Discussion 10  April 2, 2019

We will discuss chemical potential and grand canonical approach

1 [Chemical potential of ideal gas]
Consider a fluid whose Gibbs relation is \( dE = TdS - PdV + \mu dN \) so the Gibbs free energy \( G = E - TS + PV \) reads \( G = \mu N \). Thus, you should be able to get \( \mu \) directly with the aid of the so-called pressure ensemble, the ensemble with \( T-P \) constant. You may have been fed up with this ensemble, but obtain \( \mu \), using the partition function \( Y \) and \( N\mu = -k_B T \log Y \). The answer must be the same as the result given in (20.33).

2 [Colligative properties review]
The properties of dilute mixtures with or without phase transitions may be understood in terms of the chemical potentials based on the ideal gas law and mixing entropy. In short, information-theoretically calculated entropy can explain the core physics of the so-called colligative properties (Raoult, van’t Hoff (or osmotic pressure), Henry’s law, transition temperature shifts, etc.). Thus, the basic form of the chemical potential in the gas phase is

\[
\mu(T, P) = \mu^\ominus(T) + k_B T \log P,
\]

where \( P \) may be the partial pressure in a mixture. In the liquid phase

\[
\mu(T, x) = \mu^\ominus(T) + k_B T \log x,
\]

where \( x \) is the mole fraction. Both \( P \) and \( x \) in ideal systems are related to the probability (or the relative probability) to find the relevant particle.

An important feature of (DH10.2) is that \( \mu \) can be indefinitely small \( (\downarrow -\infty) \) if \( x \downarrow 0 \). Thus, if a reaction can produce a molecule that does not exist in the system, extremely large drop of \( \Delta G \) may be realized by the reaction.

(0)* What is the implication of this observation?
(i) In the hydrolysis of ATP: \( \text{ATP} \rightarrow \text{ADP} + \text{Pi} \), inorganic phosphate ion Pi is produced. If the concentration of Pi is very low, then this reaction can drive difficult reactions irreversibly. For example, if a codon correctly matches with the anticodon
this reaction occurs and the correct translation of the codon to the corresponding 
amino acid is secured. Explain.
(ii) [As discussed in the lecture] We could produce indefinitely large mechanical 
work from this type of reaction. This is a correct thermodynamic conclusion, but 
still sounds too good. This highlights a major distinction among thermal, chemical, 
and electromechanical energies. Explain.

Traditionally, the chemical physics properties studied within these ‘information 
theoretical chemical potential’ are called colligative properties. Representative prob-
lems we can at least approximately answer within this framework look as:
(1) If 2 g of a non-volatile extract from pitch is dissolved in 100 g of benzene, the 
vapor pressure of benzene at 300 K is reduced to 99.1 mmHg from 100 mmHg. What 
is the average molecular weight of this extract?
(2) How many weight % of methanol is required to prevent water from freezing at 
260 K?
(3) 1.23 g of a kind of globular protein is in 100 cm$^3$ aqueous solution. The osmotic 
pressure of this solution is 7.43 cm of water column. What is the molecular weight 
of this protein?

The colligative properties may be treated in a unified fashion as follows: 
I and II denote two distinct but coexisting phases/systems. For a chemical that may 
go between I and II freely the equilibrium condition is

$$
\mu_1^0(T'_I, P'_I) = \mu_II^0(T'_II, P'_II) + k_B T'_II \log y.
$$

(DH10.3)

Here, superfix 0 means the pure state and $y$ denotes the mole fraction in II of the 
chemical being exchanged. We assume without ‘impurity’ (minority)

$$
\mu_1^0(T_I, P_I) = \mu_II^0(T_{II}, P_{II}).
$$

(DH10.4)

Combining these two, we obtain

$$
\mu_1^0(T'_I, P'_I) - \mu_1^0(T_I, P_I) = \mu_II^0(T'_II, P'_II) - \mu_II^0(T_{II}, P_{II}) + k_B T'_II \log y.
$$

(DH10.5)

The rest is to adapt this to various situations.

**Vapor pressure change**

These are about the pressure of the vapor (gas phase) coexisting with mixture liquid.
Thus, $I = G$, $II = L$, $T = T'$ is everywhere the same, so let us drop it from $\mu$s. Using (DH10.1) for the gas phase, we see

$$ k_B T \log P'_G / P_G = k_B T \log y \quad (\text{DH10.6}) $$

or $P'_G = yP_G$.\footnote{Here, we use the fact that the liquid phase volume change due to the pressure change is negligible.} This may be understood as:

- Raoult’s law: the partial pressure $P'_G$ of one component in a liquid mixture is given by its mole fraction $y$ times the vapor pressure $P_G$ of the component when it is pure, or

- Henry’s law: the amount $y$ of a gas component resolved in the liquid phase is proportional to the partial pressure of the component in the gas phase.

