Lecture Notes — Chemical Thermodynamics

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1 The bittersweet beauty everyone despises

1.1 What are we even talking about?

Thermodynamics is almost unanimously chosen as the most hated subject by both engineers, chemists and some physicists. The reason behind this is simple — *it is a very abstract subject talking about not abstract processes*. This unexpected jump in abstraction from the more or less understandable introductory electromagnetism or Newtonian mechanics courses met before makes you wonder why it even works. The other issue — *you cannot use the same level of abstraction as per se quantum mechanics* — the systems you talk in thermodynamics are real objects: engines, electric batteries etc. They are not some abstract electrons, cats in boxes and wavefunctions that you can't even measure directly.

The objective of this lecture is simple — to justify why classical thermodynamics is *a universal tool of a scientist* to describe whatever processes that involve energy transformations on a macroscopic scale and to show *how to use the general theory of thermodynamics as a tool to explain all macroscopic processes that concern a chemist.*

1.2 Systems, energy, and other convoluted words

Like in any other branch of theoretical physics, we first have to define the scope of events and objects that classical thermodynamics handles.

Important note: In this lecture we are only concerned in the classical thermodynamics. We will not discuss statistical thermodynamics except some brief mentions.

Now, let us introduce the main object of thermodynamics – *a system*. A system can be literally anything as long as it follows some rules:

- A system has to be macroscopic — there should be sufficiently many particles inside.

- A system has to have some way to distinguish it from the surroundings — a boundary surface that can be imaginary.

- There should be some parameters that can be used to quantify the system (more on that later).

A very important problem we almost immediately stumble upon is the lack of a way to describe a thermodynamic system using physical variables we are used to. You can describe the motion of a particle by its mass, velocity, coordinate... You can't feasibly do that when the amount of particles in the system is in the order of 10^{23}. This is why we have to introduce some *macroscopic variables* that can quantitatively describe the state of a system. Some examples of them include: temperature, pressure, energy, volume, mass... The thermodynamic variables can be *independent* or *dependent* variables. For example, the internal energy U can be both a function of independent temperature and volume variables $U = f(T, V)$ or a function of independent temperature and pressure variables: $U = f(T, p)$.

A thermodynamic variable can be *intensive* or *extensive*. An *intensive* variable can characterise some *point* of the system — temperature, pressure, mechanical tension... An *extensive* variable characterises *a part* of the system — volume, energy, mass... They cannot characterise a point. Some of intensive variables are referred to as *thermodynamic forces* — they are variables that have to be equal actoss the system in equilibrium, such as pressure or temperature. If an intensive variable is the same across all the system, this system is called *homogeneous*. If there is some jump in the intensive variables, the system is called *heterogeneous*. This allows us to distinguish *phases* in a system.

The system can exchange its thermodynamic quantities with the surroundings or another system. This happens via a *thermodynamic contact* between the systems. There are three types of contact:

- Mechanical contact that proceeds via an *external field*. The defined external field performs *macroscopic work* on the system, thus changing its parameter.

- Thermal contact that proceeds via *heat transfer*. This contact doesn't have an analogue in classical physics because there is no force associated with it, thus no macroscopic work as well (more on that later).

- Diffusion contact that proceeds via *matter exchange* between the system and the surroundings. The type of particles that can exit/enter the system depends on the properties of the boundary surface.

We also define types of systems in accordance to allowed contact:

- An *isolated system* has no thermodynamic contact at all.

- An *adiabatic system* doesn't have any thermal contact.

- A *closed system* has no diffusion contact.

Mention 5 different variables to describe a system that weren't mentioned yet. Classify them as intensive or extensive. Are they thermodynamic forces?

Suggest a way to experimentally implement an isolated system. Is there any feasible way to experimentally measure its thermodynamic quantities when it reaches equilibrium?

2 The four laws of thermodynamics

2.1 Zeroth law — What is equilibrium?

When we talk about thermodynamic systems, we cannot use the same terms for equilbrium state as we used in classical mechanics — this would imply *all particles of the system are not moving or moving in one direction* as per Newton's first law. We already said we cannot measure each particle on its own, this is why the classical definition of equilibrium cannot be applied here.

Hence, we have to introduce the *zeroth law of thermodynamics* that describes thermodynamic equilibrium as follows:

- Equilibrium is reached in a system when *after a significantly long time* its macroscopic thermodynamic quantities don't drastically change over time from some average value - *the equilibrium value of a quantity*. The small deviations from the average due to the chaos of the system are called *random fluctuations*.

