

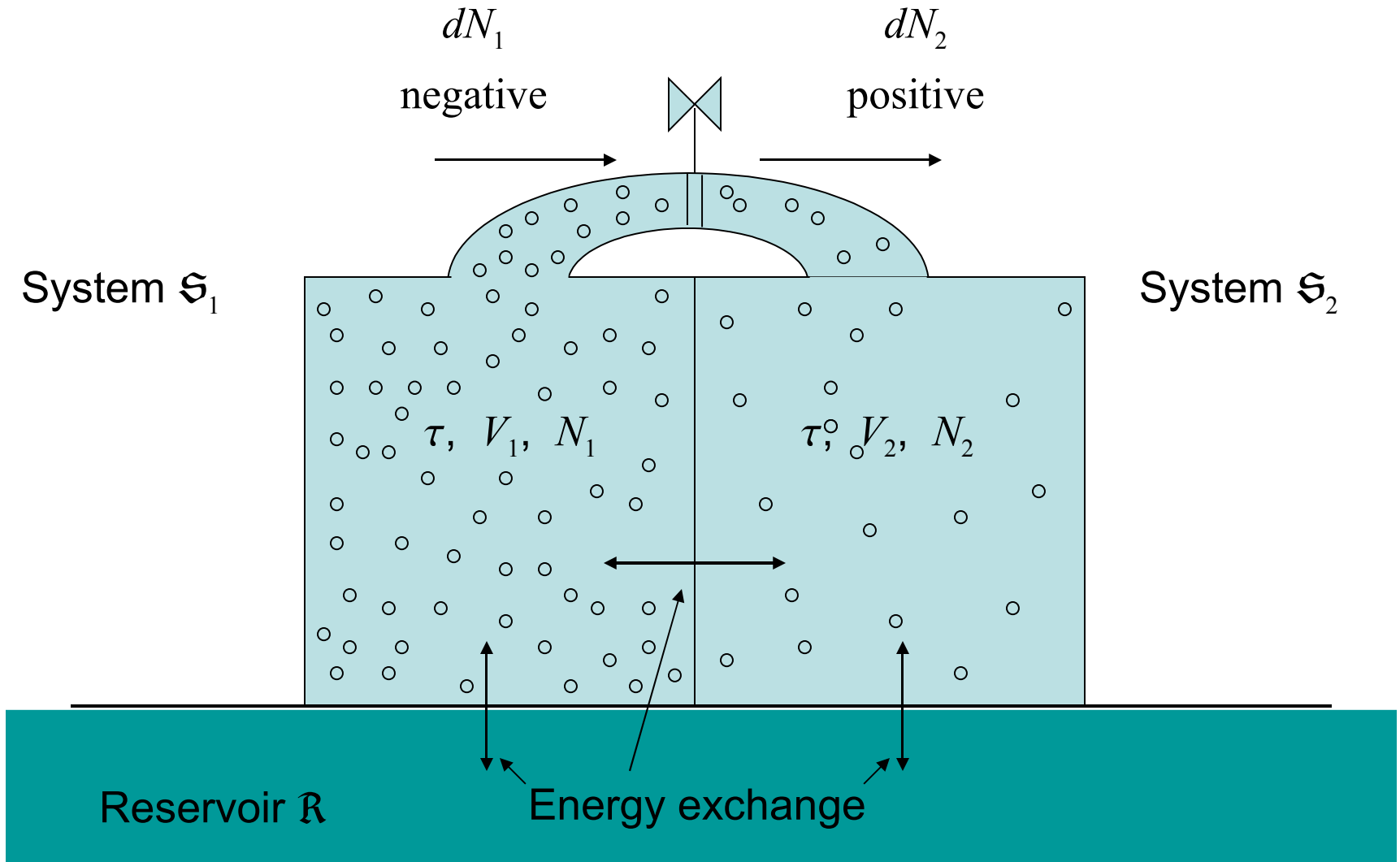
CHEMICAL POTENTIAL AND GIBBS DISTRIBUTION

Chemical Equilibrium

- Remember that T was the property, two systems share when they are in thermal equilibrium (flow of energy).
- The **Chemical Potential** $\mu(\tau, V, N)$ governs the flow of particles (diffusive contact) between the systems, just as the temperature governs the flow of energy.