**Osmotic pressure** (van’t Hoff’s law)

I is the pure liquid, and II the mixture under $P''_I = P + \pi$ (slightly pressurized). There is no temperature change (let us drop $T = T'$). Without impurity $P_1 = P''_I = P$. Let $y = 1 - x$, where $x$ is the mole fraction of the impurity in II. Thus, (DH10.5) reads

$$ \mu^0(P) = \mu^0(P + \pi) + k_B T \log(1 - x), \quad (\text{DH10.7}) $$

where $\mu^0$ is the pure liquid chemical potential.

We know generally (you must be able to derive this from the Gibbs relation),

$$ d\mu = v dP - s dT, \quad (\text{DH10.8}) $$

where $v$ is the molar volume/molecule (for a pure liquid $v = V/N$) and $s$ the molar entropy per molecule.\footnote{Here, chemical potentials are per molecule. That is why $k_B$ appears. Chemical potentials per mole reads

$$ \mu(T, x) = \mu^\ominus(T) + RT \log x. \quad (\text{DH10.9}) $$}

Therefore, we get

$$ \pi = nk_B T, \quad (\text{DH10.10}) $$

where $n = xN_A/V$ (the number density).\footnote{This same equation reads $\pi V = cRT$ where $c$ is the molarity with appropriate choice of the units.}

You could change the temperatures of I and II (instead of $P$). What will you have to do to stop the movement of the solvent from I to II (which should be at higher
temperature, I or II)?

**Phase transition point shift**

Impurities in the liquid phase are often excluded from the coexisting gas or solid phase. In such cases, II = L and I may be G or S phase. Under constant pressure, we are interested in the shift in the coexistence temperature. Combining (DH10.5) and (DH10.8) with \( y = 1 - x \), \( T_I = T_{II} = T \) (the pure substance phase transition point) and \( T'_I = T'_II = T + \Delta T \) (the phase transition point of the mixture), we get (to order \( x \))

\[
-s_I \Delta T = -s_{II} \Delta T - k_B T x
\]  

*(DH10.11)*

**Melting-point depression**: I = S, II = L. Then, \( s_{II} - s_I = L/N_A T \), where \( L \) is the melting heat (enthalpy change due to the phase transition per mole).

Therefore,

\[
\Delta T = -\frac{k_B T^2}{L/N_A} x, \text{ which is } < 0.
\]

*(DH10.12)*

**Boiling-point elevation**: I = G, II = L. Then, \( s_I - s_{II} = L/N_A T \), where \( L \) is the evaporation heat (enthalpy change due to the phase transition per mole).

Therefore,

\[
\Delta T = \frac{k_B T^2}{L/N_A} x, \text{ which is } > 0.
\]

*(DH10.13)*

Now, let us answer the above-mentioned representative questions.

(1) If 2 g of a non-volatile extract from pitch is dissolved in 100 g of benzene (C\(_6\)H\(_6\)), the vapor pressure of benzene at 300 K is reduced to 99.1 mmHg from 100 mmHg. What is the average molecular weight of this extract?

(2) How many weight % of methanol (CH\(_3\)OH) is required to prevent water from freezing at 260 K? The melting heat of ice is 334 J/g, and that of methanol is 99 J/g.

(3) 1.23 g of a kind of globular protein is in 100 cm\(^3\) solution. The osmotic pressure of this solution is 7.43 cm of water column at 25 \(^\circ\)C. What is the molecular weight of this protein?

(1) is the Raoult question. (2) is the melting point depression. (3) is a van’t Hoff question.
3 [More practical melting point depression problems]
(1) The melting point of water should be depressed by the absorbed air. What do you think is its order, 0.1 K, 0.01 K or 0.001 K? At 273 K under 1 atm, the solubility of nitrogen in water is 23.5 ml/l, and that of oxygen is 48.9 ml/l.
(2) If $m$ g of a substance is dissolved in 100 g of benzene, its melting point is decreased by 1.7 K. If the same amount is dissolved in water the melting point of water is decreased by 1.2 K. The melting heat of benzene is 127 J/g. Its melting point is 5.5 °C. How do you explain these two facts consistently?

