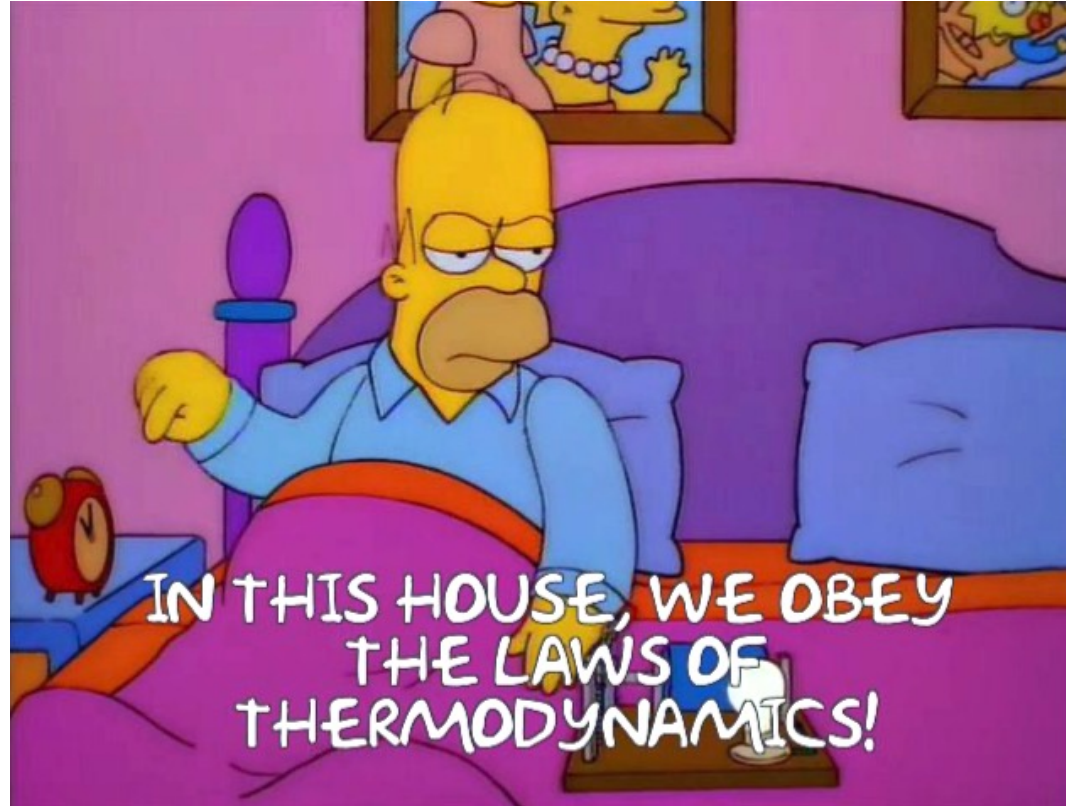


Thermodynamics (lecture 5)



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Summary lecture 4

- Gibbs and Helmholtz free energies
- Spontaneous change and equilibrium
- Four fundamental equations
 - Maxwell relations

$$G = H - TS$$

$$A = U - TS$$

$$dG_{T,p} \leq 0 \quad (\text{closed system})$$

$$dU = TdS - pdV + \mu dn$$

$$dA = -SdT - pdV + \mu dn$$

$$dH = TdS + Vdp + \mu dn$$

$$dG = -SdT + Vdp + \mu dn$$

- Gibbs energy
 - Variation with temperature and pressure
 - Chemical potential perfect gas

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

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

$$\mu(p) = \mu^\ominus + RT \ln \frac{p}{p^\ominus}$$

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

- Gibbs-Duhem relation

Content of the course

- ✓ Introduction to Thermodynamics and gases
- ✓ The First Law of Thermodynamics
- ✓ Heat Capacities, Enthalpy and Thermochemistry
- ✓ The Second Law of Thermodynamics
- ✓ Helmholtz and Gibbs free energies
- **Phase Transitions and Chemical Equilibrium** → Today, lecture 5
- Chemical Equilibrium and Electrochemistry
- Ideal solutions, Colligative properties
- Condensation in the Van der Waals Equation of State

Today's lecture (5)

- Phase equilibria
 - Phase diagrams
 - Phase boundaries and their slopes
- Chemical equilibrium
 - (Reaction) mixtures
 - Condition for chemical equilibrium: reaction Gibbs energy $\Delta_r G$
 - Reaction quotient and the equilibrium constant
 - Effects of mixing

from lecture 1:

Le Chatelier's Principle

"A system at equilibrium will respond to a perturbation so as to relieve the effect of the perturbation"



Henry Louis Le Chatelier
(1850 – 1936)