Then we also have to introduce a postulate of *transitivity of equilibrium* — If a system A is in equilibrium with system B, and system A is in equilibrium with system C, system B is also in equilibrium with system C. We can intuitively explain it by the fact that the combined A+B and A+C systems are also in equilibrium if their parts are in equilibrium with each other and on their own.

For our convenience, here we also introduce *temperature* — temperature is some quantity that is equal between two systems in thermal equilibrium.

From the zeroth law, prove that temperature should be an intensive variable and a thermodynamic force.

Suggest an experimental device setup to measure temperature of a system. Justify it would work in accordance with the zeroth law.

2.2 First law — How do we quantify energy transfer?

Now we are going to discuss the way energy is transferred from and into the system. We already mentioned that the way the system can transfer energy is via *thermodynamic contact.* But before that, we need to make an important conclusion from the zeroth law:

- In a system in equilibrium, the internal variables *are a function of external variables and the temperature*:
$$b_j = f(T, a_1, a_2, ..., a_R),$$
  this is an expression for the j-th internal variable as some function of R external variables and temperature.

Let us then say that *there is some internal quantity U that corresponds to the total energy stored in a system.* Then from the corollary we wrote just now, we can conclude that in equilibrium U is a function of all the external variables and temperature:

$$U = U(T, a_1, a_2, ...a_R) - \text{The caloric state equation.}$$

The name is related to the fact that this equation is very convenient to compute heat capacities and other *caloric properties* that are related to heat transfer.

Because we can express the initial external variable set as functions of whatever other variables as long as it's a one-to-one dependency, we also have to introduce another postulate: *Internal energy is a monotonous function of temperature*, this means that in a system with only thermal contact allowed, the internal energy increases with increasing temperature:

$$\left(\frac{\partial U}{\partial T}\right)_{a_1, a_2, ..., a_R} > 0.$$

Generally, we can write down R more state equations that describe the i-th *intensive conjugate variable* as a conjugate function of the other R external variables:

$$A_i = A_i(T, a_1, a_2, ..., a_R) - \text{The thermic state equation.}$$

Thus we obtain that *a system with R external variables has R+1 state equations*. The full set of R+1 state equations can be used to *obtain the value of any thermodynamic quantity of a system at any given conditions.*

Now we are ready to formulate the *first law of thermodynamics*:

- The internal energy is an extensive additive variable of state;

- Energy is conserved in the universe;

- Energy is transferred via thermodynamic contacts.

Now let us discuss the concept of *macroscopic work* — the work performed on a system by an *external field* that is described using an *external variable*. Analogically to how we define force in classical mechanics:

$$F = -\frac{\partial U}{\partial x},$$

we can define a *thermodynamic conjugate force for a variable a_i*:

$$A_i = -\left(\frac{\partial U}{\partial a_i}\right)_{T, a_{j \neq i}} \qquad j = 1, 2...R.$$

Because of that, for a transformation we obtain the following expression:

$$dU = \delta q - \delta w,$$

where δq is the amount of heat transferred in a process and δw is the amount of work the system has performed in the process (this sign convention is chosen because of the practical applications). Notice that we don't use the d symbol because heat and work themselves are *functionals* — their value depends on the way we chose to carry out the process.

Is there any way to experimentally measure the absolute value of the internal energy of a system?

But, if we carry out the process for some extent, the value of A_i is going to change inside of the system, this is why if the process is carried out faster than the system can reach equilibrium, the value of A_i across the system will have a gradient. On the other hand, if the process is carried out *very slowly*, at a speed slower than the time the system takes to reach equilibrium, *the system is going to sustain an equilibrium state all through the process*. Such a process is

called *a quasistatic process.* In such a process you can suppose $A_{i,0}$ — the *external value of* A_i equals A_i — the internal value of A_i. Then we can anyways rewrite the first law as:

$$dU = \delta q - \sum_{i=1}^{R} A_{i,0} da_i.$$

Because of the different ways we can run the process, the value difference of $A_{i,0}$ and A_i throughout any process also differs. This leads us to an expression for the *quasistatic process first law* that is commonly used:

$$dU = \delta Q - \sum_{i=1}^{R} A_i da_i.$$

Because in a non-quasistatic process the work required to perform the process has to be split into two parts: changing the state and fighting the equilibrium inbalance in the system, we can easily notice that without fighting the inbalance we need to perform less work ourselves. Because of that we can conclude that *in a quasistatic process the work performed by the system is maximal.*

Write the expression for the first law of thermodynamics for a closed system.