We will show that if μ of the two systems is different, particles will flow from the system with higher μ_1 to the system with lower μ_2 , until $\mu_1 = \mu_2$

Consider $\mathfrak{S}_1 + \mathfrak{S}_2$ as shown in the figure:



We have shown earlier that for a system S in thermal equilibrium with reservoir \mathfrak{R} , the Helmholtz free energy F is minimum compatible with τ, V, N and other constraints.

This is also true for $S_1 + S_2$ (here $N = N_1 + N_2 = \text{constant}$).

$$F = F_1 + F_2 = U_1 + U_2 - \tau(\sigma_1 + \sigma_2) \quad \text{is a minimum.}$$

Since N is constant,

$$\begin{aligned} dN = 0 &= dN_1 + dN_2 \\ \Rightarrow dN_1 &= -dN_2 \end{aligned}$$

At the minimum,

$$dF = 0 = \left(\frac{\partial F_1}{\partial N_1} \right)_{\tau} dN_1 + \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau} dN_2 = 0$$

Also V_1, V_2 hold constant.

$$\Rightarrow \left[\left(\frac{\partial F_1}{\partial N_1} \right)_{\tau} - \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau} \right] dN_1 = 0 \quad (*)$$

$$\Rightarrow \left(\frac{\partial F_1}{\partial N_1} \right)_{\tau} = \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau} = \mu_j(\tau, V_j, N_j) \text{ (condition for equilibrium).}$$

The chemical potential is defined as

$$\left(\frac{\partial F}{\partial N} \right)_{\tau, V} := \mu(\tau, V, N)$$

If $\mu_1 > \mu_2$ we see from (*) that $dF < 0$ when $dN < 0 \Rightarrow$ Particles flow from the system with larger μ to the system with lower μ

Since Particles are not divisible, the strict definition of μ is in terms of a difference (as opposed to derivative)

$$\mu(\tau, V, N) \equiv F(\tau, V, N) - F(\tau, V, N - 1)$$

If several chemical species are present , each has its own chemical potential

$$\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{\tau, V, N_1, N_2, \dots} .$$

Example: Chemical Potential of the Ideal Gas

Remember: The free energy of the monatomic ideal gas is

$$F = -\tau \ln Z$$

or

$$F = -\tau [N \log Z_1 - \log N!] = -\tau \log \left[\frac{Z_1^N}{N!} \right]$$

where $Z_1 = \frac{V}{\lambda_{DB}^3} = n_Q V$, $n_Q = \frac{1}{\lambda_{DB}^3}$ (Quantum concentration)

$$\text{and } \lambda_{DB} = \sqrt{2\pi m^2 / M\tau}$$

Use

$$F(N) - F(N-1) = -\tau \left[(N - N + 1) \log Z_1 - \log \frac{N!}{(N-1)!} \right]$$

$$\Rightarrow \mu = -\tau [\log Z_1 - \log N] = \tau \log(N/Z_1)$$

$$\text{or } \mu = \tau \log \frac{n}{n_Q}, \quad \text{where } n = N/V.$$

μ depends on concentration, not on N or V separately.

