PHY 341/641 Thermodynamics and Statistical Mechanics MWF: Online at 12 PM & FTF at 2 PM Record!!!

Discussion for Lecture 15:

Properties of the Gibbs free energy

Reading: Chapters 5.1-5.2

- **1. Intensive and extensive variables**
- 2. General properties of Helmholtz and Gibbs free energies
- 3. Ideal gas relationships
- 4. Gibbs free energy G

Course schedule for Spring 2021

schedule -- subject to frequent adjustment.) Reading assignments are for the **An Introduction to Therm** by Daniel V. Schroeder. The HW assignment numbers refer to problems in that text.

	Lecture date	Reading	Торіс	HW	Due date
1	Wed: 01/27/2021	Chap. 1.1-1.3	Introduction and ideal gas equations	1.21	01/29/2021
2	Fri: 01/29/2021	Chap. 1.2-1.4	First law of thermodynamics	1.17	02/03/2021
3	Mon: 02/01/2021	Chap. 1.5-1.6	Work and heat for an ideal gas		
4	Wed: 02/03/2021	Chap. 1.1-1.6	Review of energy, heat, and work	1.45	02/05/2021
5	Fri: 02/05/2021	Chap. 2.1-2.2	Aspects of entropy		
6	Mon: 02/08/2021	Chap. 2.3-2.4	Multiplicity distributions	2.24	02/10/2021
7	Wed: 02/10/2021	Chap. 2.5-2.6	Entropy and macrostate multiplicity	2.26	02/12/2021
8	Fri: 02/12/2021	Chap. 2.1-2.6	Review of entropy and macrostates	2.32	02/15/2021
9	Mon: 02/15/2021	Chap. 3.1-3.2	Temperature, entropy, heat	3.10a-b	02/17/2021
10	Wed: 02/17/2021	Chap. 3.3-3.4	Temperature, entropy, heat	3.23	02/19/2021
11	Fri: 02/19/2021	Chap. 3.5-3.6	Temperature, entropy, heat	3.28	02/22/2021
12	Mon: 02/22/2021	Chap. 4.1-4.3	Ideal engines and refrigerators	4.1	02/24/2021
13	Wed: 02/24/2021	Chap. 4.3-4.4	Real engines and refrigerators	4.20	02/26/2021
14	Fri· 02/26/2021	Chap 51	Free energy	55	03/01/2021
15	Mon: 03/01/2021	Chap. 5.1-5.2	Thermodynamic relations	1.46c-e	03/03/2021
16	Wed: 03/03/2021	Chap. 5.3	Phase transformations	3.33	03/05/2021
17	Fri: 03/05/2021	Chap. 5.3	Phase transformations	5.14а-е	03/08/2021
18	Mon: 03/08/2021				
19	Wed: 03/10/2021				
20	Fri: 03/12/2021	Chap. 1-5	Review		
0.0	Mon: 03/15/2021	No class	APS March Meeting	Take Home Exam	
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Comment – the homework assignments include problems from earlier chapters that we are now in a better position to understand. They involve evaluating material properties. For most materials, these must be determined experimentally for each different material. In some cases, we can evaluate them analytically assuming the ideal gas law.

Your questions –

From Parker – What is the advantage of using the Helmholtz versus the Gibbs free energy, when is one more appropriate than the other?

From Chao -- While expressing Gibbs free energy this time, why are we doing the summation of the chemical potentials, instead of just a single mu times dN?

From Kristen – 1. In the book it says that the entropy of the environment can increase if it acquires volume from the system, what does this mean exactly? 2. Could you explain how we get equation 5.35?

From Michael -- Could you elaborate a little more about what the book means when it says "it was crucial that the two variables being held fixed in eq 5.34, T and P, were both intensive so that all extensive quantities could grow in proportion to N"?

From Rich -- In the equation for dStotal, is T the system or environmental temperature?

Thermodynamic quantities

Among the many thermodynamic functions and variables that we have encountered, it is useful to distinguish two types in terms of how they scale with size –

Intensive – independent of system size **Extensive** – proportional to system size

Examples -

- Temperature Volume Pressure Entropy
- T Intensive or Extensive?
- V Intensive or Extensive?
- P Intensive or Extensive?
- S Intensive or Extensive?

