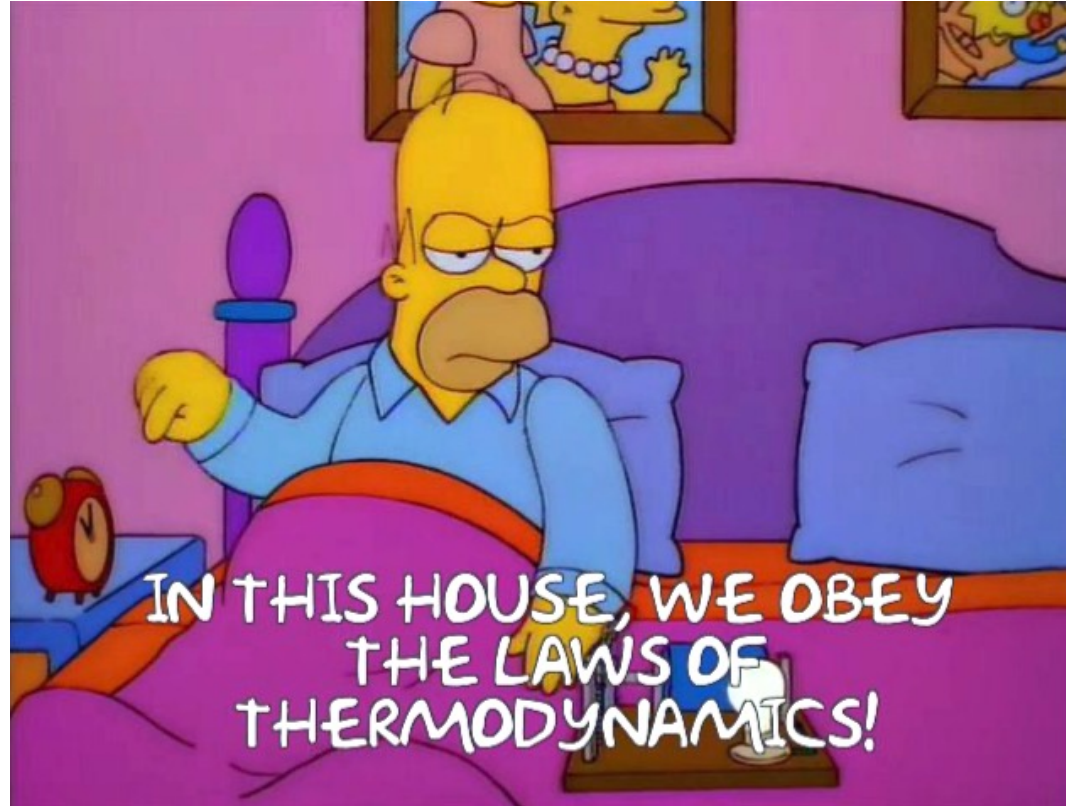


# Thermodynamics (lecture 4)



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# Summary lecture 3

- Entropy
- The Second Law of Thermodynamics
  - Clausius inequality
  
- Entropy changes of processes
  - Heating at constant volume
  - Heating at constant pressure
  
- Standard reaction entropy
- Carnot cycle

$$dS = \frac{dq_{\text{rev}}}{T} \quad S = k_B \ln W$$

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

$$\Delta S = S(T_2, V) - S(T_1, V) = \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

$$\Delta S = S(T_2, p) - S(T_1, p) = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

$$\Delta_r S^\ominus = \sum_i \nu_i S_{m,i}^\ominus(T)$$

# 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
- Electrochemistry
- Ideal solutions, Colligative properties
- Condensation in the Van der Waals Equation of State

→ Today, lecture 4

# Today's lecture (4)

- Spontaneous change and equilibrium (Clausius inequality)
  - Internal energy, enthalpy, Helmholtz energy, Gibbs energy
- Fundamental equations and total differentials
  - Maxwell relations
- Gibbs energy
  - Variation with temperature: Gibbs-Helmholtz equation
  - Variation with pressure
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previous lecture:

# The Clausius inequality (most accurate formulation of the Second Law)

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

$$(dS = dS_{\text{sys}})$$

$$\left( \Delta S = \int dS \right)$$

Clausius inequality

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

Spontaneous (irreversible) process:

Isolated system:  $dS > 0$

$$dS > \frac{dq}{T}$$

Reversible process (in any system):

Isolated system:  $dS = 0$

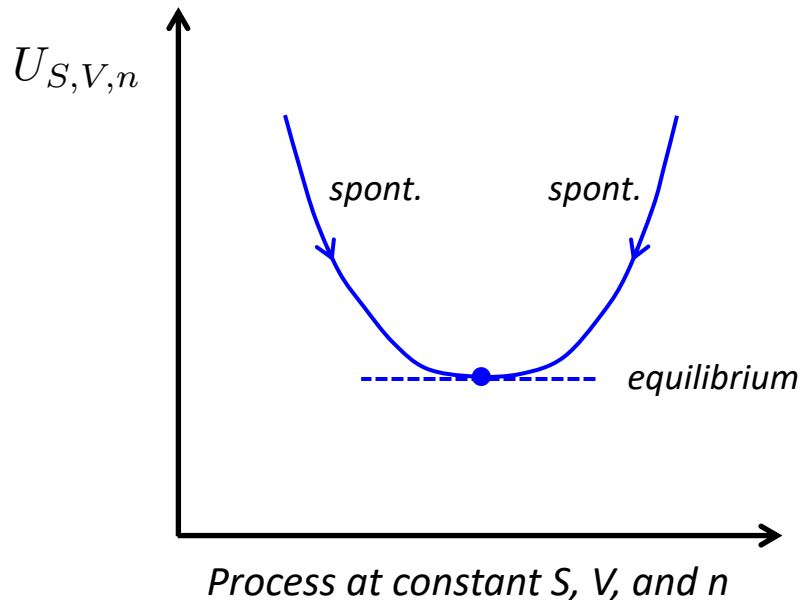
$$dS = \frac{dq_{\text{rev}}}{T}$$

# Spontaneous change and equilibrium: *internal energy*

What are the consequences of the Clausius inequality (i.e. the Second Law of Thermodynamics) for the change in internal energy?

$$dU \leq TdS - p_{ex}dV + \mu dn$$

(single component open system)



$$dU_{S,V,n} \leq 0 \quad \left\{ \begin{array}{l} dU_{S,V,n} < 0 \quad \text{spontaneous} \\ dU_{S,V,n} = 0 \quad \text{equilibrium} \end{array} \right.$$

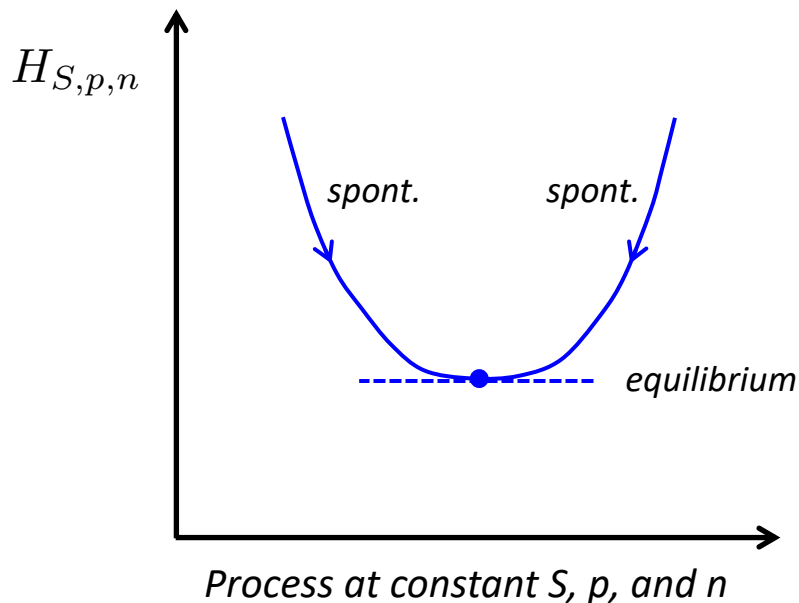
... not very useful condition ...

How do we control or fix entropy  $S$  in the lab?