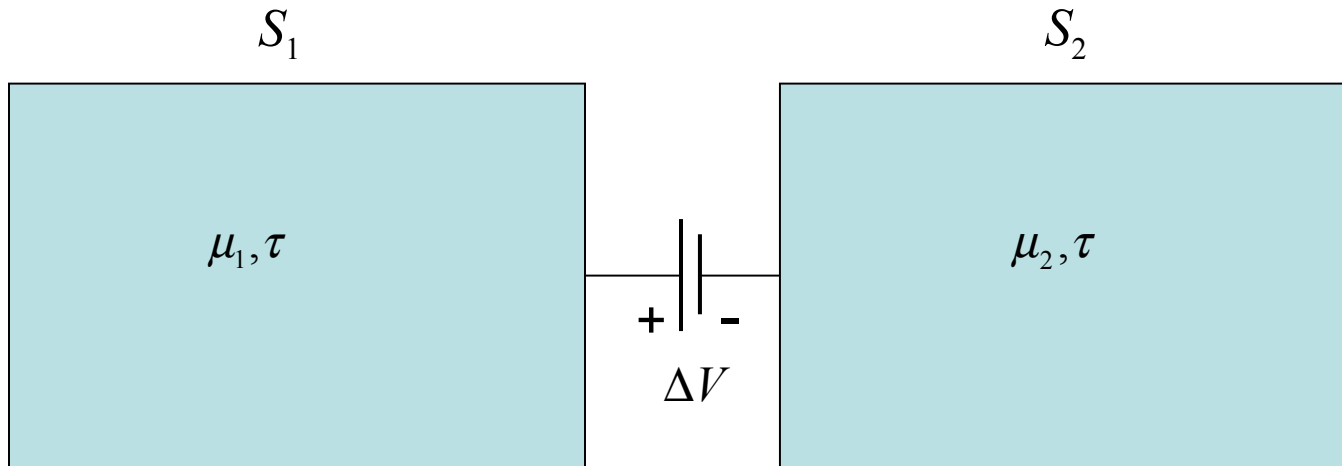
μ Increases as n increases! This is what one would expect intuitively.

Using Ideal gas law $p = n\tau$ we can write

$$\mu = \tau \log(p/\tau n_Q).$$

Internal and Total Chemical Potential

Consider the two systems of charged particles. A potential step between them can be established by applying a voltage.



Initially $\mu_2 > \mu_1$, yielding $\Delta\mu(\text{initial}) = \mu_2 - \mu_1$

Now apply ΔV to S_1 such that

$$q\Delta V = q(V_2 - V_1) = \Delta\mu(\text{initial})$$

If F_2 is fixed, the potential step rises F_1 by

$$N_1\Delta\mu(\text{initial}) \quad (\text{increase in potential energy})$$

For diffusive equilibrium we need

$$\mu_1(\text{final}) = \mu_1(\text{initial}) + \underbrace{[\mu_2(\text{initial}) - \mu_1(\text{initial})]}_{\Delta\mu(\text{initial})} = \mu_2(\text{initial}) = \mu_2(\text{final})$$

The barrier $q\Delta V$ brings S_1 and S_2 into diffusive equilibrium.

Note: The chemical potential $\hat{=}$ potential energy.

The difference in μ is equal to a potential barrier that will bring two systems into equilibrium.

When external potentials are present

$$\mu = \mu_{\text{tot}} = \mu_{\text{ext}} + \mu_{\text{int}}$$

μ_{int} : Internal chemical potential, defined as μ if no external potential is present.

The equilibrium condition $\mu_2 = \mu_1$ can then be written as

$$\begin{aligned}\Delta\mu_{\text{tot}} &= 0 \\ \Rightarrow \Delta\mu_{\text{ext}} &= -\Delta\mu_{\text{int}}.\end{aligned}$$