Write the expression for isochoric heat capacity C_V of a closed system in accordance to the first law of thermodynamics. Is it a state function? Explain why the caloric state equation is easy to derive from the C_a values.

Compare the work to isothermally compress an ideal gas confined in a piston with mass M by increasing its mass by m from volume V_i to volume V_f by: a) momentarily increasing the mass to $m + M$; b) quasistatically increasing the mass to $m + M$. Suggest an experimental setup to do so. Plot a graph of $\frac{w_{reversible}}{w_{irreversible}}$ as a function of m/M. Does it correlate with the theory?

2.3   Second law — What energy transfer is allowed?

Imagine a situation — a ball that lies on a table is suddenly thrown up at the expense of the energy of the table. It sounds too fictional to be true, and it's true. Although such a process would be totally fine according to the laws of thermodynamics we know right now, in reality they don't proceed for some reason.

This problem is tackled by the second law of thermodynamics. It introduces an extensive additive state variable called *entropy* such that:

- In any process that proceeds spontaneously in an isolated system, the entropy of the system increases.

  Use the second law of thermodynamics to prove that the entropy of the universe reaches its maximum at equilibrium.

Now we have to somehow quantify entropy with a real process. Let us imagine an isolated system split into two subsystems α and β that only have thermal contact in between each other. If we distort the equilibrium between two systems, we see that there will be some heat transfer such that their temperatures equalise due to the zeroth law for the system to reach equilibrium. On the other side, the second law says that during that the entropy of the combined $\alpha + \beta$ system has to increase. This leads us to a very important conclusion — *entropy is inherently connected with heat transfer.*

Now, let us make another important derivation. Suppose the systems α and β are parts of one isolated system in thermal equilibrium. The entropies and internal energies of the parts of the system are:

$$S = S_\alpha(U_\alpha) + S_\beta(U_\beta);$$
$$U = U_\alpha + U_\beta = const.$$

Now let's assume there is an imaginary infinitisemal transfer of energy between the systems. Thus, $\delta U_\alpha = -\delta U_\beta$ from the isolation requirements. Because, if this transfer is allowed, the total entropy still remains in a state of maximum, for the imaginary infinitisemal change of entropy δS the following holds:

$$\delta S = \frac{dS_\alpha}{dU_\alpha}\delta U_\alpha + \frac{dS_\beta}{dU_\beta}\delta U_\beta = 0,$$

or, by rearrangement,

$$0 = \delta U_\alpha \left(\frac{dS_\alpha}{dU_\alpha} - \frac{dS_\beta}{dU_\beta} \right).$$

But, because the value of δU_α can be an arbitrary number, the only way this can hold is when

$$\frac{dS_\alpha}{dU_\alpha} = \frac{dS_\beta}{dU_\beta}.$$

Here, we refer to the zeroth law — in thermal equilibrium between two systems they have the same temperature. Thus we can deduce that

$$\frac{dS}{dU} = \frac{1}{T}. \qquad \text{The inverse is chosen for convenience.}$$

Thus we obtain for the quasistatic process:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,a}.$$

Use the second law of thermodynamics to prove that entropy is monotonously increasing with temperature, thus heat can only flow from a hotter body to a colder body.

For a quasistatic process of transfer of finite entropy, the same considerations of thermal equilibrium throughout all the process lets us finally substitute the value of δq in the equation. Because of the second law, we can thus say that *any quasistatic process is reversible.* Thus we can obtain the *fundamental theorem of thermodynamics*: for a reversible process the differential of internal energy converts to:

$$dU = TdS - \sum_{i=1}^{R} A_i da_i.$$

Prove the Clausius inequality — in a process the entropy increase of the system is greater or equal to the ratio of heat to temperature. Use the second law and the corollary from the first law.

2.4 Third law — What happens at zero temperature?

Because internal energy is a monotonous function of temperature, when temperature approaches zero entropy has to approach some value as well:

$$S = \int_0^T \frac{\delta q}{T} dT + const.$$

Unlike energy where you can ignore this constant by carefully choosing reference states to measure absolute values from, there *simply does not exist a state with known entropy.* This leads us to the need to introduce another law of thermodynamics — the third law:

- The entropy of whatever equilibrium system is zero at zero temperature.