# Spontaneous change and equilibrium: *enthalpy*

$$H = U + pV$$

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



$$dH_{S,p,n} \leq 0 \left\{ \begin{array}{l} dH_{S,p,n} < 0 \quad \text{spontaneous} \\ dH_{S,p,n} = 0 \quad \text{equilibrium} \end{array} \right.$$

*... still not very useful condition ...*

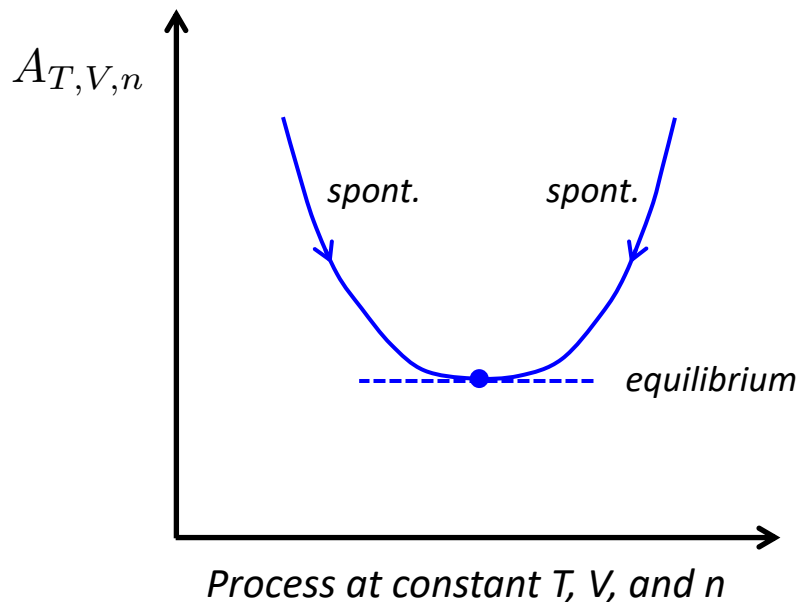
*How do we control or fix entropy  $S$  in the lab?*

**We need (two) other thermodynamic potentials**

# Spontaneous change and equilibrium: *Helmholtz energy*

$$A = U - TS$$

$$dA \leq -SdT - p_{ex}dV + \mu dn$$



$$dA_{T,V,n} \leq 0 \quad \left\{ \begin{array}{l} dA_{T,V,n} < 0 \quad \text{spontaneous} \\ dA_{T,V,n} = 0 \quad \text{equilibrium} \end{array} \right.$$

... more useful condition ...

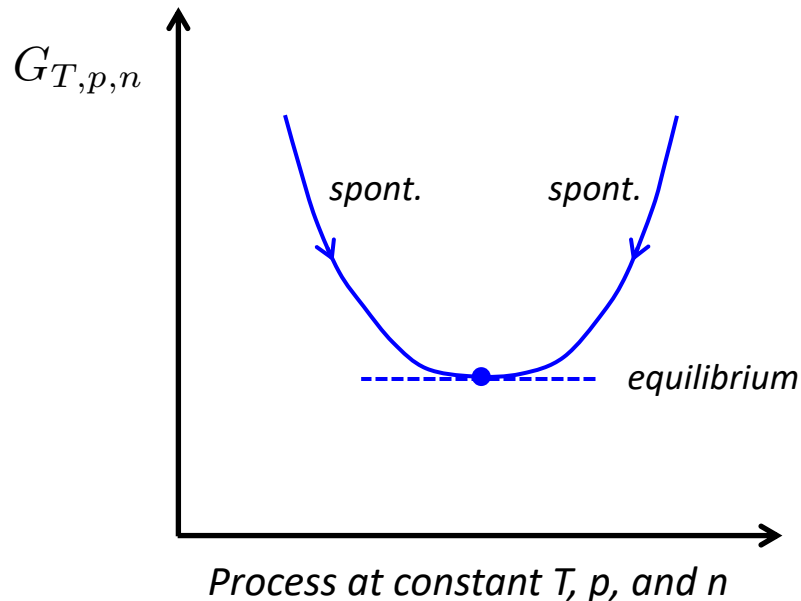
But processes in the lab happen at constant pressure ... ( $p = p_{ex}$  ... recall  $dq_p$  vs  $dq_v$ )



