Notes for today

- Reading: Today finishing chapter 2. Then, read Ch. 3.

- HW presentations for tomorrow: Looking for volunteers for problems 3, 4, 5.

Recall:

① **Fundamental equation**: $\boldsymbol{S(U,V,N_1,N_2\ldots)}$ **or** $\boldsymbol{U(S,V,N_1,N_2\ldots)}$

First law 2 versions:

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

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{VN}$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{SN}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{SV}$$

② **Equations of state**

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{VN}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{UN}$$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{UV}$$

③ ***equilibrium*** between systems 1 and 2,

$T_1 = T_2$ thermal

$P_1 = P_2$ mechanical

$\mu_1 = \mu_2$ ← Matter flow of equivalent particles. Or, interchange of particle types:

$$H_{2-ortho} \Leftrightarrow H_{2-para}$$

Examples:

$$U = C(VNS)^{1/3}$$

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

Examples:

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

$$U = \frac{3}{2}Nk_BT$$

$$PV = Nk_BT$$

$$\mu = -k_BTln\left[\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right]$$

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Can derive from phase-space multiplicity (HW) (& see ch. 16)

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$$PV = Nk_BT$$

$$\mu = -k_BTln\left[\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right]$$

$$= -k_BTln\left[\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right]$$

Decreases with *T* as could expect

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{SV}$$

This is spinless monatomic ideal gas, where *U* measures only the particles' KE.

Spin adds e.g. $-k_BTln[2]$ term

More on particle interchange/chemical equilibrium:

Section 2.9, with specific application to ideal gases & ionization
(Saha equation I don't think is in the text)

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN \quad \Longrightarrow \quad \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{VN}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{UN}, \quad -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{UV}$$

Yields, for ***equilibrium*** between systems 1 and 2,

$T_1 = T_2$ (thermal) $\quad P_1 = P_2$ (mechanical) $\quad \mu_1 = \mu_2$

More general, $\mathrm{H} \Leftrightarrow e^- + p^+$

$$\mathrm{CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O}$$

etc.

$$dN_H = -dN_e = -dN_p$$

$$\mu_H = \mu_e + \mu_p$$

For *S* at equilibrium (extremum)

Equilibrium ionization process (all considered ideal gases):

$$H \Leftrightarrow e^- + p^+ \qquad dN_H = -dN_e = -dN_p, \qquad \mu_H = \mu_e + \mu_p$$

- Assume all H atoms in ground state (valid if *T* not too high)
- Also *H* atoms at effective negative potential energy (-13.6 eV) relative to ions:

$$\mu_{\mathrm{H}} = -13.6 \text{ eV} + [\mu_{\mathrm{translational}}]$$

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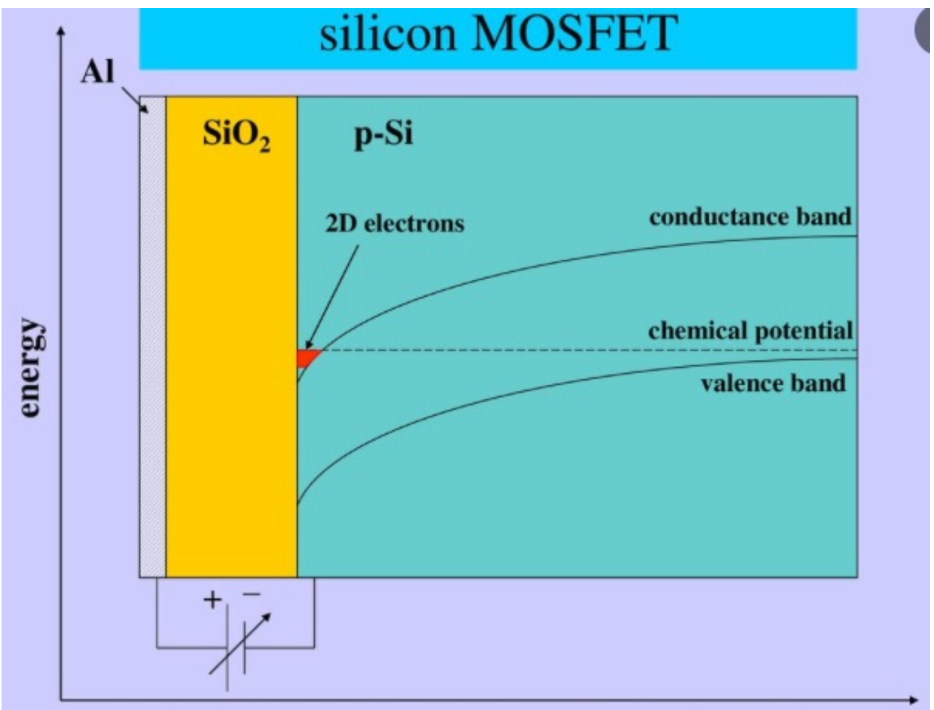

MOSFET (basis for CMOS memory); renormalization of electron translational energies vs. chemical potential caused by applied potential energy is simlar.
Applied voltage causes switching.

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Result:

$$13.6\ \mathrm{eV} = k_B T ln\left[\frac{n_H}{n_e n_p}\left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2}\right]$$

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$$\frac{1}{\lambda_{th}^3}$$

Thermal (electron) DeBroglie wavelength

- $n = 1/\lambda_{th}^3$ is also approx. crossover for quantum-gas behavior (section 18.3 of text)
- Note Room temperature, $1/\lambda_{th}^3 \approx\ 10^{25}\ m^{-3}$ for electrons; heavier particles (atoms) much smaller

Equilibrium ionization process (all considered ideal gases):

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- Assume all H atoms in ground state (valid if *T* not too high)
- Also *H* atoms at effective negative potential energy (-13.6 eV) relative to ions:

$$\mu_{\mathrm{H}} = -13.6\ \mathrm{eV} + [\mu_{\mathrm{translational}}]$$

Result:

$$\frac{n_e n_p}{n_H(1/\lambda_{th}^3)} = e^{-\Delta E_{ioniz}/k_B T}$$

- This is Saha equation: important in astronomy (Stellar atmospheres)
- Exponential term is Boltzmann probability distribution; product of densities is *law of mass action*, results from equality of chemical potentials.

Equilibrium ionization process (all considered ideal gases):

Further result:

$$\mu_{\mathrm{e}} = -k_B T ln\left[\frac{1/\lambda_{th}^3}{n_e}\right]$$

- So e.g. suppose all densities are equal (approximate crossover point for complete ionization): result is,

$$\mu_{\mathrm{e}} \approx -13.6 \text{ eV}$$

Electron chemical potential found to be lowest when it is thermally more stable than H-atom.

We will return to this later in the course (relation of μ to Gibbs free energy).

Brief summary, chapter 2:

Fundamental equation: $\boldsymbol{S(U, V, N_1, N_2 \ldots)}$ **or** $\boldsymbol{U(S, V, N_1, N_2 \ldots)}$

& First law :

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

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

$$\boldsymbol{T = \left(\frac{\partial U}{\partial S}\right)_{VN}} \qquad \boldsymbol{\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{VN}}$$

$$\boldsymbol{-P = \left(\frac{\partial U}{\partial V}\right)_{SN}} \qquad \boldsymbol{\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{UN}}$$

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

Equations of state

equilibrium,

$T_1 = T_2$ thermal

$P_1 = P_2$ mechanical

$\mu_1 = \mu_2$ matter flow

$\mu_H = \mu_e + \mu_p$ chemical