Show that any isothermal process between two equilibrium states at 0K doesn't change the entropy.

Show that a temperature of 0 K cannot be reached in a finite amount of thermodynamic operations.

There is also a fact that because thermal motion slows down with decreasing temperature, when a system approaches zero temperature, it might not be able to relax into an equilbrium state, thus it freezes in time with some *residual entropy.*

3 Potentially, the most important part of chemical thermodynamics

3.1 The transformed state functions

We have mentioned that full description of a system and all its associated thermodynamic quantities at any arbitrary conditions can be carried out if we are given R+1 state equations for all the variables. There is, however, a workaround for this — *fundamental equations in their natural variables* that allow us to generate all R+1 state equations from one function. For an experimenter, obviously obtaining one dependency is a lot simpler than obtaining a couple dozen dependencies, this is why extrapolating the fundamental equations is the Holy Grail of

an experimenter who does thermodynamics research.

> *Show that the equation of $U = U(S, V, a_i, ...a_R)$ is a fundamental equation, i.e. derive the R+1 thermic and caloric state equations from it.*

You could just say that internal energy and entropy is totally enough to do thermodynamics and be totally right. However, we already mentioned *too many times* that experimentally setting entropy as an external variable is too inconvenient. This leads us to a search for other fundamental equations — something whose external variables can actually be easy to handle in a real laboratory setting.

The easiest external variables to control are temperature, pressure and volume. This wants us to make up some fundamental equation that has them as their independent variables. Here we come by the Legendre transformations of the internal energy — a transform that swaps the conjugate force as a new independent variable. Let us see this as an example:

Let us find the differential of a function $H = U + pV$ that we are going to call *enthalpy*:

$$dH = dU + d(pV) = TdS - pdV + pdV + Vdp - \sum_{i=1}^{R} A_i da_i = TdS + Vdp - \sum_{i=1}^{R} A_i da_i.$$

We see that the independent variables of this function are S and p, so we de facto have swapped the V and p independent and conjugate variables from a pair in the differential.

> *Show that the equation of $H = H(S, p, a_i, ...a_R)$ is a fundamental equation.*

> *Show that the enthalpy change of an isobaric process equals the heat added during the process.*

Analogically, we can transform $U(S, V, a_i, ...a_R)$ with respect to entropy and obtain the two

most commonly used thermodynamic fundamental equations:

$$dG(T, p, a_i, ...a_R) = V dp - S dT - \sum_{i=1}^{R} A_i da_i \qquad \text{where } G = H - TS,$$

$$dF(T, V, a_i, ...a_R) = -p dV - S dT - \sum_{i=1}^{R} A_i da_i \qquad \text{where } F = U - TS.$$

$F(T, V, a_i, ...a_R)$ is called the *Helmholtz free energy* and $G(T, p, a_i, ...a_R)$ is called the *Gibbs free energy*. You may wonder why the name of the function contains the word free. This is because they are related by *maximum work of a system*. It's proven by exactly the same proof as we did for enthalpy that those quantities are also fundamental equations.

> *Show that the Helmholtz energy change in a reversible isothermal process equals the full work applied to a system during the process.*

> *Show that the Gibbs energy change in a reversible isothermal annd isobaric process equals the total non-expansion work applied to a system during the process. This work is also referred to as useful work.*

3.2   The sign to determine the reality

The first lesson in a general chemistry course usually mentions the fact that negative Gibbs energy change of a reaction implies it is spontaneous. It is not always true. Now we are going to discuss when this phrase is relevant and how to formulate it in a general manner.

We can say that the entropy of an isolated system is a *thermodynamic potential* — some quantity the sign of whose change is sufficient and necessary to predict spontaniety of a process. Indeed, if the entropy of an isolated system increases, a transformation is spontaneous; if it reaches maximum, the system reaches equilibrium in accordance to the second law. Again, because entropy cannot be directly measured in an experiment, it is a very inconvenient thermodynamic potential to actually predict real experiment results. This is why we need to introduce other thermodynamic potentials.

> *Use the Clausius inequality to show that in a spontaneous process in an adiabatic isobaric*

system $dH_{S,p,a} < 0$. Explain why this is sufficient to justify that at constant entropy and pressure enthalpy is a thermodynamic potential.