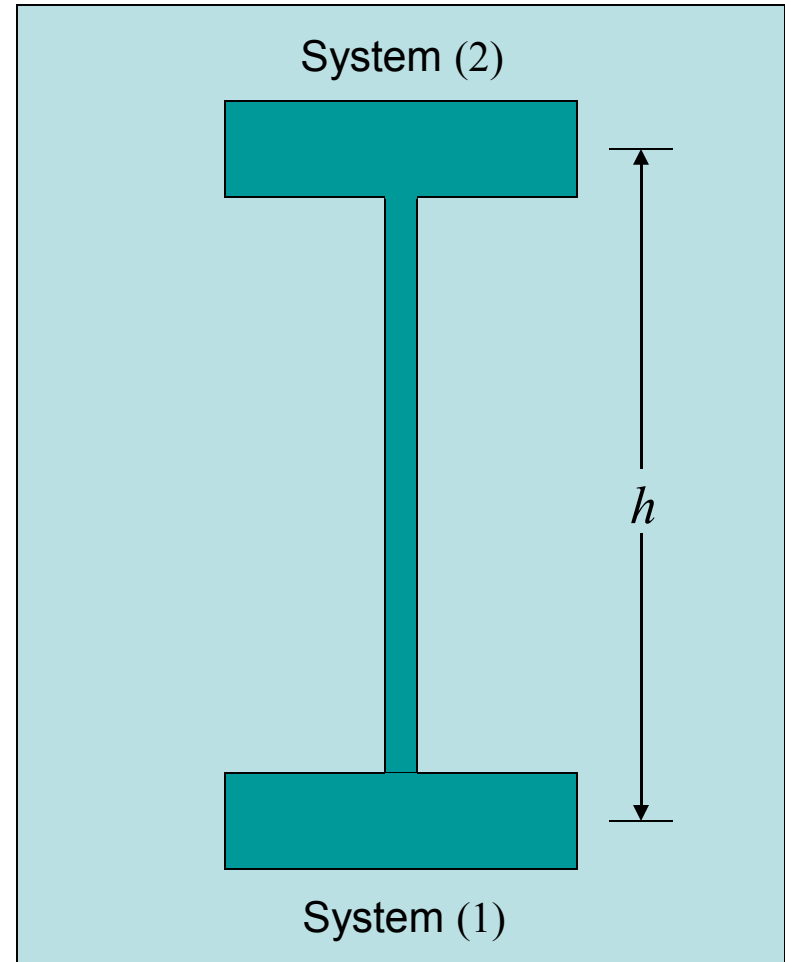
Example: Variation of barometric pressure with altitude.

Place the zero of the potential energy at ground level, then the potential energy per molecule at height h is Mgh , where M is the particle mass and g the gravitational acceleration.

The internal chemical potential of the particles is given by

$$\mu_{\text{int}} = \tau \log \left(\frac{n}{n_Q} \right)$$

$$\mu_{\text{ext}} = Mgh.$$



A model of the variation of atmospheric pressure with altitude.

The total chemical potential is

$$\mu(h) = \tau \log\left(\frac{n(h)}{n_0}\right) + Mgh$$

In equilibrium, the chemical potential μ must be every where identical:

$$\begin{aligned} \tau \log\left[\frac{n(h)}{n_0}\right] + Mgh &= \tau \log\left[\frac{n(0)}{n_0}\right] \\ \Rightarrow n(h) &= n(0) \exp\left(\frac{-Mgh}{\tau}\right) \end{aligned}$$

For an ideal gas $p = n\tau$

$$p(h) = p(0) \exp\left(\frac{-Mgh}{\tau}\right) = p(0) \exp\left(\frac{-h}{h_c}\right)$$

$$\text{where } h_c = \frac{\tau}{Mg}.$$

This is **barometric pressure equation**.

Barometric pressure equation gives us dependence of the pressure on altitude in an isothermal atmosphere of a single chemical species.

At the characteristic height $h_c = \frac{\tau}{Mg}$ the atmospheric pressure decreases by the fraction $e^{-1} \approx 0.37$. To estimate the characteristic height, consider an isothermal atmosphere composed of nitrogen molecules with a molecular weight of 28.

Mass of an N_2 molecule is 48×10^{-24} gm. .

At temperature 290K the value of $\tau \equiv k_B T$ is 4.0×10^{-14} erg.