# Spontaneous change and equilibrium: *Gibbs energy*

$$G = H - TS$$

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



$$dG_{T,p,n} \leq 0 \left\{ \begin{array}{l} dG_{T,p,n} < 0 \quad \text{spontaneous} \\ dG_{T,p,n} = 0 \quad \text{equilibrium} \end{array} \right.$$

*... most useful condition ...*

*Most useful in chemical thermodynamics!*

# Spontaneous change and equilibrium: *Gibbs energy*

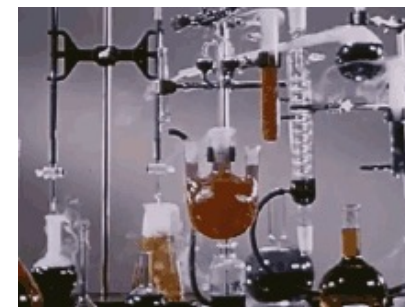
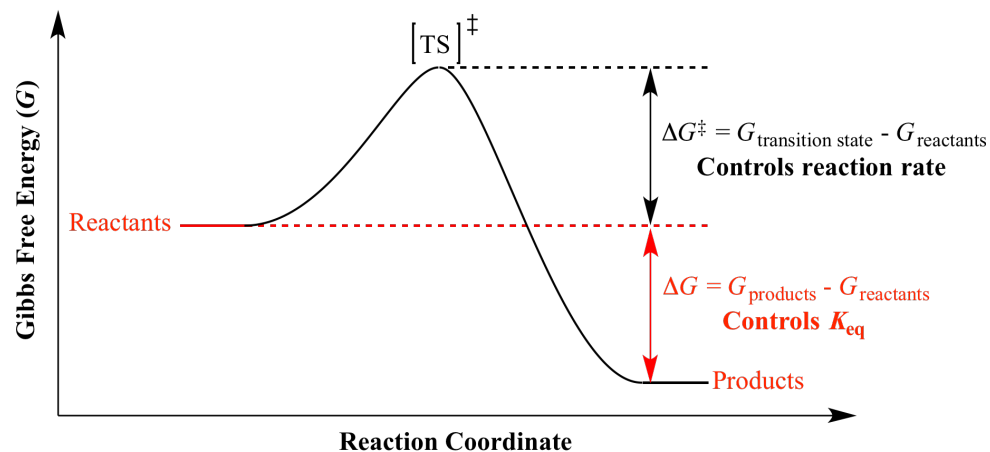
$$dG_{T,p,n} \leq 0 \left\{ \begin{array}{ll} dG_{T,p,n} < 0 & \text{spontaneous} \\ dG_{T,p,n} = 0 & \text{equilibrium} \end{array} \right. \longrightarrow \begin{array}{l} \Delta G < 0 \\ \Delta G = 0 \end{array}$$

*Most useful in chemical thermodynamics!*

*For example: used in 'Organic Chemistry 1' by Dr Paul Kouwer (3<sup>rd</sup> quarter)*



In the chemistry lab we also obey the Laws of Thermodynamics!



# Today's lecture (4)

- Spontaneous change and equilibrium (Clausius inequality)
  - Internal energy, enthalpy, Helmholtz energy, Gibbs energy
- **Fundamental equations and total differentials**
  - Maxwell relations
- Gibbs energy
  - Variation with temperature: Gibbs-Helmholtz equation
  - Variation with pressure
- Gibbs-Duhem relation
- Helmholtz and Gibbs *free* energies