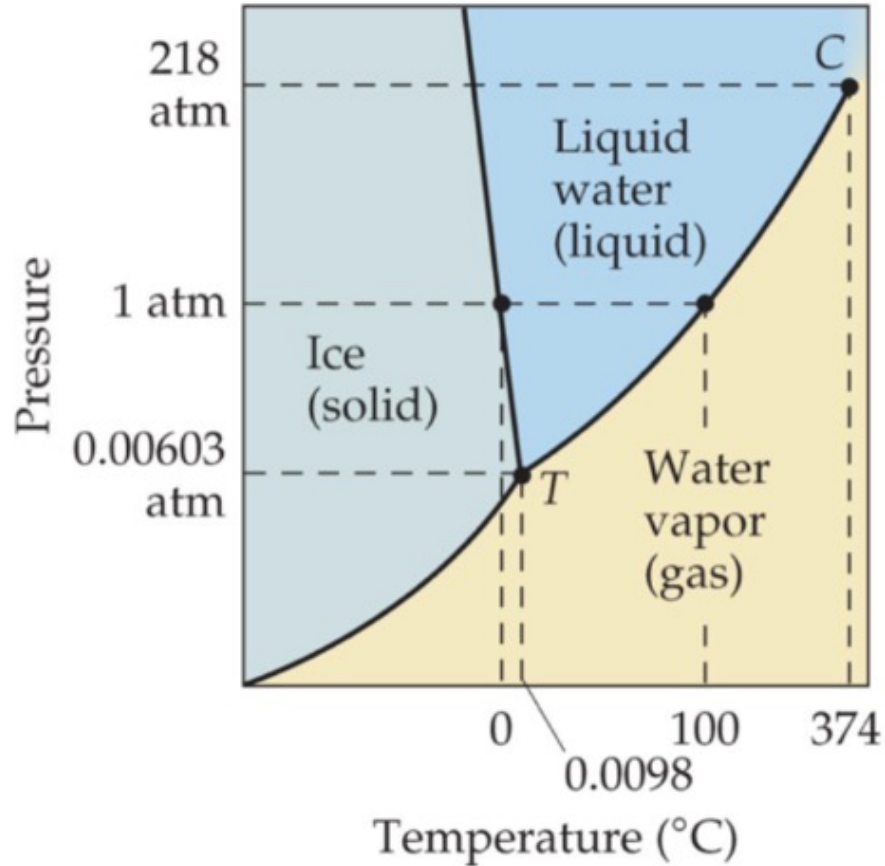
2. Phase diagram of water



Thermodynamics:

- **calculate** the slope of the ice-water phase boundary (lecture 5)

Single component phase diagram: water



Phase boundaries

solid-gas, liquid-gas and solid-liquid

Triple point (T)

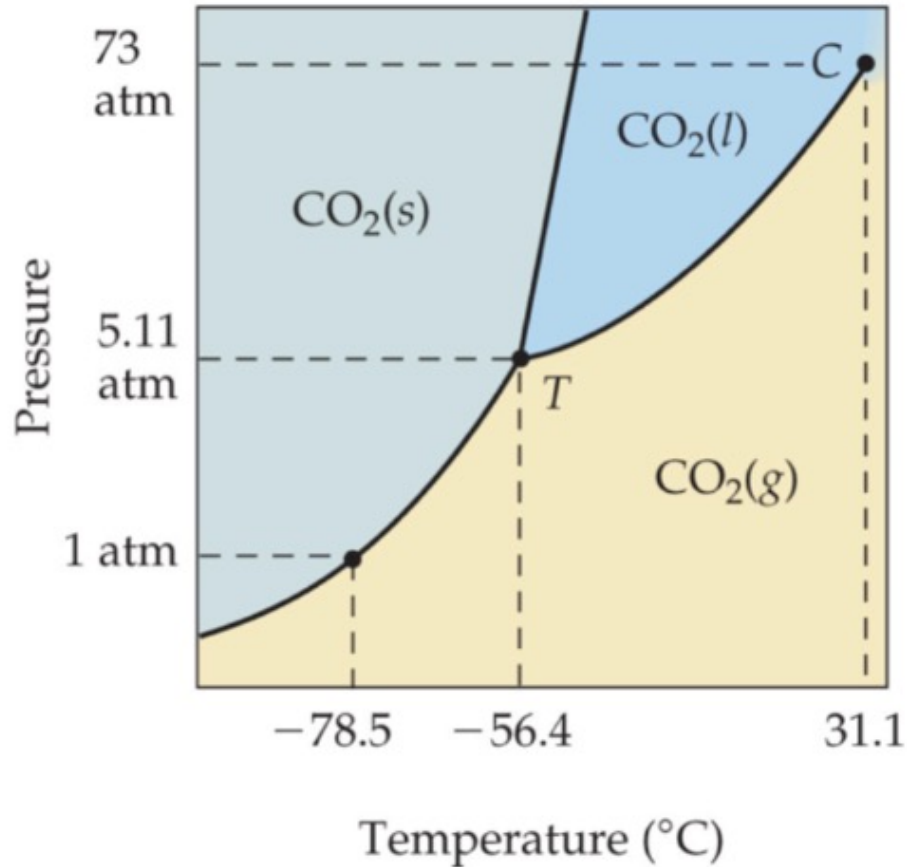
equilibrium between solid, liquid and gas

Critical point (C)

where the liquid-gas boundary terminates

<https://youtu.be/Y6S7bZbx4-s> (for chlorine)

Single component phase diagram: CO₂



Critical point (C)