Analogically to enthalpy you can show that *for all the characteristic functions in their fundamental form, in a spontaneous process where the natural variables remain constant the characteristic function decreases.*

Explain at which conditions a system reaches equilibrium simultaneously with the minimum of a) Helmholtz energy; b) Gibbs energy; c) internal energy.

3.3 The chemical potential

Notice that beforehand we intentionally left all the *unimportant* external variables masked beneath the a_i signs — they actually didn't matter beforehand. When we are handling chemical reactions, we understand that one extra thing that matters is the *effect of the amount of matter on the energy.* This is why we end up into introducing n as another variable in the fundamental equation. Then we also need to have its conjugate force — *the chemical potential*:

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,a_{i \neq j}}.$$

As long as there is only one chemical everything sounds just right. You take some amount of a chemical out, the energy changes. Seemingly, no issues arise.

Prove that in a system with only one component the chemical potential equals the molar Gibbs energy of the system.

The thing is, because Gibbs energy is additive, for a system that has more than one component (*Note: a component is an independent compound whose amount is needed to specify the exact composition of a system.* For example, the equilibrium system of H_2 gas and its dissociated form is still a one-component system because the degree of dissociation depends on the temperature and pressure, so that the amount of the molecular hydrogen is always known assuming we know the amount of total H_2 gas in the vessel.), this simple trick won't work. Indeed, the total Gibbs energy of a mixture of $n_1, n_2, ...n_k$ moles of k components would be also proportional to the molar Gibbs energy:

$$G_{full} = G_{molar} \cdot \sum_{i=1}^{k} n_i.$$

The variables in which G_{molar} is expressed are *amounts of a given component in one mole of the system...* Because that multiplied by the total amount of moles in the system gives the amount of moles of a certain component, this variable is nothing else than *the ratio of moles of one component to the total amount of moles.* If you remember your general chemistry, this variable is called the *molar fraction of the i-th component* χ_i:

$$\chi_i = \frac{n_i}{n_{total}}.$$

Thus we obtain that the molar Gibbs energy in a mixture depends from the *molar fractions*:

$$G_{molar} = G_{molar}(T, p, \chi_1, \chi_2, ...\chi_k).^1$$

So, let us try the same approach we had applied to derive the chemical potential of the i-th component:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{i \neq j}} = \left(\frac{\partial}{\partial n_i} \cdot n_{total} \cdot G_{molar}(T, p, \chi_1, \chi_2, ...\chi_k) \right)_{T,p,n_{i \neq j}} =$$

$$= G_{molar}(T, p, \chi_1, \chi_2, ...\chi_k) \cdot \left(\frac{\partial n_{total}}{\partial n_i} \right)_{T,p,n_{i \neq j}} + n_{total} \cdot \left(\frac{\partial}{\partial n_i} \cdot G_{molar}(T, p, \chi_1, \chi_2, ...\chi_k) \right)_{T,p,n_{i \neq j}}.$$

This thing looks ridiculously painful to simplify. To counter that, we *intentionally* introduce a new type of variable — *partial molar quantities.* We define them using quite a bit of math I will not justify in this lecture[2] such that the partial molar quantity $\bar{Y}$ equals to the partial derivative of the total quantity at constant pressure and temperature:

$$\bar{Y}_i = \left(\frac{\partial Y}{\partial n_i} \right)_{T,p,n_{i \neq j}}.$$

Here the Gibbs energy shines at its best — for other fundamental equations temperature and pressure aren't natural variables, there would be some factor figurative in the formula for the partial molar quantity. But for the Gibbs energy,

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{i \neq j}} = \mu_i!$$

This thus concludes that *partial molar Gibbs energy equals to the chemical potential.* Even more, because of another propery of partial molar functions (that I will not justify mathematically),

$$G = \sum_{i=1}^{k} \mu_i n_i.$$

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[1]For the brevity, from here I will omit the other external variables in the fundamental equations unless I explicitly bring them up.

[2]You can read Borshevskiy Chapter 9 if you are interested in the mathematical justification of this equation. It is very much out of the scope of this lecture. He also beautifully explains why the constant variables must be pressure and temperature.

Use the definition of the molar fraction to show that $G_{molar} = \sum_{i=1}^{k} \chi_i \mu_i$.