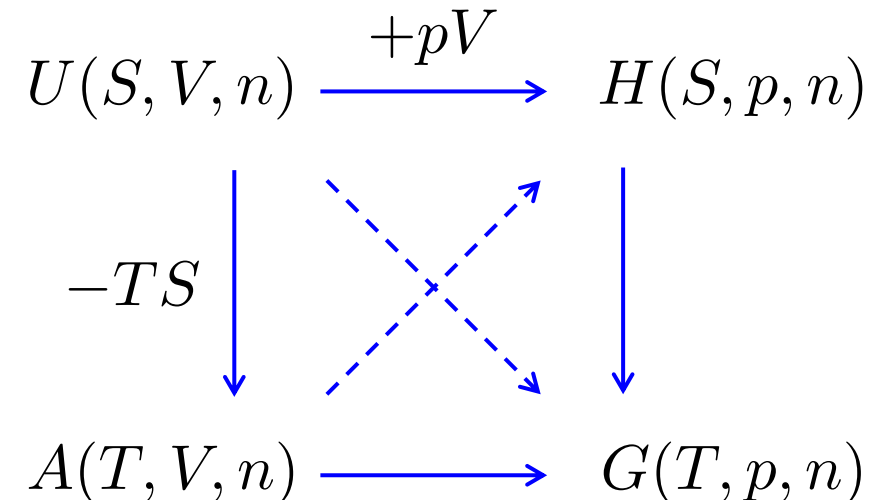
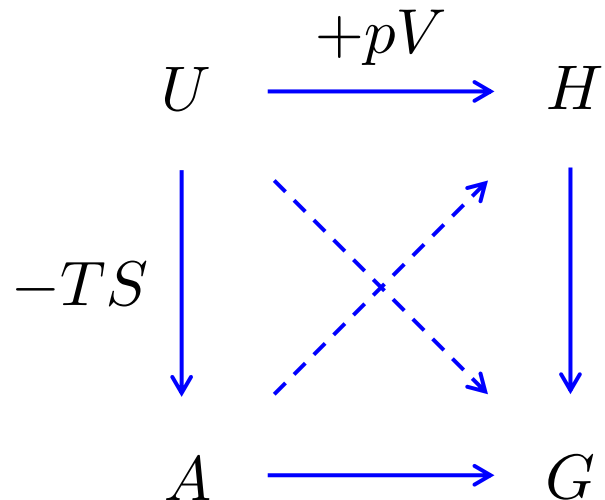
# The four energy state functions (thermodynamic potentials)

*Internal energy*  $U$

*Enthalpy*  $H = U + pV$

*Helmholtz energy*  $A = U - TS$

*Gibbs energy*  $G = H - TS = A + pV = U + pV - TS$



# The four fundamental equations

How the four energy state functions  $U$ ,  $H$ ,  $A$  and  $G$  vary with state variables  $n$ ,  $p$ ,  $V$ ,  $S$ ,  $T$

$$\begin{array}{llll} dU = TdS - pdV + \mu dn & \rightarrow & U(n, V, S) & \text{(hmm ...)} \\ dH = TdS + Vdp + \mu dn & \rightarrow & H(n, p, S) & \text{(hmm ...)} \\ dA = -SdT - pdV + \mu dn & \rightarrow & A(n, V, T) & \text{(better ...)} \\ dG = -SdT + Vdp + \mu dn & \rightarrow & G(n, p, T) & \text{(best!)} \end{array}$$

natural variables

*Most useful and appropriate energy state function (thermodynamic potential)?*

- *Depends on the context of the problem*
- *What are the relevant constraints/boundary condition/variables?*
- *In chemistry, the natural control variables are  $p$  and  $T \rightarrow$  Gibbs energy*

# Total differentials ('well-behaved functions')

Four energy state functions:  $U$ ,  $H$ ,  $A$  and  $G$  → all 'well-behaved'

$$f = f(x, y, z)$$

$$df = \left( \frac{\partial f}{\partial x} \right)_{y,z} dx + \left( \frac{\partial f}{\partial y} \right)_{x,z} dy + \left( \frac{\partial f}{\partial z} \right)_{x,y} dz$$

- Integral over closed path is zero:

$$\oint df = 0$$

- Order of differentiation is arbitrary:

$$\left( \frac{\partial^2 f}{\partial x \partial y} \right)_z = \left( \frac{\partial^2 f}{\partial y \partial x} \right)_z$$

# Maxwell relations

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

For example:

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

$$\begin{aligned}\left(\frac{\partial \mu}{\partial p}\right)_{T,n} &= \left(\frac{\partial V}{\partial n}\right)_{T,p} \\ &= V_m\end{aligned}$$

- entropy change with pressure for a perfect gas
- change of chemical potential with pressure  
(lecture 7)

Problem set 4: use Maxwell relation derived from fundamental equation for  $dA$  to show  $\Delta S = nR \ln \frac{V_2}{V_1}$

