Thermodynamics

Remedial Lecture 3

03 – 03 – 2022

Course outline

- 5 sessions:
  - 1 Basics, (state) functions, ideal gas, internal energy, work, heat, Enthalpy
  - 2 Energy, Entropy
  - **3 Energy, chemical reactions**
  - 4 Electrochemistry
  - 5 Colligative properties & statistical thermo

Course today

- Energy effects during reaction
- Activity and activity coefficient
- Chemical equilibrium constant
- ξ

- Goals of today:
  - To be able to calculate enthalpy, entropy and gibbs free energy of reactions via the formation energies
  - Calculate equilibrium reactions
  - Know what acitivity is and activity coefficient

Study material

- Study guide (page ….. & ..)
- Atkins (see study guide)
- Relevant formulas on formula sheet

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \Delta_r G^{\ominus} + RT\ln Q \quad \text{with} \quad Q = \prod_i a_i^{\nu_i}$$

$$RT\ln K = -\Delta_r G^{\ominus}$$

$$\mu_i = \mu_i^{\ominus} + RT\ln a_i = \mu_i^{\ominus} + RT\ln\frac{P_i}{P^{\ominus}}$$

$$G_{P,T} = \sum_i \mu_i n_i$$

$$\sum_j n_j \mathrm{d}\mu_j = 0$$

Activity instead of concentration

- activity (symbol a) is a measure of the *“effective concentration”* of a species in a mixture
- the activity depends on any factor that alters the chemical potential. Such factors may include: concentration, temperature, pressure, interactions between chemical species, electric fields, etc. Depending on the circumstances, some of these factors may be more important than others.
- The difference between activity and other measures of composition arises because molecules in non-ideal gases or solutions interact with each other, either to attract or to repel each other.

i.e ion – ion and ion – water interactions

- **Used to explain discrepancies between ideal solutions and real solutions (or mixtures of gases)**

- activity is dimensionless (so, there's no unit)
- Activity of a gas, use the ratio of the effective pressure to the standard state pressure:

  $a_{gas} = P / Pº$ a_{gas} is a ratio with **no units.**

- Activity of a solute in solution:

  $a_{solute} = C / Cº$ a_{solute} is a ratio with **no units.**

- The activity of pure substances in condensed phases (solid or liquids) is taken as unity (the number 1)
- Relation between concentration and activity by $a = \gamma [C]$ mol/L
  - *γ = activity coefficient*
- Relation between molality and activity by $a = \gamma\ b$ mol/kg solvent
  - *γ = activity coefficient*
- Relation between mol fraction and activity by $a = \gamma\ x$ mol/mol total
  - *γ = activity coefficient*
- ***ALL THREE*** **γ 's have different values………..**
- The lower the concentration of all solute particles in the solution, the closer the value of γ for each solute approaches 1

ξ

- Progress of the reaction
- ξ = 1 when one of the reactants is depleted
  - So find out which reactant is depleted first
  - In equilibrium reactions, ξ will never be 1

Q versus K

- Q is always twata/twifota $Q = \prod_i a_i^{\nu_i}$

- In general

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \Delta_r G^{\ominus} + RT \ln Q$$

- At equilibrium only; K = Q and $(\mathrm{d}G)_{P,T,W'} = 0.$

$$RT \ln K = -\Delta_r G^{\ominus}$$

Calculation on reactions

- See tutor hour next two slides
- Followed by the formal way of presenting

How much heat is released during a chemical reaction?

If the reaction takes place under normal (laboratory) conditions, we may assume that the pressure is not influenced by the reaction.

$$Q_p = \Delta H$$

$\Delta_r H^\Theta$ is defined as the $\Delta_f H^\Theta$ (products) – $\Delta_f H^\Theta$ (reactants)

The $\Delta_f H^\Theta$ of elements = 0.