In chemistry we are mainly using the chemical potentials of multi-component systems as a function of molar fractions (or concentrations, due to the convenience). However, this results in weird standardisation conditions etc. that are required to describe mixtures (one-molar infinite diluted solution of an isolated aqueous sodium ion would be a very good example).[3]

The only thing we are only going to mention about mixtures is that we need some way to describe the change of the chemical potential via change of composition. This is why we introduce *chemical activity.* It is an imaginary quantity that behaves in a way we like as chemists:

- Activity of a gas equals the pressure of an *ideal gas with the same chemical potential*;

- Activity of a solid or the solvent equals unity (we just assume that their contributions to the total energy are so large/small compared to other constituents they don't change the total energy with change of composition);

- Activity of a solute equals to the activity of an *ideal solute with the same chemical potential*.[4]

Again, because of the convenient way we chose the activity to be related to ideal gases, we can also say that the chemical potential would behave similarly to one of an ideal gas (with the standard state included into the equation; we suppose at standard states all activities are unity):

$$\mu_i = \mu_i^0 + RT \ln \alpha_i.$$

Show that in a dilute solution, $\chi_{solute} \approx c_{solute} \cdot \frac{M_{solvent}}{\rho_{solution}}$.[5]

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[3] We are not going to discuss solutions and their chemical behaviour in the scope of this lecture, but you can read more in Borshevskiy Chapters 9, 10, 11, 12 and 14.

[4] Here it's vital to remember there are two types of *good* solutes — Raoult law solutes that have their activity proportional to $\ln \chi$ and the vapour pressure that behaves as per ideal gas law, or Henry law solutes that have their activity proportional to the molar concentration. The former one is used for activity definition, but the Henry solutions are more convenient to work with.

[5] This justifies why we can simplify molar fraction for concentration for a sufficiently dilute solution and still get about the same activity.

4 Reactive and approaching equilibrium

4.1 Chemical reactions with all this arsenal

Having all the arsenal from the previous chapter, it's very easy to characterise a chemical reaction. A chemical reaction can be characterised by a *balanced reaction equation*:

$$\nu_1 A_1 + \nu_2 A_2 + ... \longrightarrow \nu_j A_j + ... + \nu_k A_k$$
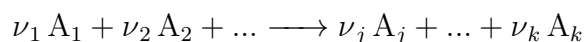
Here A_i is some i-th reactant/product involved in the reaction and ν_i is the *stoichiometric coefficient*. Because a reaction equation is... an equation, we can rearrange it to a more convenient form:

$$\sum_{i=1}^{k} \nu_i A_i = 0.^6$$

Now, let us leave the reaction mixture reach equilibrium at constant temperature, pressure and total amount of reactants. The molar Gibbs energy, because chemical potential is the partial molar Gibbs energy, at any given extent of reaction would be equal to:

$$G_{RM} = \sum_{i=1}^{k} \mu_i n_i.$$

If the reaction could proceed spontaneously in some direction, it would have minimised the Gibbs energy of the entire reaction mixture. Thus, *at the equilibrium composition the reaction mixture Gibbs energy reaches a minimum.* Then we define $\Delta_r G$ — *the molar Gibbs energy change of the reaction mixture with respect to equilibrium:*

$$\Delta_r G = \left(\sum_{i=1}^{k} \mu_i \nu_i \right)_{now} - \left(\sum_{i=1}^{k} \mu_i \nu_i \right)_{equilibrium}.$$

Analogically we define the *standard molar reaction Gibbs free energy change* $\Delta_r G^0$:

$$\Delta_r G^0 = \left(\sum_{i=1}^{k} \mu_i \nu_i \right)_{standard} - \left(\sum_{i=1}^{k} \mu_i \nu_i \right)_{equilibrium}.$$

Now we are also going to define some imaginary variable to describe the extent of the reaction, let's name it ξ, such that $dn_i = d\xi * \nu_i$. *It is just needed to take accountability for the stoichiometric coefficients.* Because we decided the reaction proceeds at constant T,p,n the only variable that can affect the Gibbs energy of the reaction mixture is the extent variable. Even more, at some reaction extent equilibrium is reached and G is minimised:

$$\left(\frac{\partial G_{RM}}{\partial \xi} \right)_{T,p,n_{total}} = 0.$$

Now let us take the extent derivative from the equilibrium reaction mixture composition (remember $dn_i = d\xi \cdot \nu_i$):

$$\left(\frac{\partial G_{RM}}{\partial \xi} \right)_{T,p,n_{total}} = \sum_{i=1}^{k} \frac{\partial n_i}{\partial (n_i/\nu_i)} \mu_i = \sum_{i=1}^{k} \mu_i \nu_i = 0.$$

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[6]The ν_i now get their signs. We choose them such that the signs of product stoichiometric coefficients are +, and of reactant stoichiometric coefficients are -.

