General Physics I

Lect.22 Analytical Thermodynamics

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An overview

- So far, we have been using a series of interdependent state variables to discuss thermodynamic: P, V, N

- T, defined from the 0th law, what's a thermal equilibrium

- U, defined from the 1st law, Energy conservation and transfer

- S, or rather ΔS, defined from the 2nd law, (need to wait for the 3rd law to see the exact value)

- And we have defined a number of other alphabets, H, F, G…as a combination of the above. We sometimes refer to them as "thermodynamic potentials"

Missing piece: chemical potential

Recall dU can be written as the following:

$$dU = TdS - pdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

But we should note that the state variables of a single component system in flux that could achieve equilibrium are uniquely defined by specifying the size of the box, N and U. *We essentially need to let the particles flow.* This means that any function of state of such a system, such as its entropy, should be expressed as a function of U,V and N, i.e. S(U,V,N) and U(S,V,N).

From which we can deduce that we can add an extra term to our equation for dU to give what becomes the entry point of analytical thermodynamics:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

We call this the "master equation": $\mathbf{dU = TdS - PdV + \mu dN}$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}$$

chemical potential

Systems

We can define systems according to whether they allow flow of particles and/or energy:

- An **open** system is one in which particles and energy can move between the system and its surroundings.
- A **closed** system is one in which particles do not flow between the system and its surroundings, but energy can.
- - An **isolated** systems is one where no energy or particles can flow between the system and its surroundings.

In this class we mostly talk about closed system, so we can assume ΔN=0 (one less variable to worry about for every potential).
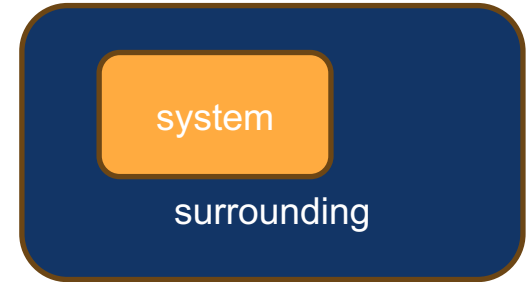
Entropy for ideal gas

- For ideal gas, we can work out the entropy change from the master equation (1st law expressed in state variables)

$$dU = C_v dT = TdS - pdV$$

$$dS = \frac{C_v dT}{T} + \frac{pdV}{T} = \frac{C_v dT}{T} + \frac{nRdV}{V} \quad \text{(using } pV = nRT\text{)}$$

$$S = C_v \ln T + nR \ln V + S_0(n)$$

- The S_0 term we cannot directly derive from thermodynamical analysis, though we can probably guess it's proportional to n (imagine we increase the number n to 2n).

- If we set S=0, we have the adiabatic process, so
$$C_{V,m}\ln T_1 + R\ln V_1 = C_{V,m}\ln T_2 + R\ln V_2 ,$$

$$\text{or } T_1 V_1{}^{\gamma-1} = T_2 V_2{}^{\gamma-1}$$

Entropy for ideal gas (cont)

- Note: Introduction of entropy does not increase the number of independent thermodynamic variables; i.e., S(T,V,n), just like what we have derived

$$S = C_v \ln T + nR \ln V + S_0(n)$$

- We can see that C_v is also proportional to n, where we have $C_{v=}nC_{V,m}$
- Now consider that we have two portion of the same gas, the number of particles and volume should be doubled, so should be the entropy, but here
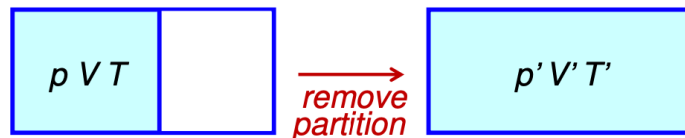
$$2nR\ln 2V = 2nR\ln V + 2nR\ln 2 \neq 2(nR\ln V)$$

- To make the expression extensive, we let $S_0(n) = nS'_0 - nR\ln n$, S'_0 can be constant but material dependent:

$$S = nC_{v,m} \ln T + nR \ln V + nS'_0 - nR \ln n$$

$$= nC_{v,m} \ln T + nR \ln \left(\frac{V}{n}\right) + nS'_0$$

'heat'　　　'configuration'

Example

Consider the free expansion of gas into vacuum: ΔU = ΔQ = ΔW = 0

There is no work done nor heat exchange, so the internal energy U stays the same, so that for ideal gas T = T'.