where the liquid-gas boundary terminates

Triple point

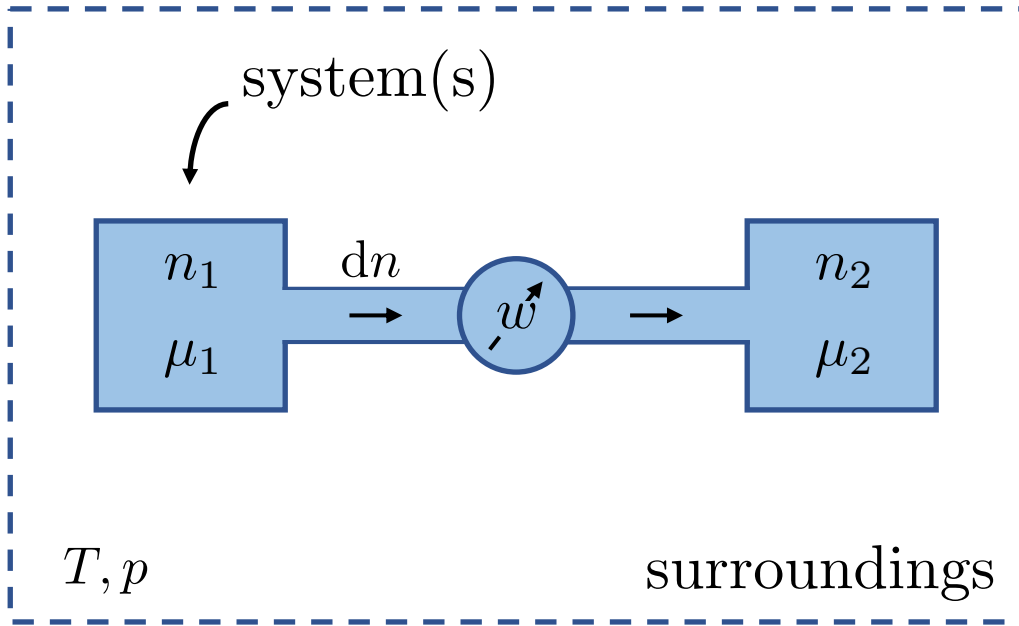
Pressure at triple point > p = 1 bar

Sublimation of dry-ice (solid CO₂) at p = 1 bar

<https://youtu.be/8Gj8dr6AsYg>

Condition for phase equilibrium

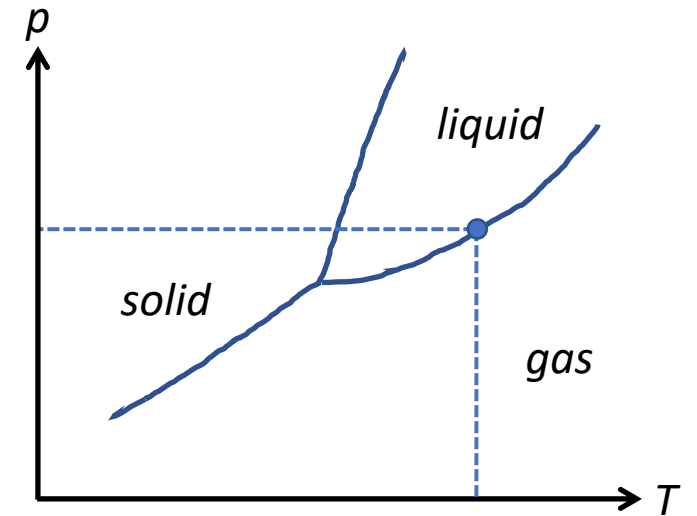
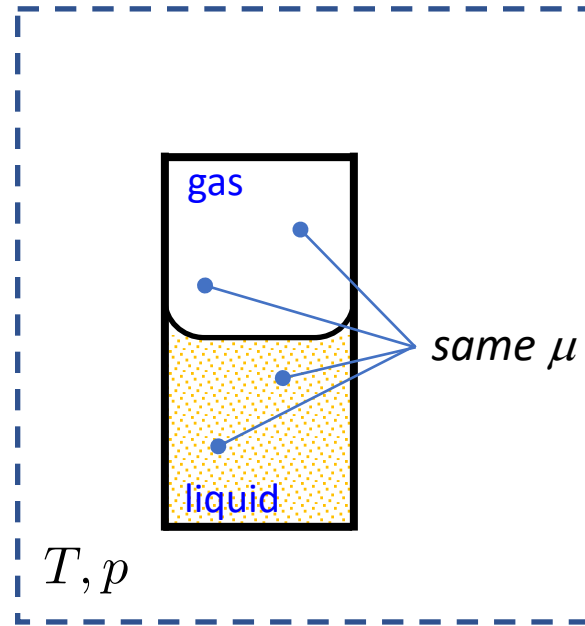
from lecture 1: chemical potential



$$\mu_1 = \mu_2$$

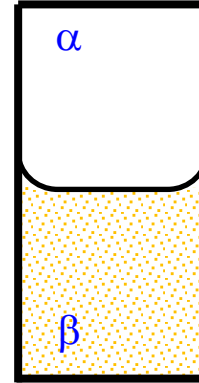
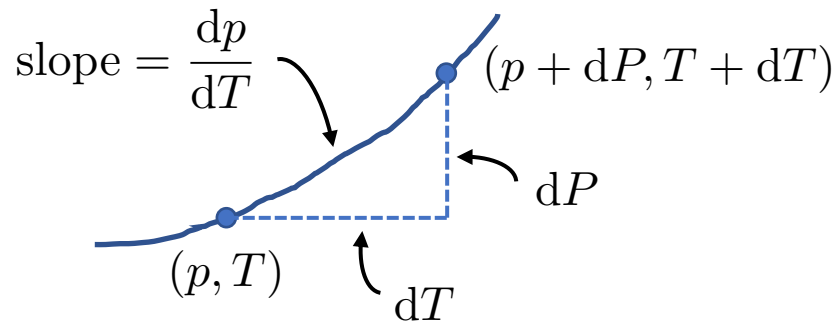
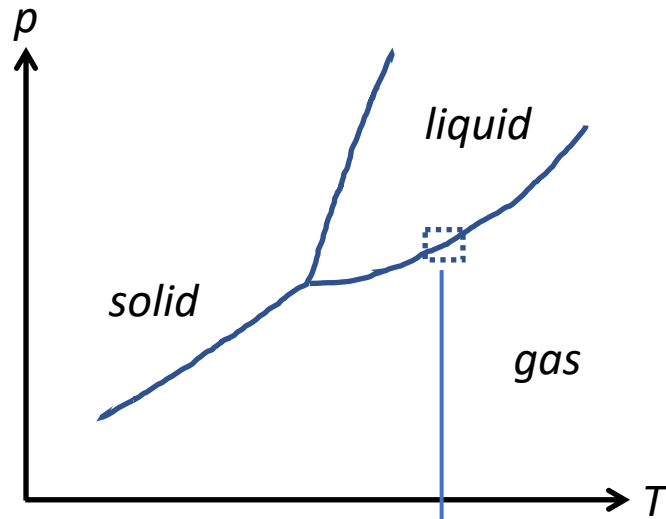
Chemical Equilibrium