In formula:

$$\Delta_\mathrm{r} H = \sum H_{\mathrm{f},products} - \sum H_{\mathrm{f},reactants}$$

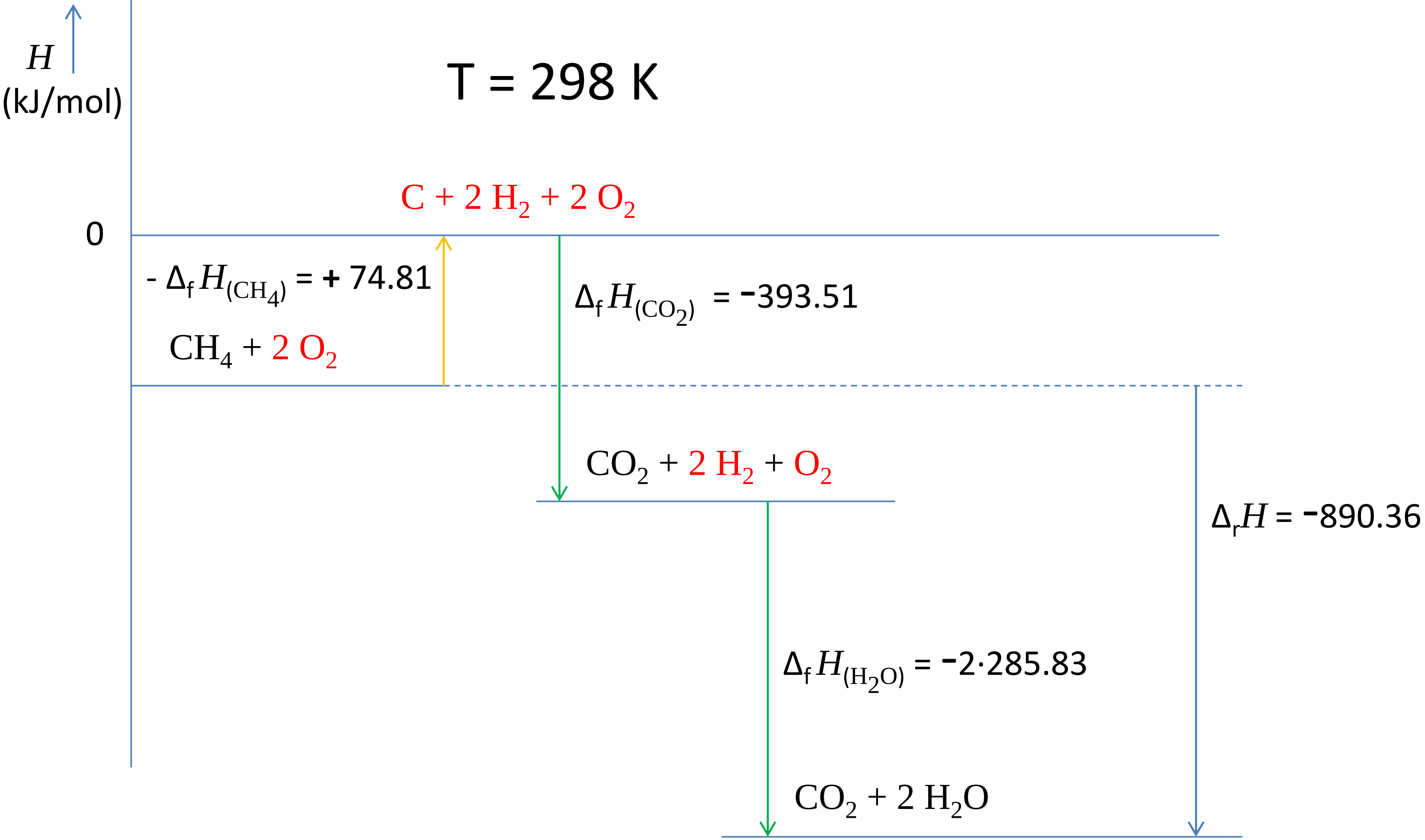
For example: the combustion of methane

$$CH_4(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l)$$

$\Delta_r H = -(-\,74.81) - 2 \cdot 0 + (-\,393.51) + 2 \cdot (-\,285.83) = -\,890.36$ kJ/mol CH_4

The combustion of methane in an enthalpy diagram:

T = 298 K



H (kJ/mol)