Thus, we get an obvious conclusion in a reaction mixture for an isothermal isobaric reaction in a closed vessel: *the sum of equilibrium activity coefficients times the signed stoichiometric coefficients equals zero.*

Now, let us remember that $\mu_i = \mu_i^0 + RT \ln \alpha_i$ — the expression of chemical potential from chemical activity. Here it found its use. Now let us calculate the expression for $\Delta_r G - \Delta_r G^0$ by subtracting their corresponding definitions:

$$\Delta_r G - \Delta_r G^0 = \left(\sum_{i=1}^k \mu_i \nu_i \right)_{now} - \left(\sum_{i=1}^k \mu_i \nu_i \right)_{standard} = \sum_{i=1}^k \nu_i \left(\mu_i - \mu_i^0 \right) =$$

$$= \sum_{i=1}^k \nu_i \left(\mu_i^0 + RT \ln \alpha_i - \mu_i^0 \right) = \sum_{i=1}^k \nu_i RT \ln \alpha_i.$$

Now we are going to define the *reaction quotient Q* and the *equilibrium constant K — the reaction quotient of the equilibrium reaction mixture*:

$$Q = \prod_{i=1}^k \alpha_i^{\nu_i}.^7$$

Show that a reaction with negative $\Delta_r G^0$ will spontaneously proceed in a direction of products from the standard state.

Show that $\Delta_r G^0 = \sum_{i=1}^k \nu_i G_{m,i}^0$ and because that $\Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0$.

Use the formulae we just derived to derive the only two formulas of physical chemistry you actually end up using in problem sets: $\Delta_r G = \Delta_r G^0 + RT \ln Q$ and $\Delta_r G^0 = -RT \ln K$.

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[7]This weird Π sign indicates a product of activities for all k compounds involved in the reaction with their signed stoichiometric coefficients on the exponent. Because for the reactant the coefficients are negative, they automatically end up in the denominator. Do not be scared of this writing, it is the same as you learned before.

5 Shocking applications of the theory

5.1 Electrochemical potential and equilibrium

We have already seen the universality of thermodynamics because we could choose any arbitrary external forces as variables of the quantities we are dealing with without changing the ideas behind the laws. So, when treating electrochemical cells, we will work exactly the same way. We recall from ninth grade physics that work needed to move a charge q in a constant field with potentia φ equals $w = q \cdot \varphi$. This is why we introduce the charge of the system as another *external variable*. Its conjugate can thus reasonably be the electric potential:

$$\varphi = \left(\frac{\partial U}{\partial q}\right)_{S,V,a_i}.$$

From electrodynamics (if there is a potential difference and charge can move across the potential boundary, an electric current will flow across the potential difference) and the requirements to φ being a thermodynamic force, we can say that *if a system is in equilibrium, the electric potential across the system is also in equilibrium.*[8]

The problem now is simple: *charge is not a virtual thing. Charge is carried by charged particles.* We need to introduce a way to express how much energy changes *when a charged particle moves into/out of the system.* This energy change is a part of two changes: *the change due to chemical potential of the particle and the change due to electric field potential.* The problem we meet — chemical potential is measured in energy per mole, meanwhile electric potential is measured in joules per coulomb. In order for the sum to be some physically sound quantity, we need to convert them into one unit — joules per mole charged particle. Luckily enough, a charged particle has its charge as an integer amount of electrons added or removed to the neutral particle. This *elementary charge* will be denoted as z_i. This allows us to introduce the *electrochemical potential* χ:

$$\chi_i = \mu_i + \varphi F z_i \qquad F = 96485 \, C/mol.$$

Derive the expression for χ_i written above from the fact it is a sum of two contributions to the energy.

Show that χ_i also has to be equal across the system that reached chemical and electrical equilibrium.