For example: liquid-gas equilibrium



$$\mu_{\text{liquid}}(p, T) = \mu_{\text{gas}}(p, T)$$

Phase boundaries and their slopes



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

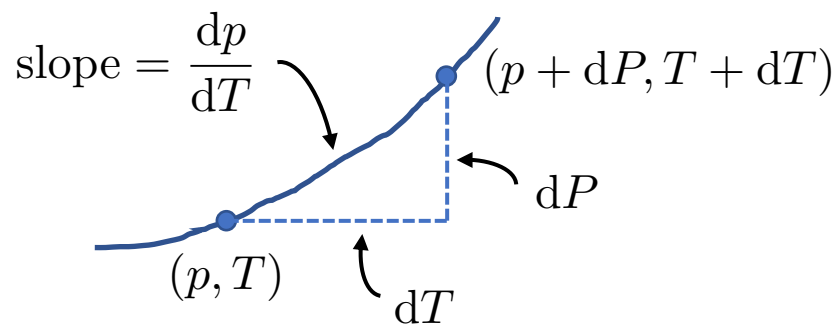
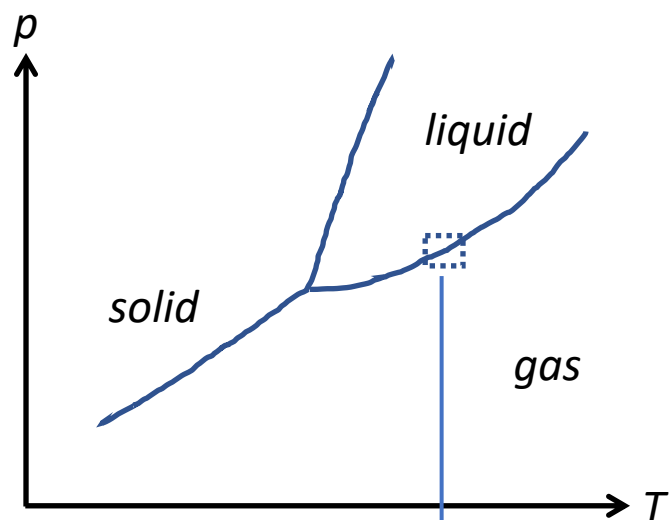
\downarrow

$$d\mu_{\alpha} = d\mu_{\beta}$$

from lecture 4: Gibbs-Duhem relation

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

Clapeyron equation



$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

$$\Delta S_m = \Delta_{\text{trs}} S = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}}$$

$$\Delta V_m = \Delta_{\text{trs}} V$$

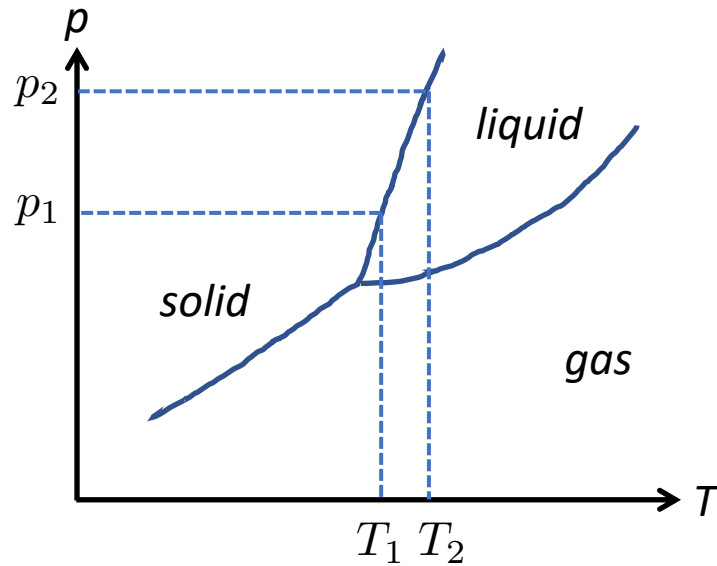
$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V} = \frac{\Delta_{\text{trs}} H}{T \Delta_{\text{trs}} V}$$

*exact and completely general
 $s \leftrightarrow l, l \leftrightarrow g, s \leftrightarrow g, \text{ etc.}$*



Benoit Clapeyron
(1799 – 1864)

Solid-liquid phase boundary

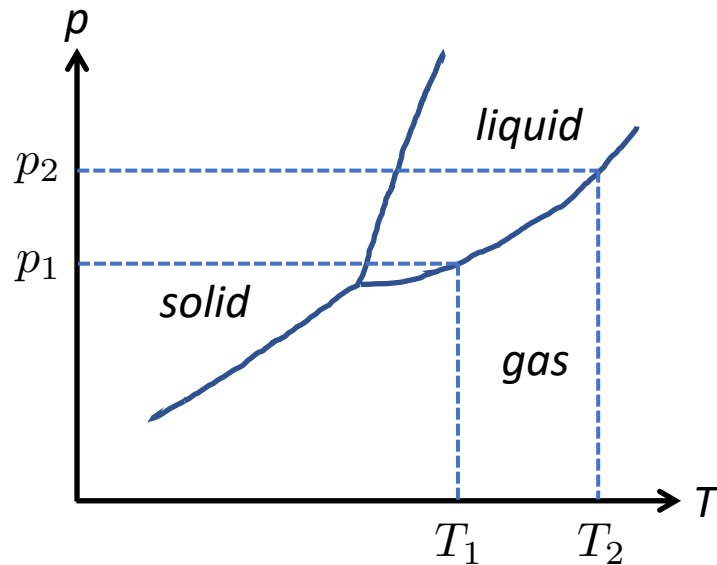


Integrated Clapeyron equation

$$p_2 - p_1 = \frac{\Delta_{\text{fus}} H}{\Delta_{\text{fus}} V} \ln \frac{T_2}{T_1}$$