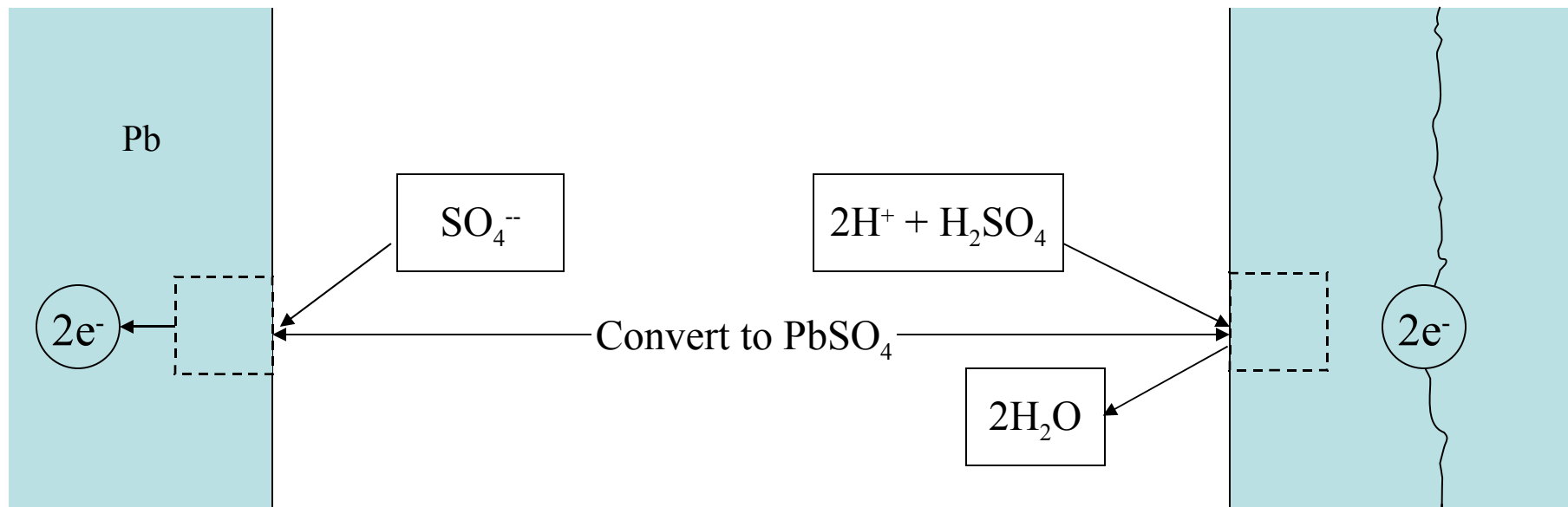
With $g = 980 \text{ cm s}^{-2}$, the characteristic height is then 8.5km.

Batteries

One of the most vivid examples of chemical potentials and potential steps is the electrochemical battery. In the lead-acid battery the negative electrode consists of metallic lead, Pb, and the positive electrode is a layer of reddish-brown lead oxide, PbO₂, on a Pb substrate. The electrodes are immersed in diluted sulfuric acid, H₂SO₄, which is partially ionized into H⁺ ions SO₄⁻ ions. It is the ion that matter.

(-) electrode

(+) electrode

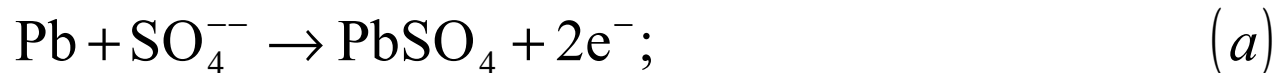


The lead-acid battery consists of a Pb and a PbO_2 electrode immersed in partially ionized H_2SO_4 . One SO_4 ion converts one Pb atom into $\text{PbSO}_4 + 2e^-$; two H^+ ions plus one un-ionized H_2SO_4 molecule convert one PbO_2 molecule into $\text{PbSO}_4 + 2\text{H}_2\text{O}$, consuming two electrons.