## Further Maxwell relations ...

$$dU = TdS - pdV + \mu dn \quad \longrightarrow \quad \left( \frac{\partial T}{\partial V} \right)_{S,n} = - \left( \frac{\partial p}{\partial S} \right)_{V,n}$$

$$dH = TdS + Vdp + \mu dn \quad \longrightarrow \quad \left( \frac{\partial T}{\partial p} \right)_{S,n} = \left( \frac{\partial V}{\partial S} \right)_{p,n}$$

$$dA = -SdT - pdV + \mu dn \quad \longrightarrow \quad \left( \frac{\partial p}{\partial T} \right)_{V,n} = \left( \frac{\partial S}{\partial V} \right)_{T,n}$$

... there are more ...

**In general: very useful for calculations in thermodynamics**

(but please don't learn them off the top of your head!)



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# Variation of Gibbs energy with temperature

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

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

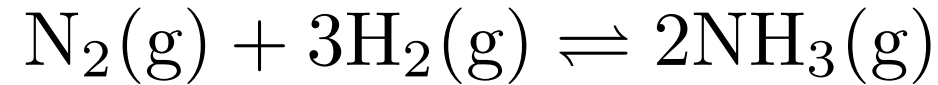
Gibbs-Helmholtz equation

Applies to both reactant and products in a chemical reaction under standard conditions

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

Lecture 6:  $T$ -dependence of equilibrium constant  $K_p$  (Van 't Hoff equation)

# Standard reaction Gibbs energy: $\Delta_r G^\ominus$



tabulated for  $T = 298 \text{ K}$

$$\Delta_r G^\ominus = \sum_i \nu_i \Delta_f G_{m,i}^\ominus(T)$$

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

compare:  $\Delta_r H^\ominus = \sum_i \nu_i \Delta_f H_{m,i}^\ominus(T)$

$$\Delta_r S^\ominus = \sum_i \nu_i S_{m,i}^\ominus(T)$$

at constant temperature

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

# Variation of Gibbs energy with pressure

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

For a perfect gas:

$$G(p_2, T) = G(p_1, T) + nRT \ln \frac{p_2}{p_1}$$

For solids and liquids:

$$G(p_2, T) = G(p_1, T) + V(p_2 - p_1)$$

Problem set 4:

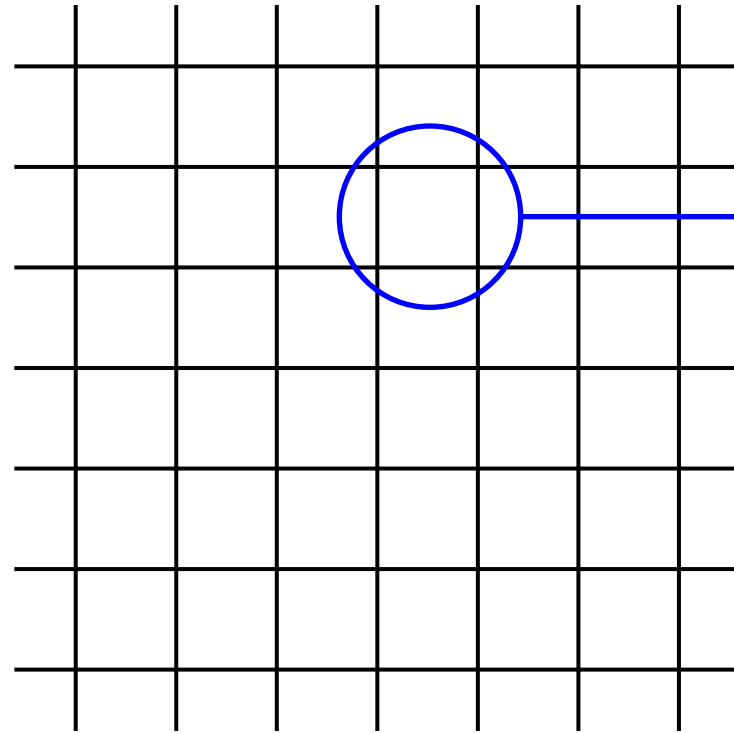
use this to calculate pressure at which the graphite  $\rightarrow$  diamond transition becomes favourable