Tells us how the melting temperature changes with the pressure

Liquid-gas and solid-gas phase boundaries



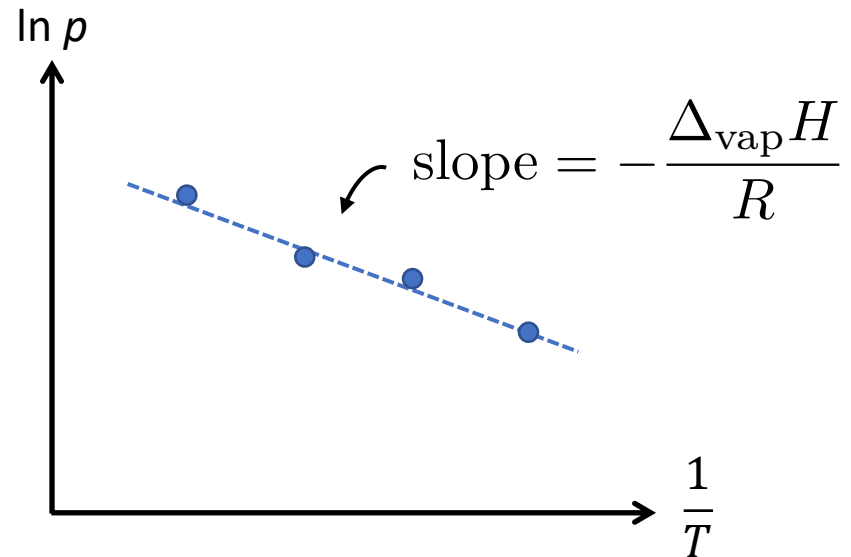
Clausius-Clapeyron equation

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{trs}} H}{RT^2}$$

Approximate and only applicable to $l \leftrightarrow g$ and $s \leftrightarrow g$

Tells us how the sublimation or boiling temperature changes with the pressure

Measuring $\Delta_{\text{trs}}H$ from (p, T) values along phase boundary



For example for liquid-gas equilibrium

Integrated Clausius-Clapeyron equation

$$\ln \frac{p_2}{p_1} = -\frac{\Delta_{\text{trs}}H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

See Problem Set 5 – Exercise 23

Today's lecture (5)

- Phase equilibria
 - Phase diagrams
 - Phase boundaries and their slopes
- **Chemical equilibrium**
 - (Reaction) mixtures
 - Condition for chemical equilibrium: reaction Gibbs energy $\Delta_r G$
 - Reaction quotient and the equilibrium constant
 - Effects of mixing

So far: single component systems

from lecture 4:

Fundamental equation: $dG = -SdT + Vdp + \mu dn$

$$G = \mu n$$

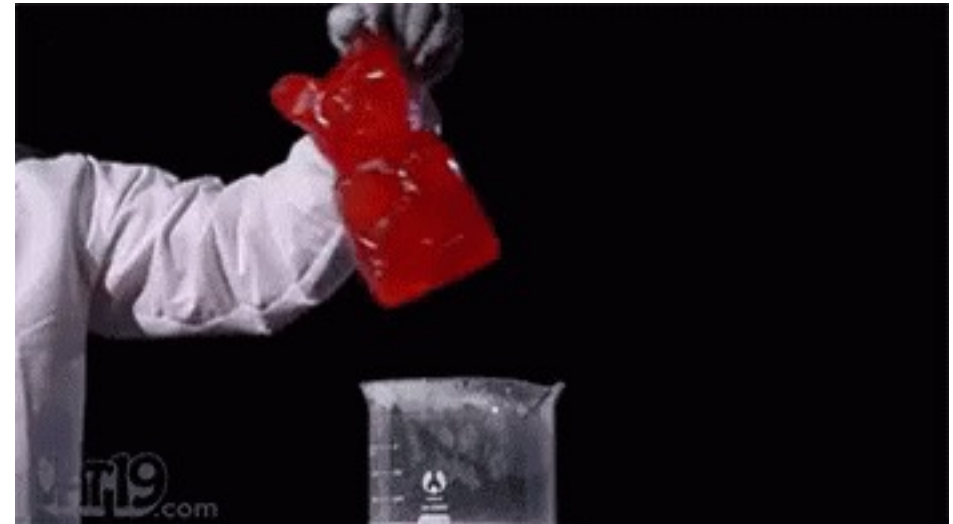
Gibbs-Duhem: $nd\mu = -SdT + Vdp$

Intensive variables μ , T and p are **not** independent of each other

But ... chemical reactions ...



MIXTURES!