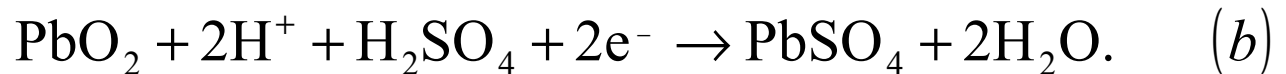
In the discharge process both the metallic Pb of the negative electrode and the PbO₂ of the positive electrode are converted to lead sulfate, PbSO₄.

Discharge Process:

Negative electrode:

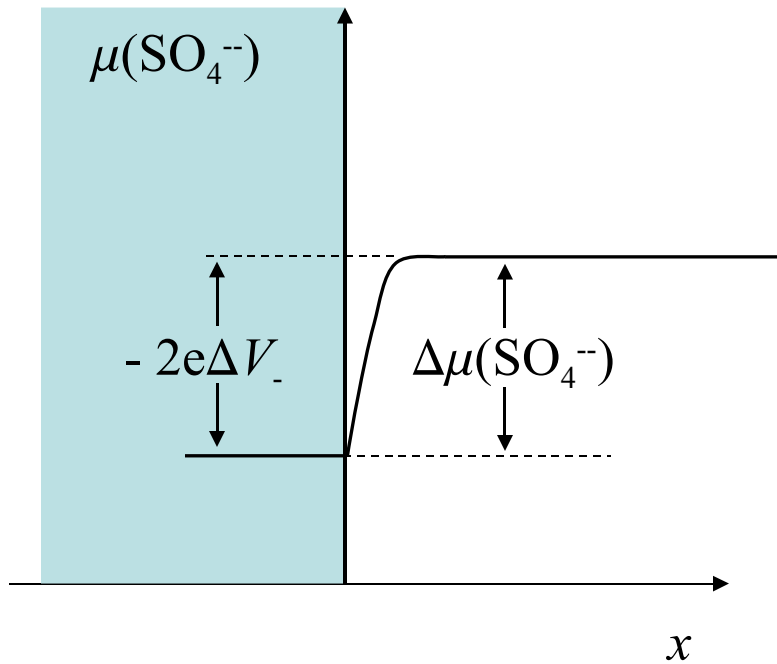


Positive electrode:

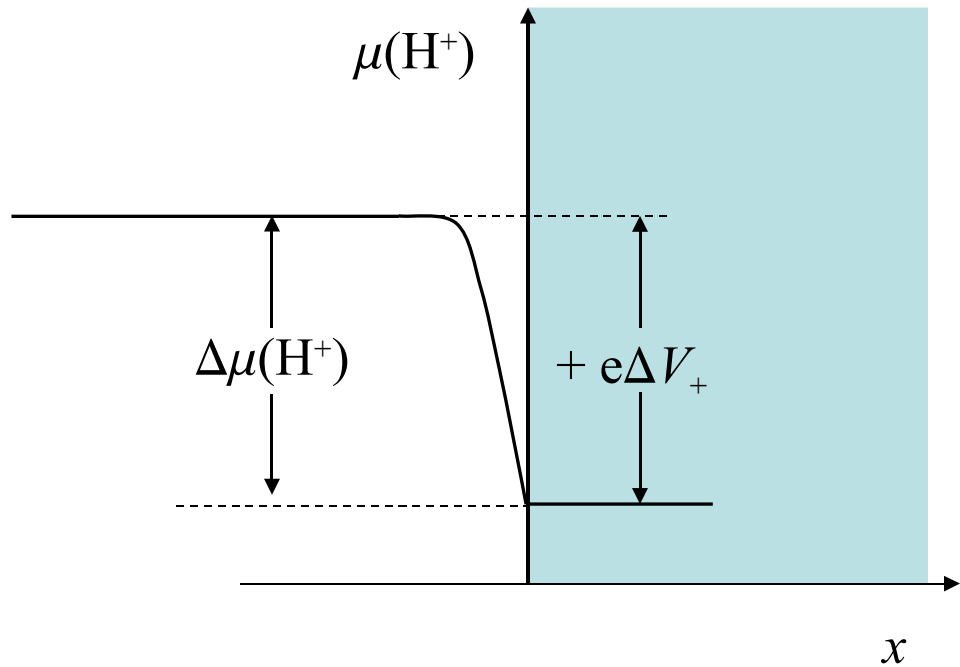


Because of (a) the negative electrode acts as a sink for SO₄⁻ ions, keeping the internal chemical potential $\mu(\text{SO}_4^{--})$ of the sulfate ions at the surface of the negative electrode lower than inside the electrolyte.

(-) electrode



(+) electrode

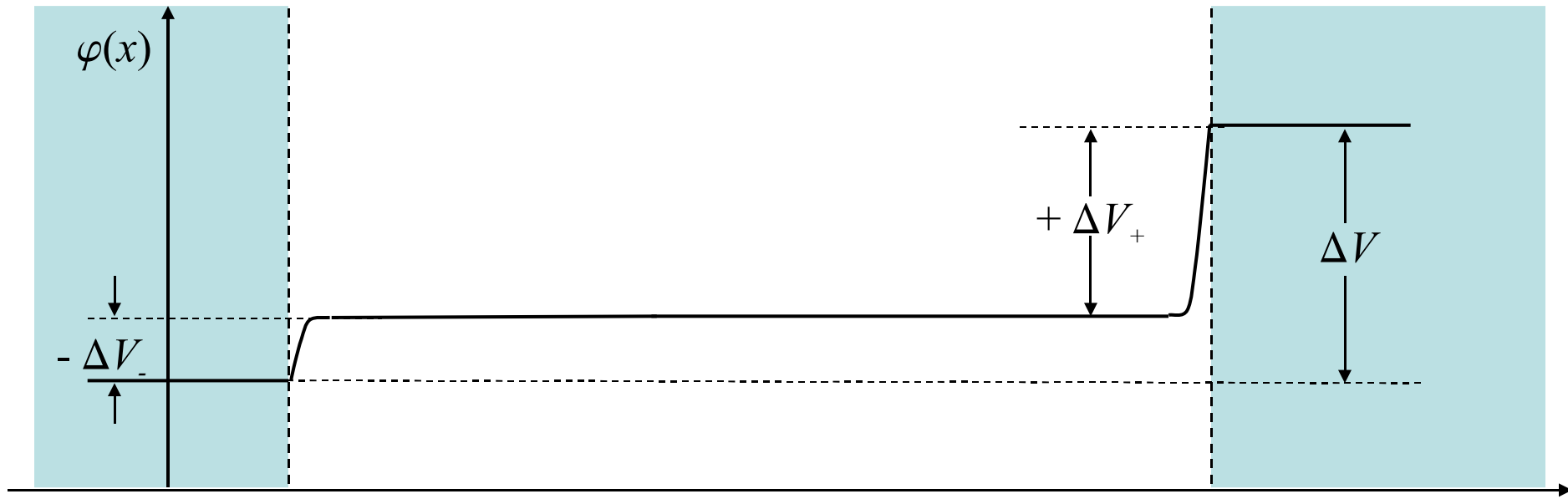


The electrochemical potentials for SO_4^{2-} and H^+ before the development of internal potential barriers that stop the diffusion and the chemical reaction.

Because of (b) the positive electrode acts as a sink for H^+ ions, keeping the internal chemical potential $\mu(H^+)$ of the hydrogen ions lower at the surface of the positive electrode than inside the electrolyte. The chemical potential gradients drive the ions towards the electrodes, and they drive the electrical currents during the discharge process.