4 [Miscible vs immiscible]\(^4\)
There are two liquids A and B whose vapor pressures are given as $P_A^0(T)$ and $P_B^0(T)$, respectively. Assume that these chemicals do not react each other, and in the gas phase they make an ideal gas mixture.
(1) Suppose that these liquids mix well and make an ideal mixture. Then, Raoult’s law holds. If the mole fraction of A in the liquid phase is $x$, what is the vapor pressure of this mixture at temperature $T$?
(2) Suppose that these liquids does not mix at all. Still you can put them in a single vessel and heat. What is the vapor pressure of this mixture at temperature $T$?
(3) What can you say about the boiling points of case (1) and case (2)? The boiling points are $T_A$ and $T_B$, respectively, for these pure liquids.

5 [Simple adsorption problem].
Consider a two dimensional lattice with $N$ sites, each of which can adsorb at most one particle of chemical A. The energy of the adsorbing site is reduced by $\epsilon$ ($>0$) when a particle is adsorbed (or you can say an adsorbed chemical A particle has its energy reduced by $\epsilon$ relative to its non-adsorbed states).
(1) At temperature $T$, $n$ particles are adsorbed on the lattice. Using the canonical formalism, find the chemical potential $\mu$ of the adsorbed particles in terms of the covering fraction $\theta$ of the lattice by the adsorbed particles. Notice that if $n$ is fixed, $E$ is fixed, so canonical and microcanonical ensemble approaches are virtually the same. You can (but need not) follow the following steps:
   (i) Compute the canonical partition function $Z(n)$, and then calculate the Helmholtz free energy $A(n)$ of the lattice with $n$ particles on it (thus, the total $E = -n\epsilon$).

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\(^{4}\)Already discussed in a lecture.
(ii) Then, utilizing the Gibbs relation, compute the chemical potential (per particle) \( \mu \).

(2) Write down the grand canonical partition function for this lattice system, assuming that the particle chemical potential is (general) \( \mu \). Then, compute the adsorbed number \( n \) of particles, and confirm the consistency of your answer and that for (1).

(3) The 2D lattice system is immersed in a big tank of a solution of chemical A in an inert solvent. The chemical potential of the solute (particles of chemical A) is given by

\[
\mu_A = \mu_A^\ominus(T) + k_B T \log x,
\]

where \( x \) is the mole fraction of chemical A in the solution. Find the equilibrium fraction \( \theta \) of the lattice points covered by the particles.

(4) What happens to this coverage, if you raise the temperature? You may assume that \( \epsilon \) is sufficiently large (i.e., adsorption is energetically favorable). Can you comment on the relation between your observation and Le Chatelier’s principle? (Or better, guess the result first and then confirm your guess.) Assume that resolving chemical A into the solvent is energetically neutral, so \( \mu_A^\ominus \) is \( T \) independent.

6 [Small system in terms of grand-canonical formalism].

There are 100 identical spinless bosons whose \( n \)-th one-particle state has an energy \( \epsilon_n = n \epsilon \ (n \in \mathbb{N}; n = 0 \) is the one-particle ground state). These particles do not interact. When the system is in equilibrium with the particle reservoir (chemostat) of temperature \( T \) and chemical potential \( \mu \), on the average 99 particles occupy the one-particle ground state \( (n = 0) \), and one particle occupies the one-particle first excited state \( (n = 1) \). The other one-particle states are negligibly occupied.

(1) Find the chemical potential \( \mu \) in terms of \( \epsilon \) (or compute \( \mu/\epsilon \)).

(2) Is the second excited state occupied only negligibly? Compute \( \langle n_2 \rangle \). \( \langle n_2 \rangle/\langle n_1 \rangle \) is not terribly small, so you might think that the problem is not self-consistent. Give your comment on this observation.

7 [Near ground microstates].

In a system one particle state has energies 0, \( \epsilon \), 2\( \epsilon \), \( \cdots \) (equally spaced and not degenerate as illustrated in Fig 20.4 in the Lecture Notes), where \( \epsilon = 0.01 \) eV.\(^5\)

(1) There are 1000 particles in the system. What is the energy of the lowest energy

\(^5\)1 eV corresponds to 12,000 K.
microstate (= ground microstate, i.e., the ground state of the whole system) from
the origin of the one particle state energy for (1F) fermions and for (1B) bosons?
(Ignore the internal states of the particles.)
(2) Itemize all the excited microstates (of the whole system, needless to say) whose
excitation energies are less than or equal to 3ε (from the ground microstate) for
fermions (2F) and for bosons (2B).
(3) The above system with 1000 fermions is initially at T = 0. Suppose all the
fermions are converted into bosons adiabatically (that is, with E being kept con-
stant). Is the temperature of the resultant boson system in equilibrium higher than
5,000 K?
(4) [Can you make a fermion bomb?] There is a fermion gas at room temperature
with the Fermi energy 10 eV. The gas is in an adiabatic container. The fermions
are actually metastable, and are converted into stable bosons without any energy
input. The reader may assume the particles do not interact. If the transformation
from fermions to bosons is carried out adiabatically, so that the particles experience
no sudden forces, can the resulting bose gas explode the container?