Chemical reaction: mixture of reactants and products

Fundamental equation for dG and Gibbs-Duhem relation revisited

Single component system

$$dG = -SdT + Vdp + \mu dn$$

$$G = \mu n$$

$$nd\mu = -SdT + Vdp$$

Intensive variables μ , T and p are **not** independent of each other

Multicomponent system (mixture)

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

$$G = \sum_i \mu_i n_i$$

$$\sum_i n_i d\mu_i = -SdT + Vdp$$

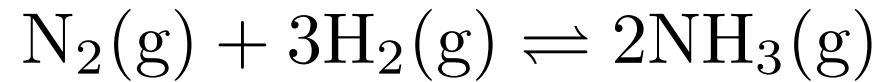
$$= 0 \quad \text{at constant } T, p$$

*Chemical potentials of different components in a mixture are **not** independent of each other*

Fundamental equation:

Gibbs-Duhem:

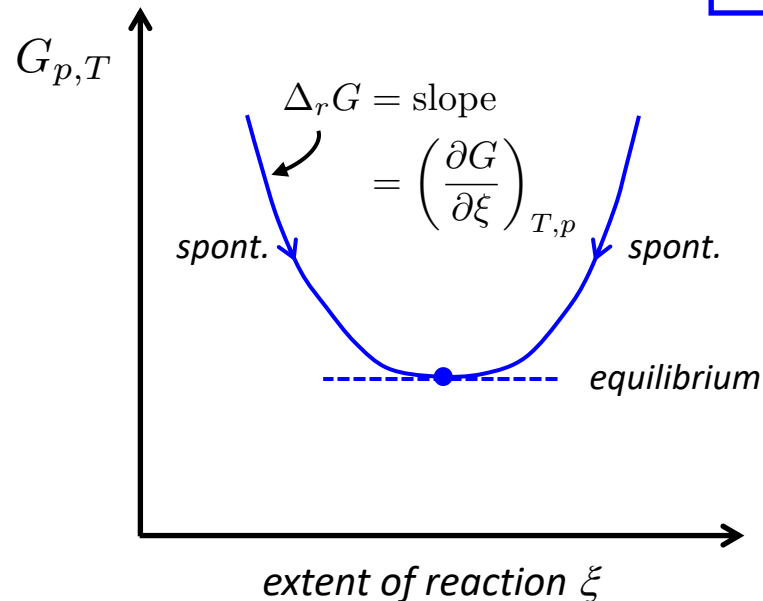
Condition for chemical equilibrium: ξ extent of reaction



$$\Delta_r G \equiv \left(\frac{\partial G}{\partial \xi} \right)_{T,p} = \sum_i \nu_i \mu_i$$

Reaction Gibbs energy

ξ : extent of reaction



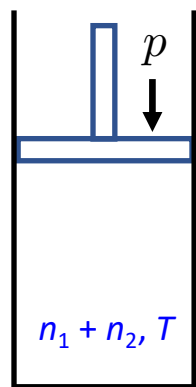
- $\Delta_r G < 0$: forward reaction ($\xi \uparrow$) spontaneous
- $\Delta_r G > 0$: backward reaction ($\xi \downarrow$) spontaneous
- $\Delta_r G = 0$: **equilibrium**

(Recall: $dG_{T,p} = 0$ at equilibrium)

The reaction quotient Q

Reaction mixture:

- All components i are perfect gases
- Chemical potentials: $\mu_i = \mu_i^\ominus + RT \ln \frac{p_i}{p^\ominus}$
- Partial pressures: $p_i = x_i p$



$$p_1 + p_2 = p$$

partial pressures

$$p_1 = x_1 p$$

$$p_2 = x_2 p$$

mole fractions

$$x_1 = \frac{n_1}{n_1 + n_2}$$

$$x_2 = \frac{n_2}{n_1 + n_2}$$

$$x_1 + x_2 = 1$$

Reaction Gibbs energy:

$$\Delta_r G = \sum_i \nu_i \mu_i$$

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

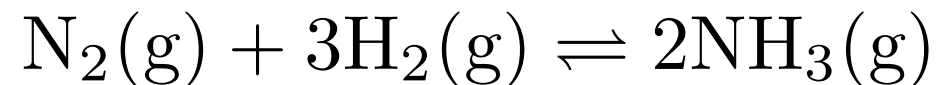
$$\rightarrow \Delta_r G^\ominus = \sum_i \nu_i \mu_i^\ominus$$

Standard reaction
Gibbs energy

$$\rightarrow Q = \prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i}$$

Reaction quotient

The reaction quotient Q : *example*



$$Q = \prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i}$$

i	ν_i	
$\text{N}_2(\text{g})$	-1	} -ve for reactants
$\text{H}_2(\text{g})$	-3	
$\text{NH}_3(\text{g})$	$+2$	} +ve for products

$$Q = \left(\frac{p_{\text{N}_2}}{p^\ominus} \right)^{-1} \left(\frac{p_{\text{H}_2}}{p^\ominus} \right)^{-3} \left(\frac{p_{\text{NH}_3}}{p^\ominus} \right)^2 = \frac{\left(p_{\text{NH}_3}/p^\ominus \right)^2}{\left(p_{\text{N}_2}/p^\ominus \right) \left(p_{\text{H}_2}/p^\ominus \right)^3}$$

The equilibrium constant K_p

Condition for chemical equilibrium:

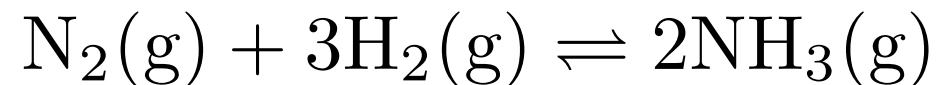
$$\Delta_r G = \sum_i \nu_i \mu_i = 0$$

$$\Delta_r G^\ominus = -RT \ln K_p \quad K_p = Q_{\text{eqm}} = \left[\prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i} \right]_{\text{eqm}}$$

Two of the most important equations in chemical thermodynamics

- Relates K_p for a chemical reaction to $\Delta_r G^\ominus = \sum_i \nu_i \Delta_f G_{m,i}^\ominus$ tabulated for $T = 298 \text{ K}$
- Note: K_p is dimensionless and independent of total pressure

