

Thermodynamics tutorhour 4

November 29th 2023

- Questions about the lecture or course matter?
- Gibbs energy

Last week in exercise 11d we were able to calculate the entropy change of one mole of water at 10 °C that is cooled to 0 °C and then freezes to form ice at 0 °C.

ΔS_{sys} turned out to be negative (!). However, the process still runs as we know, because ΔS_{tot} is positive (and thus the 2nd law of thermodynamics is obeyed). It must be noted that we were not able to calculate the latter.

So, if we want to look at our system only and predict whether the process is running spontaneously or not, it's more convenient to make use of ΔG .

The Clausius inequality (irreversible spontaneous process):

$$dq - TdS_{sys} \leq 0$$

$$\text{or} \quad dq \leq TdS_{sys}$$

- In this course S is used instead of S_{sys}

- If there is no other work involved than expansion

$$dU = dq + dw \quad \text{and} \quad dw = -p_{ext}dV + \mu dn + \dots$$

work and chemical work,

the following inequality holds: $dU \leq TdS + (-p_{ext}dV + \mu dn)$

At constant S , V and n this inequality changes in: $dU_{S,V,n} \leq 0$

For other energies holds:

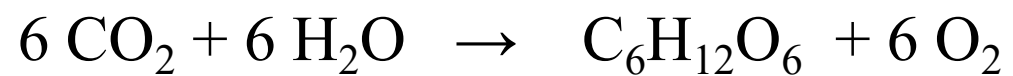
$$dH_{S,p,n} \leq 0$$

$$dA_{T,V,n} \leq 0$$

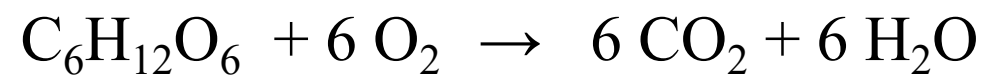
$$dG_{T,p,n} \leq 0$$



Spontaneous process?



$$\Delta_r G = + 28.3 \cdot 10^5 \text{ J mol}^{-1} > 0$$



$$\Delta_r G = - 28.3 \cdot 10^5 \text{ J mol}^{-1} < 0$$

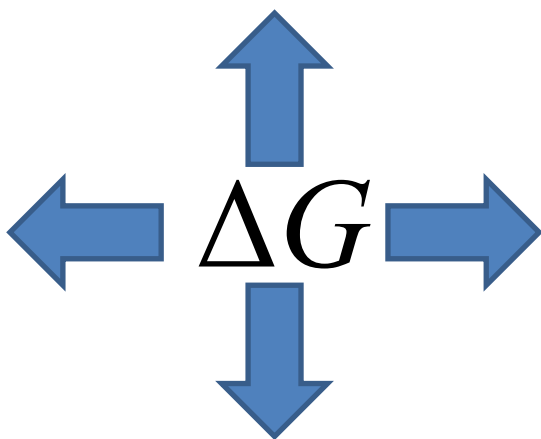
**Electro-chemistry
(lecture 6)**

$$\Delta G = w'_{\max}$$

at equilibrium:
 $\Delta G = 0$ and $Q = K$
so
 $\Delta G^\theta = -RT \ln K$
(lecture 5)

mixing
lowering of freezing point
elevation of boiling point
osmotic pressure

**Colligative
properties
(lecture 7)**



Does this
reaction
occur?
Yes, if...