We are now going to treat electrochemical reactions similarly to a chemical reaction. First,

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[8]For an actual derivation that doesn't use 'it makes sense for it to be this way' as the main argument, read Borshevskiy Chapters 15 and 16.

we are going to define a *half-cell reaction*: a reaction that only involves the electron breaking free from the compounds or the compounds absorbing an electron from the electrode surface. *Because again, electric potential cannot be measured directly*[9] *in its absolute value, there needs to be some reference potential.* Chemists choose the *standard hydrogen electrode* as such a reference. Its potential is zero at standard conditions. Now we just treat this as a chemical reaction. If equilibrium is reached, the Gibbs energy of the electrode reaches a minimum value towards the electrochemical extent:

$$\left(\frac{\partial G_{RM}}{\partial \xi}\right)_{T,p,n_{total},q_{total}} = 0.$$

Thus, we can straight differentiate by extent. Because $q_i = z_i \varphi F \cdot n_i$ and the charge is conserved, we can make a conclusion similar to the Gibbs energy of the reaction mixture in a chemical reaction:

$$G_{RM} = \sum_{i=1}^{k} \mu_i n_i + \sum_{i=1}^{k} \varphi q_i = \sum_{i=1}^{k} \left(\mu_i + \varphi z_i F\right) n_i = \sum_{i=1}^{k} \chi_i n_i.$$

This allows us to use the same mathematical apparatus as was previously demonstrated to powerfully operate with the electrochemical potentials in a cell.

Show in a way analogical to the reaction without electrochemical equilibrium, an electrochemical reaction reaches its equilibrium when $\sum_{i=1}^{k} \chi_i \nu_i = 0$.

Show in a way analogical to the reaction without electrochemical equilibrium that $\varphi = \varphi^0 - \frac{RT}{zF} \ln Q$. Here it might be useful to remember that the total charge is conserved when dealing with the charge part of the electrochemical potential.

Now we recall that Gibbs energy was initially named a *potential* for a reason of it being related

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[9]A more exact note, the electric potential field is defined up to a factor of a gradient of an arbitrary coordinate function. If you want to read more, it can be found in any decent textbook on electrodynamics. A great one is *Classical Field Theory* (Vol 2 of Course of Theoretical Physics) by Landau and Lifschitz.

with useful work the system can procure. Let us show how it's related to the electrochemical cell.

Show that $\Delta_r G^0 = -zFE^0$.

Explain why the amount of work an electrochemical cell can perform in a reversible process is equal to the value of $\Delta_r G$.

6 A small conclusion, aka *The Defence of a Fool*

You may wonder — *why even bother so much about all the formalities behind all those formulae you can simply find in the formula page of a book and plug in the numbers.* They simply exist, and you as a user can simply use the results someone else has derived. This is undoubtedly true, but this approach is absolutely detrimental to your reasoning and logics skills. I, as the lecture author, hope that this lecture was helpful enough for you to broaden your horizons and for some of those weird laws of chemical thermodynamics to *actually become sensible in terms of why they were chosen to be so weird to begin with.* It's impossible to condense the 15 chapters of *Physical Chemistry. General and Chemical thermodynamics* by Borshevskiy (the book I used to study the subject myself and to prepare this lecture) into a 2-hour, 19-page lecture with some proof problems to trick you into thinking about thermodynamics like the people who discovered it. I tried my best for it to be mathematically rigorous, brief and engaging on the same time. There are lots of books you can read in your free time if you got interested in this topic to cover up the parts I skipped due to their absence in the IChO curriculum or simply the lack of time. *I consider the job of the lecturer is mainly to make the subject more sensible and intriguing to study on your own rather than just give you templates. If at least one of you got interested to study this topic driven by self-motivation, this is the highest praise to me as a lecturer.*

The beauty and the curse of thermodynamics is the fact that it *doesn't treat systems as actual physical objects*, rather as some abstract systems with internal and external quantities that characterise them. On one hand it's convenient to the chemist because the theoretical apparatus of thermodynamics *is universal to describe any transformation.* On the other hand, it leads to very abstract wordings, measurements and equations. If you continue to study physical chemistry, you will quickly understand the scope and limitations of this tool. Thermodynamics is for sure the first *abstract physics* topic a chemist (and a physicist) has to deal with, and if you learn to appreciate the beauty behind this subject, you will be set to appreciate the beauty behind more abstract physical theories behind simple objects.
I appreciate the helpful advice and feedback in preparing this lecture and compiling the exercises from Vladislav Ivanistsev, Rostislav Rostovskiy and Jesey Tan.