0

$C + 2 H_2 + 2 O_2$

$-\ \Delta_f H_{(CH_4)} = +\ 74.81$

$CH_4 + 2 O_2$

$\Delta_f H_{(CO_2)} = -393.51$

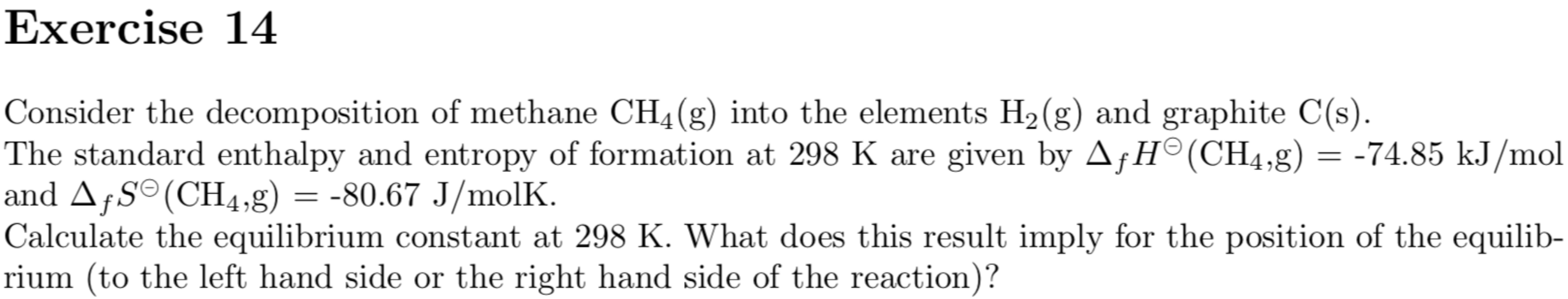
$CO_2 + 2 H_2 + O_2$

$\Delta_r H = -890.36$

$\Delta_f H_{(H_2O)} = -2\cdot 285.83$

$CO_2 + 2 H_2O$

The Formal way



Exercise 14

Consider the decomposition of methane CH_4(g) into the elements H_2(g) and graphite C(s).
The standard enthalpy and entropy of formation at 298 K are given by $\Delta_f H^\ominus(\mathrm{CH_4,g})$ = -74.85 kJ/mol and $\Delta_f S^\ominus(\mathrm{CH_4,g})$ = -80.67 J/molK.
Calculate the equilibrium constant at 298 K. What does this result imply for the position of the equilibrium (to the left hand side or the right hand side of the reaction)?

Exercise 14

The equilibrium is given by

$$CH_4(g) \rightleftarrows C(s) + 2H_2(g)$$

This is the inverse reaction of the formation of CH_4(g). The products are elements in their reference state at 298 K (C(s) and H_2(g)), so $\Delta_f G^\ominus(C,s) = \Delta_f G^\ominus(H_2,g) = 0$. The standard reaction Gibbs free energy $\Delta_r G^\ominus$ therefore is

$$\Delta_r G^\ominus = \sum_i \nu_i \Delta_f G_i^\ominus = 0 + 0 - \Delta_f G^\ominus(CH_4,g) = -\Delta_f G^\ominus(CH_4,g).$$

We can determine $\Delta_f G^\ominus(CH_4,g)$ with the standard enthalpy and entropy of formation at that (given) temperature:

$$\Delta_f G^\ominus(CH_4,g) = \Delta_f H^\ominus(CH_4,g) - T\Delta_f S^\ominus(CH_4,g) = -74850 - 298 \cdot (-80.67) = -5.081 \cdot 10^4 \text{ J/mol}.$$

The equilibrium constant K then follows with

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} = \frac{\Delta_f G^\ominus(CH_4,g)}{RT} = \frac{-5.081 \cdot 10^4}{8.314 \cdot 298} = -20.51,$$

such that $K = 1.24 \cdot 10^{-9}$.
As expected the reaction at 298 K and $P = P^\ominus$ lies almost completely on the methane side of the equilibrium.

Formation versus absolute

- G is Temperature dependent, so correct for T and activity

What is the standard….