Per mole of gas we have

$$\Delta S = C_V \ln\left(\frac{T'}{T}\right) + R\ln\left(\frac{V'}{V}\right) = R\ln\left(\frac{V'}{V}\right)$$

ΔS > 0 for V'>V

How do thermodynamic potentials work

- How a multivariable/multiparticle system behaves, from a classical mechanics point of view is a function of the basic interaction forces, i.e., **potential energy**, the kinetic energy and how much 'space' there is in which the particles have to move in.

- We are interested in macro states established at least locally as 'equilibrium' macro states via microscopic fluctuations, and how one can move from one such state to another.

- **Thermodynamic potentials** are constructed nicely s.t. under certain circumstances (e.g. temperature held constant by connection to a reservoir), changes in them allow for the entropy changes. We can easily derive their differentials regarding, e.g. S, as a function of other state variables at that condition.

Potential	Variables
$U(S, V, N)$	S, V, N
$H(S, P, N)$	S, P, N
$F(T, V, N)$	V, T, N
$G(T, P, N)$	P, T, N

Thermodynamic potentials: completeness

- Analytical thermodynamics is based on a set of 'thermodynamic potentials', from each of which all relevant state functions can be derived. Relevant thermodynamic variables can be deduced from partial derivatives of thermodynamic potentials.
- They contain all the 'relevant information' about the thermodynamical behavior of that particular system. **We just need to set up the master equation for that system.** Taking the example of U(S,V,N):

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

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{V,S} dN$$

$$\boldsymbol{T = \left(\frac{\partial U}{\partial S}\right)_{V,N}} \qquad \boldsymbol{p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}} \qquad \boldsymbol{\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}}$$

- Here, U(S,V,N) gives complete thermodynamic information about the system and variables.

Completeness not apply for non-potential

- Say we want to derive the relation on S instead of U, we write

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

$$dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN$$

- Ideally we want to have S(T,V,N), however, we do not know p as a function of T,V,N, i.e., p(T,V,N), so we cannot have the complete information of S.

- An analogy can be a spring system U(x,y)=(k_1x^2+k_2y^2)/2

- Thus the completeness only applies to the thermodynamic potentials.

Different thermodynamic potentials

Thermodynamic potentials can give complete information of the system, however, $U(S,V)$ may not always be the most convenient variables. We derive other functions that contain the same information for special circumstances:

eqn.s to recover other variables

Internal Energy

$U(S,V)$

$$dU = TdS - pdV \quad \rightarrow \quad T = \left(\frac{\partial U}{\partial S}\right)_V \quad p = -\left(\frac{\partial U}{\partial V}\right)_S$$

Enthalpy

$H(S,p) = U + pV$

$$dH = TdS + Vdp \quad \rightarrow \quad T = \left(\frac{\partial H}{\partial S}\right)_p \quad V = \left(\frac{\partial H}{\partial p}\right)_S$$

Helmholtz Free Energy

$F(T,V) = U - TS$

$$dF = -SdT - pdV \quad \rightarrow \quad S = -\left(\frac{\partial F}{\partial T}\right)_V \quad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

Gibbs Free Energy

$G(T,p) = H - TS$

$$dG = -SdT + Vdp \quad \rightarrow \quad S = -\left(\frac{\partial G}{\partial T}\right)_p \quad V = \left(\frac{\partial G}{\partial p}\right)_T$$

Enthalpy

In chemical reactions are usually performed at constant p rather than at constant V.

Enthalpy: H = U + PV

This is referred as Legendre transformation: same information, but the variable swapped for its 'conjugate' variable: $P \to -V, V \to P$

Such kind of the symmetry is exactly why we can use a simple name-swapping to derive other relations, it roots from the symmetry in math.

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \longrightarrow \left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V.$$

Some process (a fuel cell, combustion, a chemical reaction) at atmospheric pressure involves volume increases. To derive the 'useful work' of the system, one have to subtract of the 'pV' work from the work that is available to be used.