$$\Delta G \leq 0$$

$$\Delta G = \Delta G^\theta + RT \ln Q$$

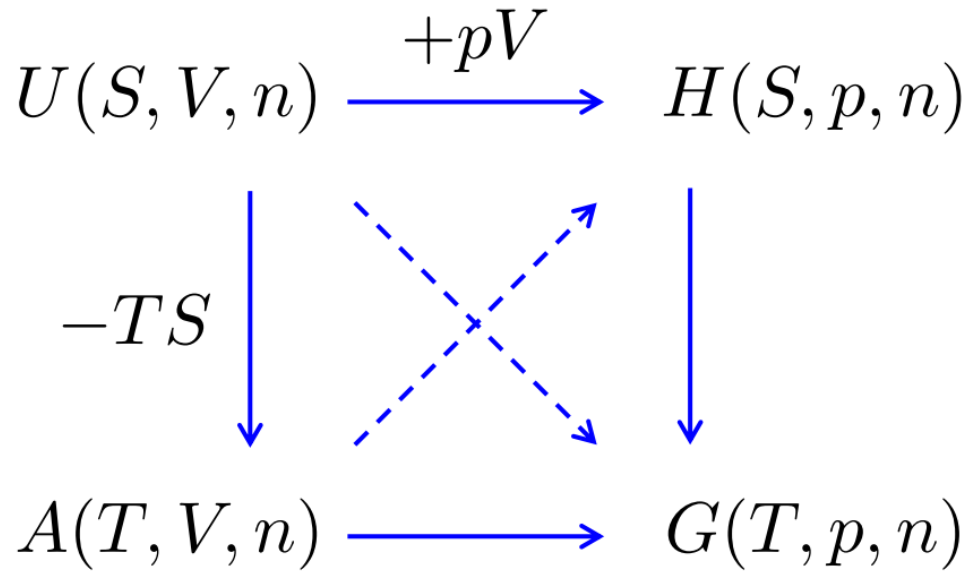
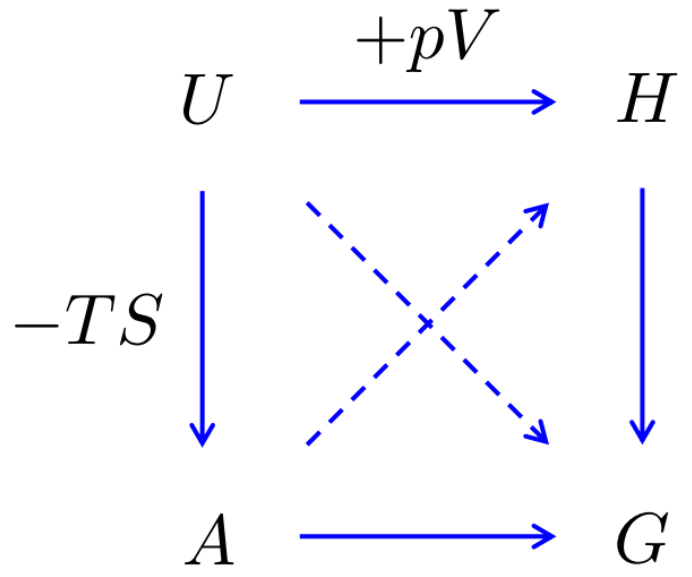
The four energy state functions (thermodynamic potentials)

Internal energy U

Enthalpy $H = U + pV$

Helmholtz energy $A = U - TS$

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



Maxwell relations

Question 1: Derive the fundamental equation of the Helmholtz energy:

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

starting from the equation of state $A \equiv U - TS$

$$A = U - TS$$

$$dA = dU - d(TS)$$

$$dA = (dq + dw) - d(TS)$$

$$dA = ~~TdS~~ + (-pdV + \mu dn) - SdT - ~~TdS~~$$

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

Maxwell relations

Fundamental equation of the Gibbs energy: $dG = -SdT + Vdp + \mu dn$

Take the partial derivative of $G(T, p, n)$ towards the variables T, p and n :

$$dG = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{p,n}}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial p}\right)_{T,n}}_V dp + \underbrace{\left(\frac{\partial G}{\partial n}\right)_{T,p}}_{\mu} dn$$

We can now find many Maxwell relations, for example how the entropy S depends on the number of moles n :

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

Maxwell relations

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

$$dG = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{p,n}}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial p}\right)_{T,n}}_V dp + \underbrace{\left(\frac{\partial G}{\partial n}\right)_{T,p}}_{\mu} dn$$

Question 2: Derive this Maxwell relation using the fundamental equation and the partial derivative of G .

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

Keep the $\partial/\partial n$ and look what S is in the fundamental equation

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

If you are deriving towards n , keep the other variables constant

Now swap ∂n and ∂T within the brackets and the boundary conditions outside the brackets. Then substitute the corresponding term from the fundamental equation.

G is our compass:

$$dG = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{p,n}}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial p}\right)_{T,n}}_V dp + \underbrace{\left(\frac{\partial G}{\partial n}\right)_{T,p}}_{\mu} dn$$

Question 3: Derive a relation to calculate ΔG going from p_1 to p_2 at constant T and n .