- Thermodynamic standard; $\Delta_f G^{\ominus}$
  - $p = p_0$
  - Listed at a temperature (eg 273 K, 298 K)
  - All activities: $a = 1$
  - Not always convenient: $a_{H+}= 1$ means pH = 0, thus need for second standard
- Biological standard conditions $\Delta_r G^{\oplus}$
  - $p = p_0$
  - Listed at a temperature (eg 273 K, 298 K, 310 K)
  - All activities $a = 1$ EXCEPT
  - $a_{H+}= 10^{-7}$ means pH = 7

A spontaneous process can be endotherm (with p constant);
So heat and enthalpy are not the energy that determines a spontaneous process

Exercise add_10

The standard formation Gibbs free energy of NH_3(g) at 298 K is $\Delta_f G^{\ominus} = -16.45$ kJ/mol. Consider the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$, in which the partial pressures of N_2, H_2 and NH_3 are 3.0, 1.0 and 4.0 bar, respectively. Assume the gases to behave as perfect gases.

a) Calculate the standard reaction Gibbs free energy at 298 K.

b) Calculate the thermodynamic equilibrium constant K.

c) Calculate the reaction Gibbs free energy at 298 K.

d) In what direction does the reaction proceed spontaneously at 298 K?

Exercise add_10

The chemical equilibrium reaction is $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \leftrightharpoons NH_3(g)$.

a) We can determine the standard reaction Gibbs free energy at 298 K with

$$\Delta_r G^\ominus = \sum_j \nu_j \Delta_f G_j^\ominus = +\left(-16.45 \cdot 10^3\right) - \frac{1}{2} \cdot 0 - \frac{3}{2} \cdot 0 = -16.45 \cdot 10^3 \text{ J/mol}.$$

b) In thermodynamic equilibrium $\Delta_r G = 0$, such that $\Delta_r G^\ominus = -RT \ln Q_{eq} = -RT \ln K$, so $K = \exp\left[-\frac{\Delta_r G^\ominus}{RT}\right] = \exp\left[-\frac{-16.45 \cdot 10^3}{8.314 \cdot 298}\right] = 765.$

c) The reaction quotient is (perfect gases and $P^{\ominus} = 1$ bar)

$$Q = \frac{\left(\frac{P_{NH_3}}{P^{\ominus}}\right)}{\left(\frac{P_{N_2}}{P^{\ominus}}\right)^{\frac{1}{2}}\left(\frac{P_{H_2}}{P^{\ominus}}\right)^{\frac{3}{2}}} = \frac{4.0}{3.0^{\frac{1}{2}} \cdot 1.0^{\frac{3}{2}}} = 2.309$$

The reaction Gibbs free energy is

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q = -16.45 \cdot 10^3 + 8.314 \cdot 298 \ln 2.309 = -14.38 \quad \text{kJ/mol.}$$

d) Since $\Delta_r G < 0$ the reaction proceeds spontaneously towards the product.

The folded state of the protein lysozyme in a solution transforms to the unfolded state at 75◦C with an enthalpy change equal to $\Delta_{\text{unfold}}H$ = 509 kJ/mol. At this temperature the folded and unfolded states are in equilibrium. The pressure change corresponding to that transition, in solution, is negligible. The difference between the isobaric heat capacity in unfolded and folded state is $\Delta c_P = c_P(\text{unfolded}) - c_P(\text{folded})$ = 6.28 kJ/molK. Furthermore, we can consider both the c_P values to be independent of temperature.

a) Calculate the entropy change of the unfolding process at 75◦C.

Next we consider the unfolding process of the protein starting in the metastable folded state at a higher temperature of 105◦C.

b) Describe a reversible path as alternative for the irreversible unfolding process at 105 ◦C. Hint: only use isobaric paths.

c) Calculate the enthalpy change of the unfolding process at 105 ◦C. Hint: Determine ΔH via the alternative reversible path and use the state function property of H.

d) Calculate the entropy change of the unfolding process at 105 ◦C.

e) Use the second law of thermodynamics to verify whether the unfolding process proceeds spontaneously at 105 ◦C.

a) At 75°C there is a (dynamic) equilibrium between the folded and the unfolded state such that at that constant temperature and pressure $0 = \mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T = \mathrm{d}H - T\mathrm{d}S$, such that $\Delta H = T\Delta S$, or $\Delta S = \frac{\Delta H}{T_{unfold}} = \frac{509\cdot 10^3}{348.2} = 1.46$ kJ/molK.

b) The unfolding process at 105 °C is irreversible (spontaneous). If we add two reversible isobars between 105 °C and 75 °C to the already reversible unfolding process at 75 °C, then we find the following diagram. So we choose the processes 1, 2 and 3 to be reversible.

