\Delta G_m = RT \ln \frac{p_f}{p_i}$$

Variation of Gibbs Free Energy with Temperature

Starting with

$$dG = Vdp - SdT$$

For an isobaric process ($\Delta p = 0$) and divide both sides by n we get

$$dG_m = -S_m dT$$

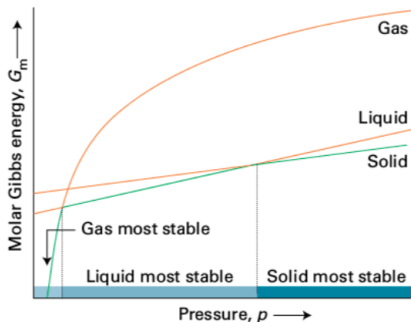
If we integrate and assume that S_m is constant

$$\int_{G_{m,i}}^{G_{m,f}} dG_m = -S_m \int_{T_i}^{T_f} dT$$
$$\Delta G_m = -S_m \Delta T$$

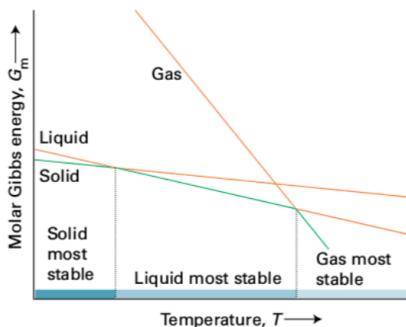
Finding the Stable Phase

We can plot both how the Gibbs free energy varies with respect to

- Pressure

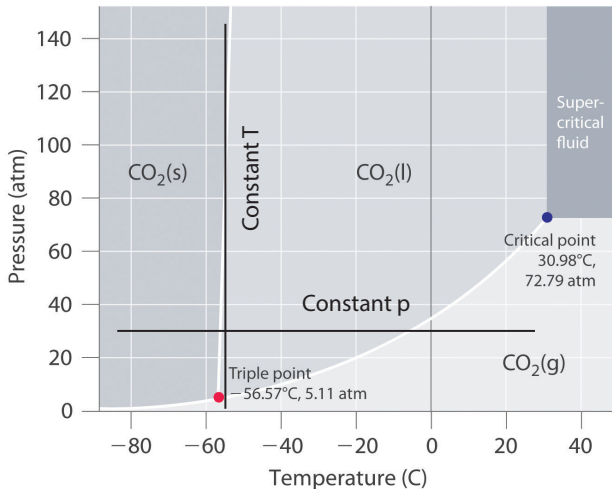


- Temperature



The phase with the lowest molar Gibbs free energy is the spontaneously formed phase.

Phase Diagram of CO_2 Revisited



Phase Diagram Example

Liquid water and ice are in equilibrium at 0°C at 1 bar. What is the effect on the difference of molar Gibbs energies of the two phases when the temperature is increased to 1°C ? Assume $S_m(\text{ice}) = 37.99 \text{ J K}^{-1} \text{ mol}^{-1}$ and $S_m(\text{water}) = 69.91 \text{ J K}^{-1} \text{ mol}^{-1}$.

The Phase Boundary

Any point lying along the **phase boundary** represents a pressure and a temperature where a dynamic equilibrium exists.

- Where the rate of the forward and the reverse phase change reaction are equal

<https://www.youtube.com/watch?v=JsoawKguU6A>

Clapeyron Equation

With two phases in dynamic equilibrium

$$dG_m(1) = dG_m(2)$$

where

$$dG_m(1) = V_m(1)dp - S_m(1)dT$$

$$dG_m(2) = V_m(2)dp - S_m(2)dT$$

Subtracting gives

$$dG_m(2) - dG_m(1) = (V_m(2)dp - S_m(2)dT) - (V_m(1)dp - S_m(1)dT)$$

$$0 = (V_m(2) - V_m(1))dp - (S_m(2) - S_m(1))dT$$

$$\Delta_{trs} V dp = \Delta S_m dT$$

Where $\Delta_{trs} V = \underline{V_m(2) - V_m(1)}$ and $\Delta S_m = S_m(2) - S_m(1)$

Clapeyron Equation (cont.)

Since $\Delta G = 0 = \Delta H - T\Delta S$ (system at equilibrium) then

$$\Delta S = \frac{\Delta H}{T}$$

Substituting this in

$$\Delta_{trs} V dp = \frac{\Delta_{trs} H}{T} dT$$

Rearranging gives

$$dp = \frac{\Delta_{trs} H}{T \Delta_{trs} V} dT$$

For this result, we assume that $\Delta_{trs} H$ and $\Delta_{trs} V$ are independent of T , and P over the range we are interested in.

Clapeyron Equation Example

- 1 Use the Clapeyron Equation to estimate the slope of the solid-liquid phase boundary of water given the enthalpy of fusion is $6.008 \text{ kJ mol}^{-1}$ and the densities of ice and water at 0°C are 0.91671 and $0.99984 \text{ g cm}^{-3}$, respectively.

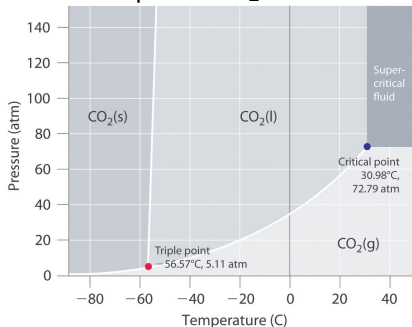
Hint: Molar mass of H_2O is $18.01529 \text{ g mol}^{-1}$

- 2 Estimate the pressure required to lower the melting point of ice by 2°C .