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

$$dG = V dp$$

$$\int dG = \int V dp$$

in case of a perfect gas

$$pV = nRT$$

$$\int dG = \int \frac{nRT}{p} dp = nRT \int \frac{1}{p} dp$$

$$\Delta G = nRT \ln \frac{p_2}{p_1}$$

$$\text{or: } G(p_2) = G(p_1) + nRT \ln \frac{p_2}{p_1}$$

in case of a solid or liquid

V is more or less constant

$$\int dG = \int V dp = V \int dp$$

$$\Delta G = V \Delta p$$

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

Fundamental equation of the internal energy: $dU = TdS - pdV + \mu dn$

Take the partial derivative of $U(S, V, n)$ towards the variables S, V and n :

$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,n}}_T dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,n}}_{-p} dV + \underbrace{\left(\frac{\partial U}{\partial n}\right)_{S,V}}_{\mu} dn$$

Mathematics and extensive quantities:

$$U = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,n}}_T S + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,n}}_{-p} V + \underbrace{\left(\frac{\partial U}{\partial n}\right)_{S,V}}_{\mu} n$$

This leads to Euler's equation:

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

Question 4: Show, starting from the definition of G and Euler's equation,

that $d\mu = -S_M dT + V_M dp$ (Gibbs-Duhem relation)

$$G = H - TS = U + pV - TS = \cancel{TS} - \cancel{pV} + \mu n + \cancel{pV} - \cancel{TS} = \mu n$$

$$\text{so: } dG = \mu dn + nd\mu$$

fundamental equation: $dG = -SdT + Vdp + \mu dn$ leads to: $nd\mu = -SdT + Vdp$

dividing each term by n leads to the Gibbs-Duhem relation: $d\mu = -S_M dT + V_M dp$

Exercise 16

a) $n = 1.0$ mole, $T_i = 25\text{ °C} = 298\text{ K}$, $p_i = 5.0$ bar, $p_f = 1.0$ bar
 $dT = 0$ (isothermal), $p = p_{\text{ext}}$ (reversible)

- $dT = 0 \Rightarrow T_f = T_i = 298\text{ K}$

- $dw = -pdV = -(nRT/V) dV$

$$w = -\int (nRT/V) dV = -nRT \int (1/V) dV = -nRT \ln(V_f/V_i) = -nRT \ln(p_i/p_f)$$

$$w = -1.0 \times 8.3145 \times 298 \times \ln(5.0/1.0) = -4.0\text{ kJ}$$

- $U = 3/2 nRT \Rightarrow \Delta U = 3/2 nR \Delta T$

$$\Delta T = 0 \Rightarrow \Delta U = 0\text{ J}$$

- $dU = dq + dw = 0 \Rightarrow dq = -dw$

$$q = -w = +4.0\text{ kJ}$$

- $dS = dq_{\text{rev}} / T$

$$\int dS = \int dq_{\text{rev}} / T \Rightarrow \Delta S = q_{\text{rev}} / T = +4.0 \cdot 10^3\text{ J} / 298\text{ K} = 13.4\text{ J/K}$$

- $A = U - TS \Rightarrow dA = dU - TdS - SdT$

$$dT = 0 \text{ and } dU = 0 \Rightarrow dA = -TdS \Rightarrow \Delta A = -T \Delta S = -298 \times 13.4 = -4.0\text{ kJ}$$

- $G = H - TS \Rightarrow dG = dH - TdS - SdT$

$$dT = 0 \text{ and } dH = dU + d(pV) = dU + d(nRT) = dU + nRdT = 0 + 0 = 0\text{ J}$$

$$\Delta G = -T \Delta S = -298 \times 13.4 = -4.0\text{ kJ}$$

Exercise 16

b) $n = 1.0$ mole, $T_i = 25\text{ °C} = 298\text{ K}$, $p_i = 5.0\text{ bar}$, $p_f = 1.0\text{ bar}$

$dT = 0$ (isothermal), at constant p : $p_{\text{ext}} = 1.0\text{ bar}$ (irreversible)

- state functions are independent of the path, so they will be the same as for the reversible process:

$$T_f = 298\text{ K}$$

$$\Delta U = 0\text{ J}$$

$$\Delta S = 13.4\text{ J/K}$$

$$\Delta A = -4.0\text{ kJ}$$

$$\Delta G = -4.0\text{ kJ}$$

- q and w are non-state-functions

c) $w = \int dw = - \int p dV = -p \int dV = -p_{\text{ext}}(V_f - V_i)$

$$pV = nRT \quad \Leftrightarrow \quad V_i = nRT/p_i \quad \text{and} \quad V_f = nRT/p_f$$

$$w = -p_{\text{ext}}(V_f - V_i) = -p_{\text{ext}} nRT (1/p_f - 1/p_i)$$

$$= -1.0 \times 1.0 \times 8.3145 \times 298 \times (1 - 1/5.0) = -2.0\text{ kJ}$$

$$dU = dq + dw = 0 \quad \Leftrightarrow \quad dq = -dw$$

$$q = -w = +2.0\text{ kJ}$$