$$\begin{tikzcd}
\begin{matrix}\text{folded}\\ 105^{\circ}\text{C}\end{matrix} \arrow[r, "\text{spontaneous}", "T{,}P"'] \arrow[d, "P", "1"'] & \begin{matrix}\text{unfolded}\\ 105^{\circ}\text{C}\end{matrix} \\
\begin{matrix}75^{\circ}\text{C}\\ \text{folded}\end{matrix} \arrow[r, "T{,}P", "2"'] & \begin{matrix}75^{\circ}\text{C}\\ \text{unfolded}\end{matrix} \arrow[u, "P", "3"']
\end{tikzcd}$$

c) $\Delta c_P = c_P(unfolded) - c_P(folded) = 6.28$ kJ/molK and we consider it to be independent of T between 75 °C and 105 °C.
H is a state function so ΔH is independent of the path. Obviously, we choose the path 1-2-3 as reversible alternative for the spontaneous unfolding process.
For (reversible) isobars $\mathrm{d}H = \mathrm{d}Q + V\mathrm{d}P = \mathrm{d}Q$, such that $\mathrm{d}H = c_P\mathrm{d}T$.
•Process 1 is isobaric, so $\mathrm{d}H_1 = c_P(folded)\mathrm{d}T$, such that $\Delta H_1 = c_P(folded)\cdot(75-105)$. ($c_P$ is independent of temperature and of course we can express ΔT in both K and °C).
•Process 3 is isobaric, so $\mathrm{d}H_3 = c_P(unfolded)\mathrm{d}T$, such that $\Delta H_3 = c_P(unfolded)\cdot(105-75)$.
•Process 2 is isothermal and $\Delta H_2 = \Delta H_{unfold}(75\,^{\circ}C) = 509$ kJ/mol.
Therefore $\Delta H_{unfold}(105°C) = c_P(folded)\cdot(75-105) + c_P(unfolded)\cdot(105-75) + 509\cdot 10^3 = (105-75)\Delta c_P + 509\cdot 10^3 = 30\cdot 6.28\cdot 10^3 + 509\cdot 10^3 = 697.4$ kJ/mol.

d) S is a state function, so ΔS is also independent of the path.

- Process 1 is isobaric, so $\mathrm{d}Q = \mathrm{d}Q_P = \mathrm{d}H$ and reversible, hence $\mathrm{d}S = \frac{\mathrm{d}Q_{rev}}{T} = \frac{\mathrm{d}H}{T} = \frac{C_P \mathrm{d}T}{T}$.
The temperature changes, so $\Delta S = c_P(folded) \int_{378.2\ \mathrm{K}}^{348.2\ \mathrm{K}} \frac{dT}{T} = c_P(folded) \ln \frac{348.2}{378.2}$.
- Process 3 is reversible and isobaric, so $\Delta S = c_P(unfolded) \int_{348.2\ \mathrm{K}}^{378.2\ \mathrm{K}} \frac{dT}{T} = c_P(unfolded) \ln \frac{378.2}{348.2}$.

- Process 2 is isothermal and reversible, so $\Delta S = \frac{Q_{rev}}{T_2} = \frac{509 \cdot 10^3}{348.2} = 1462$ J/mol.

So $\Delta S = c_P(folded) \ln \frac{348.2}{378.2} + c_P(unfolded) \ln \frac{378.2}{348.2} + 1462 = \Delta c_P \ln \frac{378.2}{348.2} + 1462 = 6.28 \cdot 10^3 \ln \frac{378.2}{348.2} + 1462 = 519.0 + 1462 = 1981$ J/molK.

e) The heat during the isobaric process, $\Delta H_{unfold}(105°C)$, is delivered to the surroundings.
$\Delta S_{env} = \frac{-Q}{T_{env}} = \frac{-\Delta H_{unfold}(105°C)}{T_{env}} = \frac{-697.4 \cdot 10^3}{378.2} = -1844$ J/molK.
The second law of thermodynamics requires that $\Delta S_{tot} > 0$ for a spontaneous process.
$\Delta S_{tot} = \Delta S + \Delta S_{env} = 1981 - 1844 = 137$ J/molK.
Thus the total entropy increases, such that the process proceeds indeed spontaneously.