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6 the core part of UIUC Qual Spring 2002; notice the year.
Homework 10 due 9 am on April 9 (Tu), 2019.
Submit to compass2g

You may discuss with your friends AFTER you have made due efforts of your own to solve the problems. I trust you. I wish you to fully understand the solutions when you submit your homeworks (and get the full credit).

No solution without your justification will get any credit.

As to the use of TeX: It was announced that from week 10 use of TeX (of some version) would be strictly imposed. The purpose is that you learn how to write mathematics properly, so if proper math orthography would be met, anything, including extremely neat hand writing, will be accepted. You must use proper aligning of formulas, correct punctuations, and correct fonts,\footnote{italicized or not in particular; basically, all the formulas are in italic and all the ordinary English sentences are in upright} etc., even with handwriting. Errors in math orthography will be penalized (but at most 20\% of the total score). Except for punctuations most requirements will be automatically satisfied, if you use (La)TeX.\footnote{Although I have no intention to recommend my own macros, if you use something like them, then you need only to be able to ‘read formulas loud.’ That is why I posted all the source files; in most cases you can copy some parts of them with modifications.} With Words (and handwriting) you will have to struggle to meet the requirement.

You may send me (yoono@illinois.edu) TeX questions like: how to write/program “…”?

1. [Easy colligative property questions]
(1) 12.3 g of an unknown substance (with negligible vapor pressure) is dissolved in 100 g of water. Its vapor pressure is 743 mmHg at 100 \( ^\circ \)C. What is its molecular weight \( M \)?

(2) A 1 l solution containing 25 g of a substance at 0\( ^\circ \)C exhibits the osmotic pressure 2.34 atm. What is the osmotic pressure of the solution containing 31 g/l of the same substance (with the same solvent) at 30\( ^\circ \)C?

2. [Steam distillation]
According to the Clapeyron-Clausius equation, the vapor pressure of a liquid obeys

\[ \frac{dP}{dT} = \frac{\Delta H}{T \Delta V}, \]

where \( \Delta H \) denotes the evaporation heat, and \( \Delta V \) is the volume increase by evaporation. Usually, the vapor is approximated as an ideal gas and the liquid volume is ignored, so \( \Delta V = V_{\text{vapor}} = RT/P \) is used. Therefore, the original Clapeyron-Clausius equation may be written as

\[ \frac{dP}{dT} = \frac{P \Delta H}{RT^2}. \]

(1) Show that this implies \( P = ce^{-\Delta H/RT} \), where \( c \) is a positive constant, if we may assume \( \Delta H \) is constant.

(2) There are two immiscible liquids A and B with the vapor pressure (in atm) \( (T \) in K) \[ P_A(T) = 942293e^{-5135/T}, \quad P_B(T) = 605380e^{-5364/T}. \]

What is the boiling point of the A, B mixture? [You can use graphic method to solve this. For example, you can use http://dlippman.imathas.com/graphcalc/graphcalc.html]

(3) What is the mole fraction of B in the vapor phase? [In this example, A is actually water.]

3. [Adsorption question]
Consider a surface with \( N \) adsorption centers, each of which can accommodate at most one particle. The energy of the adsorbing site is reduced by \( \epsilon > 0 \), that is the one particle energy is \( -\epsilon \) when a particle is adsorbed. On the surface there is a conversion reaction between A and B, which is \( \Delta > 0 \) more stable than A. B cannot detach from the surface. The surface is placed in a large tank filled with gas of A with chemical potential \( \mu \).

(1) Write down the grand canonical partition function for the adsorbing surface.

(2) Find the total coverage fraction \( \theta \) (i.e., the number of sites occupied by A or B divided by \( N \)).

(3) What do you expect to happen to the chemical potential of A, if you change \( \Delta \) while fixing the total coverage \( \theta \)?
4. [Elementary ideal quantum particles]
The one particle state energies are equally spaced (with spacing $\epsilon$) for a particle.

(1) There are $N = 1232$ identical fermions in the system and its ground state has energy $E_0 = 2311$ eV (relative to the one-particle ground state).

(i) What is the spacing $\epsilon$ and the Fermi level $\mu_F$ of the system?
(ii) What is the specific heat of the system at very low temperatures? You may assume $\beta \epsilon \gg 1$.

(2) Now, let us assume these particles are identical bosons and $\epsilon$ is the same.

(i) What is the the specific heat of the system at very low temperatures?
(ii) The system is expanded and $\epsilon$ becomes smaller. What do you expect to happen to the specific heat of the system?