Examples of intensive variables

Temperature T Pressure P Chemical potential µ Number density N/V

Examples of extensive variables

Number of particles N Volume V Entropy S Internal energy U Enthalpy H Helmholtz free energy F Gibbs free energy G

Summary of thermodynamic energies

Internal:U(S,V,N) $dU = TdS - PdV + \mu dN$ Enthalpy:H(S,P,N) = U + PV $dH = TdS + VdP + \mu dN$ Helmholtz:F(T,V,N) = U - ST $dF = -SdT - PdV + \mu dN$ Gibbs:G(T,P,N) = F + PV $dG = -SdT + VdP + \mu dN$

Note that, in order to maintain constant T, P, etc. we need to introduce the notion of interaction of our system with a "reservoir". For the moment, we will assume that the effects of the reservoir are negligible and that all processes in our "system" are performed under quasi-static conditions. More generally, corrections from reservoir effects lead to the inequalities mentioned in our textbook.

Summary of thermodynamic functions

Internal energy
$$U = U(S,V,N)$$
 $dU = TdS - PdV + \mu dN$ Entropy $S = S(U,V,N)$ $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$ Enthalpy $H = H(S,P,N)$ $dH = TdS + VdP + \mu dN$ Helmholtz free energy $F = F(T,V,N)$ $dF = -SdT - PdV + \mu dN$ Gibbs free energy $G = G(T,P,N)$ $dG = -SdT + VdP + \mu dN$

Various first derivative relationships Some first derivative relationships --

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{\partial H}{\partial S}\right)_{P,N} \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$
$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \qquad V = \left(\frac{\partial H}{\partial P}\right)_{S,N} = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$
$$\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S} = \left(\frac{\partial H}{\partial N}\right)_{P,S} = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$
$$\frac{3/01/2021}{PHY 341/641} \text{ Spring 2021 -- Lecture 15}$$

Properties of the Helmholtz free energy

Helmholtz: F(T, V, N) = U - ST $dF = -SdT - PdV + \mu dN$ \Rightarrow Under quasi-static conditions of constant T,V, and N: dF = 0 so that at equilibrium, the system is characterized by the minimum value of F. Why "free" energy? $\Delta F = \Delta U - \Delta (TS)$ From first law: $\Delta U = \Delta Q + \Delta W = \Delta Q + \Delta W_{mechanical} + \Delta W_{other}$ Under conditions of constant temperature, $\Delta Q = \Delta(TS)$ Under conditions of constant volume, $\Delta W_{mechanical} = 0$ $\Rightarrow \Delta F = \Delta W_{other}$

Properties of the Gibbs free energy

Gibbs: G(T, P, N) = U - ST + PV $dG = -SdT - VdP + \mu dN$ \Rightarrow Under quasi-static conditions of constant *T*,*P*, and *N*: dG = 0 so that at equilibrium, the system is characterized by the minimum value of G. Why "free" energy? $\Delta G = \Delta U - \Delta (TS) + \Delta (PV)$ From first law: $\Delta U = \Delta Q + \Delta W = \Delta Q + \Delta W_{mechanical} + \Delta W_{other}$ Under conditions of constant temperature, $\Delta Q = \Delta(TS)$ Under conditions of constant pressure, $\Delta W_{mechanical} = 0$ and VdP = 0 $\Rightarrow \Delta G = \Delta W_{other}$

Helmholtz free energy for monoatomic ideal gas [We have only worked out the entropy for this case.]

For monoatomic ideal gas --Equation of state: $PV = Nk_BT$

Internal energy: $U = \frac{3}{2} N k_B T$

Entropy: $S = Nk_B \left(\ln \left(\frac{V}{N} \left(\frac{4\pi MU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right)$

Helmholtz:
$$F = U - TS = -Nk_BT \left(\ln \left(\frac{V}{N} \left(\frac{2\pi MNk_BT}{Nh^2} \right)^{3/2} \right) + 1 \right)$$

Helmholtz
$$\mu$$
: $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_B T \left(\ln \left(\frac{V}{N} \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\right) \right)$