The equilibrium constant K_p : *example*



$$\Delta_r G^\ominus = -32.9 \text{ kJmol}^{-1}$$

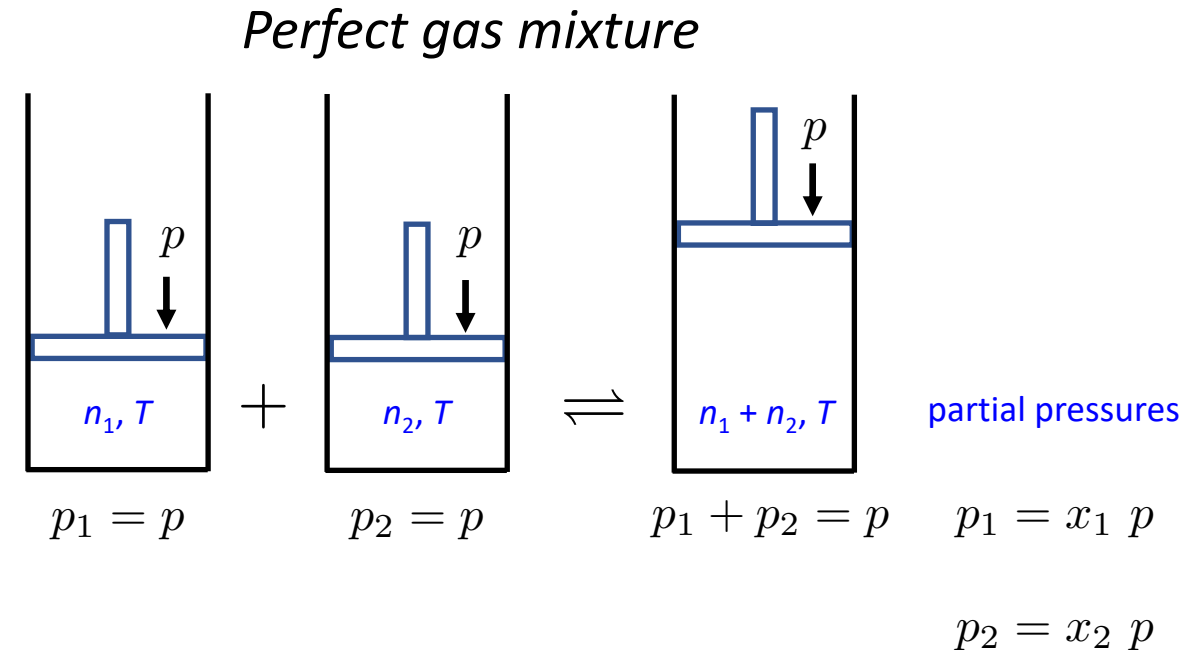
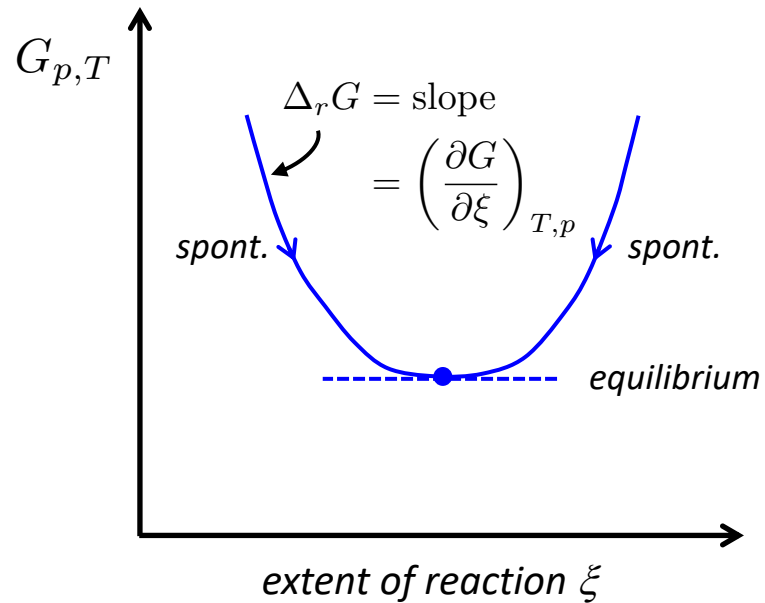
$$K_p = e^{-\Delta G^\ominus / RT} \longrightarrow K_p = 5.8 \cdot 10^5 = \frac{\left(p_{\text{NH}_3}/p^\ominus\right)^2}{\left(p_{\text{N}_2}/p^\ominus\right) \left(p_{\text{H}_2}/p^\ominus\right)^3}$$

- Equilibrium position: far to the right (products)
- Next: calculate the *composition* and how this *changes* with T and p

Today's lecture (5)

- Phase equilibria
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 - Condition for chemical equilibrium: reaction Gibbs energy $\Delta_r G$
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 - Effects of mixing

Why is there a minimum in the Gibbs energy? Mixing!



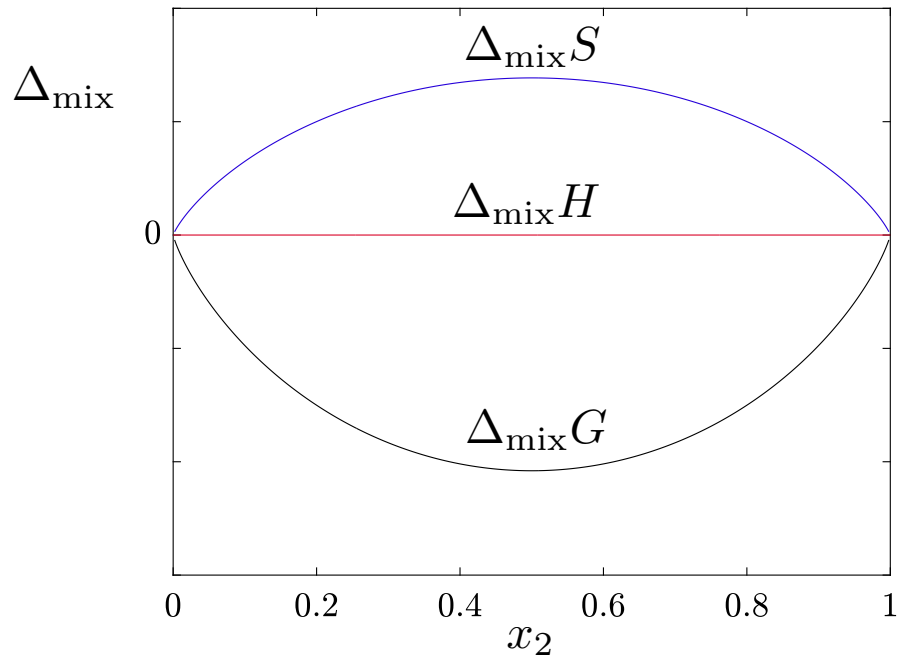
Show this by calculating:

$$\begin{aligned} \Delta_{\text{mix}} G &= G_{\text{after mixing}} - G_{\text{before mixing}} \\ &= G_{\text{final}} - G_{\text{initial}} \end{aligned}$$

$$\left(\text{Recall: } G = \sum_i \mu_i n_i \quad \text{and} \quad \mu_i = \mu_i^\ominus + RT \ln \frac{p_i}{p^\ominus} \right)$$

Effect of mixing leads to minimum in Gibbs energy

$$\Delta_{\text{mix}}G = nRT (x_1 \ln x_1 + x_2 \ln x_2) < 0$$



- Mixing of perfect gases is spontaneous ($\Delta_{\text{mix}}G < 0$)
- Mixing is purely entropy-driven

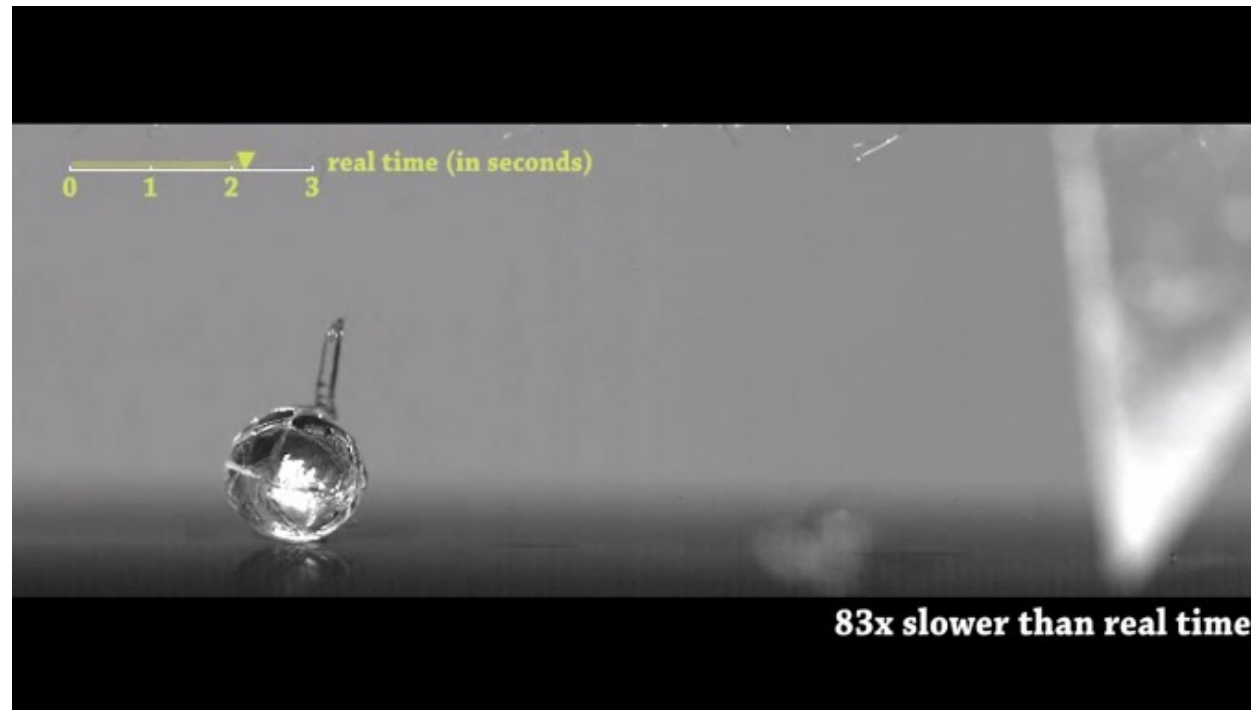
$$\Delta_{\text{mix}}S = - \left(\frac{\partial \Delta_{\text{mix}}G}{\partial T} \right)_p \rightarrow \Delta_{\text{mix}}H = 0$$

- Minimum in $\Delta_{\text{mix}}G \rightarrow$ minimum in $G_{p,T}(\xi)$

We will see the thermodynamics of mixing again in Lecture 7

And now for something completely different ...

My weekly 'freezing of undercooled water' clip



Freezing of undercooled water droplets from the outside in

Wildeman et al, Phys. Rev. Lett. 118, 084101 (2017)

Content of the course

- ✓ Introduction to Thermodynamics and gases
- ✓ The First Law of Thermodynamics
- ✓ Heat Capacities, Enthalpy and Thermochemistry
- ✓ The Second Law of Thermodynamics
- ✓ Helmholtz and Gibbs free energies
- ✓ Phase Transitions and Chemical Equilibrium
- **Chemical Equilibrium and Electrochemistry** → lecture 6
- Ideal solutions, Colligative properties
- Condensation in the Van der Waals Equation of State