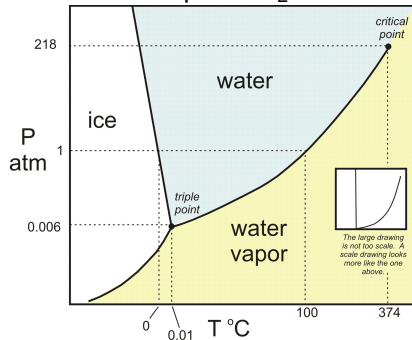
Anomalous Liquids

Anomalous liquids are when the slope of the solid-liquid state boundary is negative.

Normal Liquid - CO₂

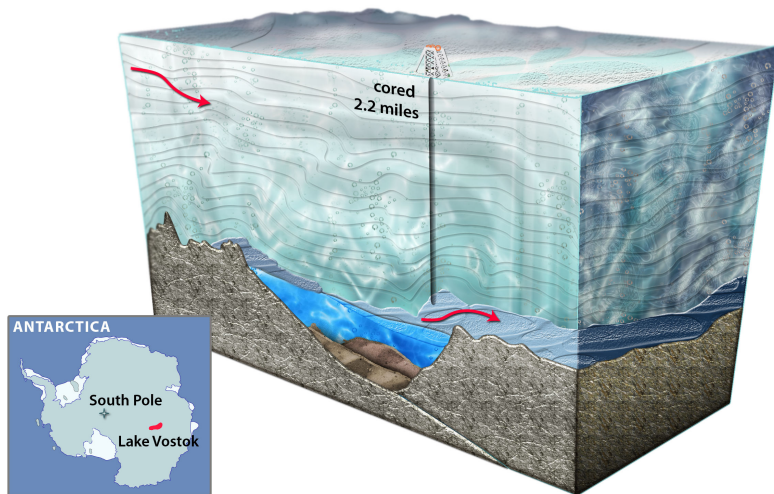


Anomalous Liquid - H₂O



One Reason Why Water Helps Support Life - Lake Vostok

As the pressure increases, the melting temperature of water decreases



The Clausius-Clapeyron Equation

For state changes involving gases, the Clapeyron equation cannot be used because we cannot assume the volume of the vapour is independent of pressure. So starting with the Clapeyron Equation:

$$\frac{dp}{dT} = \frac{\Delta_{trs}H}{T(V_{m,g} - V_{m,l/s})}$$

Since the molar volume of a gas is much larger than that of a liquid or a solid:

$$\frac{dp}{dT} = \frac{\Delta_{trs}H}{TV_{m,g}}$$

Assuming that the gas is ideal

$$\frac{dp}{dT} = \frac{p\Delta_{trs}H}{RT^2} \quad \text{where } V_{m,g} = \frac{RT}{p}$$

The Clausius-Clapeyron Equation (cont.)

Rearranging so that all the pressure terms are on one side and all the temperature terms are on the other and integrating gives:

$$\int_{p_i}^{p_f} \frac{dp}{p} = \int_{T_i}^{T_f} \frac{\Delta_{trs}HdT}{RT^2}$$
$$\ln \frac{p_f}{p_i} = \frac{\Delta_{trs}H}{R} \left(\frac{1}{T_i} - \frac{1}{T_f} \right)$$

This equation assumes that:

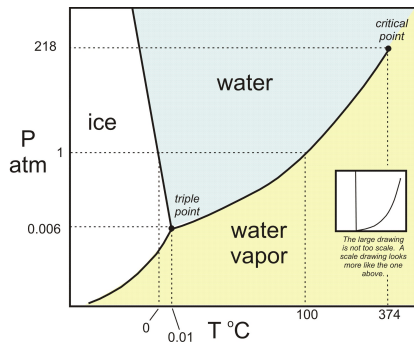
- V_m gas \gg V_m other state
- The vapour behaves ideally
- $\Delta_{trs}H$ is independent of T and p for the region of interest

A Note on Vapour Pressure

The **vapour pressure** of a substance

- Is the pressure of a vapour in equilibrium with its condensed phase.
- Is shown by the phase boundary
- When the vapour pressure matches the external pressure, the substance vapourises.

This is why, for instance, it takes longer to cook things at altitude, since the boiling point of water is lower.



Clausius-Clapeyron Example

Pikes Peak in Colorado is approximately 4300 m above sea level. If the pressure there is $0.5836 P_{sea\ level}$ what is the boiling point of water at the summit?

Hint: $\Delta_{vap}H$ for water is $40.79 \text{ kJ mol}^{-1}$.

The Phase Rule

The **phase rule** is defined as

$$f = c - p + 2$$

where

- c is the number of substances in the system
- p is the number phases present
- f is the number of variables (temperature, pressure, composition) that can be independently chosen without disturbing the number of phases in equilibrium

For example with water

- Water vapour

$$c = 1; p = 1; f = 2$$

This means temperature and pressure can be independently chosen

- Gas/Liquid phase boundary

$$c = 1; p = 2; f = 1$$

Once the temperature or pressure is determined, the other must be a specific value

Summary

- Free energies define if a process is spontaneous (ΔA or $\Delta G < 0$)
- The Helmholtz Free Energy (A) quantifies the total work possible by a process
- the Gibbs Free Energy (G) quantifies the total non-expansion work that is possible
- In single component systems, we can use how the the Gibbs Free Energy varies with respect to temperature and pressure to draw phase diagrams
- The Clapeyron Equation can be used to define phase boundaries where the molar volume changes little wrt T or p for both phases (fx phase transitions between liquid and solid phases)
- The Clausius-Clapeyron Equation should be used when the molar volume of one of the phases changes dramatically wrt T or p (fx phase transitions with a gas phase)