Gibbs free energy for monoatomic ideal gas

[We have only worked out the entropy for this case.] For monoatomic ideal gas --

Equation of state: $PV = Nk_BT$

Internal energy: $U = \frac{3}{N} N k_{\scriptscriptstyle B} T$

$$S = Nk_B \left(\ln \left(\frac{V}{N} \left(\frac{4\pi MU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right)$$

Entropy:

 $G = U - TS + PV = -Nk_BT \left(\ln \left(\frac{V}{N} \left(\frac{2\pi MNk_BT}{Nh^2} \right)^{3/2} \right) \right)$ Gibbs:

$$= -Nk_{B}T\left(\ln\left(\frac{k_{B}T}{P}\left(\frac{2\pi Mk_{B}T}{h^{2}}\right)^{3/2}\right)\right)$$

Gibbs
$$\mu$$
: $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = -k_B T \left(\ln \left(\frac{k_B T}{P} \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\right) \right)$
B/01/2021 PHY 341/641 Spring 2021 -- Lecture 15

12

Summary of results for chemical potential of ideal gas --

Helmholtz
$$\mu$$
: $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_B T \left(\ln \left(\frac{V}{N} \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\right) \right)$
Gibbs μ : $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = -k_B T \left(\ln \left(\frac{k_B T}{P} \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\right) \right)$

Are these equivalent?

a. Yes? b. No?

Note that for the constant *T* and *P* case:

$$\mu = \mu(T, P) = \mu(T_0, P_0) + \left(\mu(T_0, P) - \mu(T_0, P_0)\right)$$
$$= \mu(T_0, P_0) + k_B T_0 \ln\left(\frac{P}{P_0}\right)$$

One further comment about chemical potential using ideal gas example

Gibbs:

$$G = -Nk_{B}T\left(\ln\left(\frac{k_{B}T}{P}\left(\frac{2\pi Mk_{B}T}{h^{2}}\right)^{3/2}\right)\right) = G(T, P, N)$$
Gibbs μ :

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = -k_{B}T\left(\ln\left(\frac{k_{B}T}{P}\left(\frac{2\pi Mk_{B}T}{h^{2}}\right)^{3/2}\right)\right) = \mu(T, P)$$
Also note that $G(T, P, N) = N\mu(T, P)$

Note that for most materials, the equation of state and equations describing thermodynamic energies are much more complicated than that of the ideal gas. We rely on experimental measurements to find values of the parameters to analyze the systems. Some useful parameters are as follows.

Thermal expansion coefficient: (See problem 1.7)

$$\beta(T) \equiv \left(\frac{\partial V}{\partial T}\right)_{N,P} \frac{1}{V}$$

Example --

Volumetric Temperature Coefficients - β - for some Fluids

- water at 0°C: -0.000050 (1/°C)
- water at 4°C: 0 (1/°C)
- water at 10°C: 0.000088 (1/°C)
- water at 20°C: 0.000207 (1/°C)
- water at 30°C: 0.000303 (1/°C)
- water at 40°C: 0.000385 (1/°C)
- water at 50°C: 0.000457 (1/°C)
- water at 60°C: 0.000522 (1/°C)
- water at 70°C: 0.000582 (1/°C)
- water at 80°C: 0.000640 (1/°C)
- water at 90°C: 0.000695 (1/°C)

https://www.engineeringtoolbox.com/volumetric-temperature-expansion-d_315.html

Isothermal compressibility: (See problem 1.46)

$$\kappa(T) \equiv -\left(\frac{\partial V}{\partial P}\right)_{N,T} \frac{1}{V}$$

Note the following relationship for partial derivatives:

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{\left(\frac{\partial V}{\partial T}\right)_{P,N}}{\left(\frac{\partial V}{\partial P}\right)_{T,N}}$$

Heat capacity at constant volume: (See problem 3.33)

$$C_V(T) \equiv T\left(\frac{\partial S}{\partial T}\right)_{N,V}$$

Behavior of Gibbs free energy for a material that changes phase http://hacker.faculty.geol.ucsb.edu/geo124T/lecture.html



Coexistence line as a function of T and P for phases of water



Figure 5.11. Phase diagram for H_2O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994). Copyright ©2000, Addison-Wesley.