Heat capacities:

$$C_p = \left(\frac{dQ}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p \quad c.f. \quad C_v = \left(\frac{dQ}{dT}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v$$

Helmholtz free energy

Helmholtz Free Energy is a thermodynamic potential that measures the "useful" work obtainable from a closed thermodynamic system at a <u>constant temperature and volume</u>.

$$F=U-TS \text{ and } dF=-SdT-PdV$$

$$S = -\left(\frac{\partial F}{\partial T}\right)\bigg|_V \quad P = -\left(\frac{\partial F}{\partial V}\right)\bigg|_T$$

$$dF=-SdT-PdV= -dQ + dW - TdS - SdT = -dQ_{res} + dW - TdS \text{ (const. T)}$$
$$= TdS_{res} + dW - TdS \text{ (const. T)}$$
$$= T(dS_{res} - dS) +dW \leqq dW \text{ (const. T)}$$

$$-dF \geq -dW \text{ (maximum work done by the system)}$$

The maximum amount of energy which can be converted to work is given by -dF

Gibbs free energy

$$G=U+PV-TS$$
$$dG=-SdT+VdP$$

- Compare with $dU = TdS - PdV$, we can see the S,V dependence is completely flipped to T and P, so we have more control on them, but fundamentally the two potentials are equivalent
- Note that if there are "useful"(non-PV) work, W_{npv}, then we have $dG=-SdT+VdP+dW_{npv}$ where $dG=dW_{npv}$ if we keep p and T constant. If $\Delta G<0$, the chemical reaction is spontaneous.

Gibbs free energy per particle

- If N is not constant, but P and T are, then $dG=-SdT+VdP+\mu dN => dG=\mu dN => G=\mu N$
- Recall in high school, this is the condition for the equilibrium of a chemical reaction. Gibbs free energy does not change.
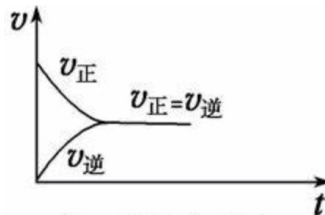
Gibbs vs. Helmholtz: Chemistry vs. Physics

- A lot of chemistry (including phase changes) is done at constant pressure, and temperature, G(P,T) has been used often by chemists.

- In physics we often focus more on F(T,V), because
1. in statistical thermodynamics F is easier to evaluate than G
2. in quantum mechanics, if you change the size of the box you change the nature (including energy) of the fundamental states, which significantly complicates the math.

- Chemists want something that is useful in the real world, while physicists typically want to know how it works on a finer scale, with simpler math.

- The powerful thing about both G and F is that they allow the entropy change of the surroundings to be written in terms of the properties of the system, i.e. the total entropy change of the "system-plus-surroundings" is written in system variables.

Maxwell Relations

Consider $dU = TdS - pdV$

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \text{and} \quad p = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$\left(\frac{\partial^2 U}{\partial S \partial V}\right)_{V,S} = \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V}$$

$$\boxed{\partial^2 f / \partial x \partial y = \partial^2 f / \partial y \partial x}$$

We have 4 sets of relations from U, F, H, G:

$\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial p}{\partial S}\right)_V$	$\left(\dfrac{\partial T}{\partial p}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_p$
$\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial p}{\partial T}\right)_V$	$-\left(\dfrac{\partial S}{\partial p}\right)_T = \left(\dfrac{\partial V}{\partial T}\right)_p$

equivalent $\longleftrightarrow$ $\left(\dfrac{\partial T}{\partial V}\right)_p = -\left(\dfrac{\partial p}{\partial S}\right)_T$

If we want to apply the chain rules for partial differentials, e.g.

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1$$

One need to be careful about the negative sign, arise from cyclic relation of the mixed partial derivatives. Proof:

$$
\left.
\begin{array}{l}
dx = \left(\dfrac{\partial x}{\partial y}\right) dy + \left(\dfrac{\partial x}{\partial z}\right) dz \\[4mm]
dy = \left(\dfrac{\partial y}{\partial x}\right) dx + \left(\dfrac{\partial y}{\partial z}\right) dz
\end{array}
\right\}
\quad
dx = \left(\frac{\partial x}{\partial y}\right) \left[\left(\frac{\partial y}{\partial x}\right) dx + \left(\frac{\partial y}{\partial z}\right) dz\right] + \left(\frac{\partial x}{\partial z}\right) dz
$$

$$\left(\frac{\partial x}{\partial y}\right) \left(\frac{\partial y}{\partial z}\right) + \left(\frac{\partial x}{\partial z}\right) = 0$$