<https://youtu.be/JyHFPV-j8Gs>

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# Extensive and intensive variables



Extensive:  $dU, dV, dn, \dots$   
Intensive:  $T, P, \mu, \dots$

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Extensive:  $U, V, n, \dots$   
Intensive:  $T, P, \mu, \dots$

# Extensive vs intensive properties (Euler's equation)

A problem from your maths course:

4. The internal energy  $U$  of a thermodynamical system depends on the quantities  $S$  (entropy),  $V$  (volume) and  $n$  (amount of substance). This means that  $U = U(S, V, n)$  is a function in several variables. According to the First and Second Laws of Thermodynamics, the infinitesimal change  $dU$  in the internal energy of a system (if only expansion work is done on the system) is given by

$$dU = T dS - P dV + \mu dn$$

with  $T$  the temperature of the system,  $P$  the pressure and  $\mu$  the chemical potential.

- (a) Show that the temperature, the pressure and the chemical potential are given by

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n}, \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,n}, \quad \mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}.$$

- (b) Using the fact that  $U(S, V, n)$  is a well-behaved function, show that

$$\left(\frac{\partial P}{\partial n}\right)_{S,V} = -\left(\frac{\partial \mu}{\partial V}\right)_{S,n}$$

which is one of the Maxwell relations that can be derived from the laws of thermodynamics.

- (c) The internal energy  $U$  is an extensive property of a system. Mathematically, this implies that

$$U(\lambda S, \lambda V, \lambda n) = \lambda U(S, V, n).$$

Take the derivative of both sides of this property with respect to  $\lambda$  (using the chain rule) and substitute  $\lambda = 1$  to show that

$$U(S, V, n) = S \frac{\partial U}{\partial S} + V \frac{\partial U}{\partial V} + n \frac{\partial U}{\partial n}.$$

- (d) Conclude from the previous parts that  $U(S, V, n) = TS - PV + \mu n$ .

- (e) Derive the Gibbs-Duhem equation:

$$S dT - V dP + n d\mu = 0.$$

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



Extensive properties machinery

$$U(\lambda S, \lambda V, \lambda n) = \lambda U(S, V, n)$$

$$U = \sum_i \left(\frac{\partial U}{\partial x_i}\right)_{x_{j \neq i}} x_i$$



$$U = TS - pV + \mu n$$

Euler's equation

# Gibbs-Duhem relation

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

Gibbs-Duhem relation

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

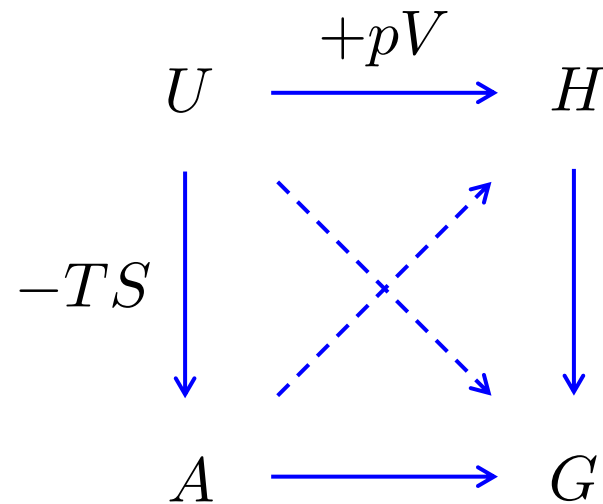
Key equation:

- Intensive variables  $\mu$ ,  $T$  and  $p$  are **not** independent of each other
- Phase transitions (lecture 5)
- Chemical equilibrium (lectures 5 and 6)
- Chemical potential of perfect gas, etc..



# Helmholtz and Gibbs *free* energies

*parts of the internal energy that is available (free) for (useful) work*



**Internal energy:**

$$U = TS - pV + \mu n$$

**Helmholtz free energy:**

that part of the internal energy available for work

$$A = -pV + \mu n$$

**Gibbs free energy:**

that part of the internal energy available for non-expansion work

$$G = \mu n$$

And now for something completely different ...

*My weekly 'freezing of undercooled water' clip*



# Content of the course

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