(-) electrode

(+) electrode



The electrostatic potential $\varphi(x)$ after the formation of the barrier.

x

If battery terminals are not connected, an electrical potential $\varphi(x)$ develops until they equalize the chemical potential steps. Diffusion stops when:

at - electrode $-2q \Delta V_- = \Delta\mu(\text{SO}_4^{2-})$

at + electrode $+q \Delta V_+ = \Delta\mu(\text{H}^+)$.

The two potentials ΔV_- and ΔV_+ are called half-cell potentials.

The total electrostatic potential difference developed across one full cell of the battery, as required to stop the diffusion reaction, is

$$\Delta V = \Delta V_+ - \Delta V_- = 2.0 \text{ volt.}$$

This is the open-circuit voltage or EMF (electromotive force) of the battery.

There is a small electron current through the electrolyte, however it is negligible! Otherwise a battery would discharge quickly. Electrons dominantly flow through external connection

An alternative way to calculate the chemical potential.

Now the number of quantum states has to depend on the number of particles

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

Assume isotropic process $dV = 0$, select $d\sigma, dU, dN$ in such a way that $d\tau = 0$, call these values $(\delta\sigma)_\tau, (\delta U)_\tau, (\delta N)_\tau$ respectively then

$$d\tau = 0$$

when

$$(\delta\sigma)_\tau = \left(\frac{\partial \sigma}{\partial U} \right)_N (\delta U)_\tau + \left(\frac{\partial \sigma}{\partial N} \right)_U (\delta N)_\tau,$$

After division by $(\delta N)_\tau$,

$$\frac{(\delta\sigma)_\tau}{(\delta N)_\tau} = \left(\frac{\partial \sigma}{\partial U} \right)_N \frac{(\delta U)_\tau}{(\delta N)_\tau} + \left(\frac{\partial \sigma}{\partial N} \right)_U.$$

$$\left(\frac{\partial \sigma}{\partial N}\right)_{\tau, V} = \left(\frac{\partial \sigma}{\partial U}\right)_{\tau, V, N} \left(\frac{\partial U}{\partial N}\right)_{\tau, V} + \left(\frac{\partial \sigma}{\partial N}\right)_{U, V}$$

$$\Rightarrow \tau \left(\frac{\partial \sigma}{\partial N}\right)_{\tau, V} = \left(\frac{\partial U}{\partial N}\right)_{\tau, V} + \tau \left(\frac{\partial \sigma}{\partial N}\right)_{U, V}$$

By the original definition of chemical potential

$$\Rightarrow -\tau \left(\frac{\partial \sigma}{\partial N}\right)_{\tau, V} + \left(\frac{\partial U}{\partial N}\right)_{\tau, V} \equiv \tau \left(\frac{\partial F}{\partial N}\right)_{U, V} \equiv \mu(\tau, V, N)$$

and on comparison with above equation

$$\mu = -\tau \left(\frac{\partial \sigma}{\partial N}\right)_{U, V} .$$

Thermodynamic identity

We can generalize the statement of the thermodynamic identity to include systems in which the number of particles is allowed to change.

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

$$\Rightarrow \tau d\sigma = dU + pdV - \mu dN$$

or

$$dU = \underbrace{\tau d\sigma}_{\text{Thermal heat}} - \underbrace{pdV}_{\text{Mechanical work}} + \underbrace{\mu dN}_{\text{Chemical work}}$$

Grand Canonical Ensemble and Grand Potential

Canonical Ensemble

Volume is fixed

Can exchange energy with
reservoir

Concept of thermal equilibrium

Definition of temperature
(energy fluctuates)

Boltzmann factor

Canonical partition function

Free energy

Grand Canonical Ensemble

Volume is fixed

Can additionally exchange
particles with reservoir

Concept of chemical/diffusive
equilibrium

Definition of chemical potential
(particle number fluctuates)

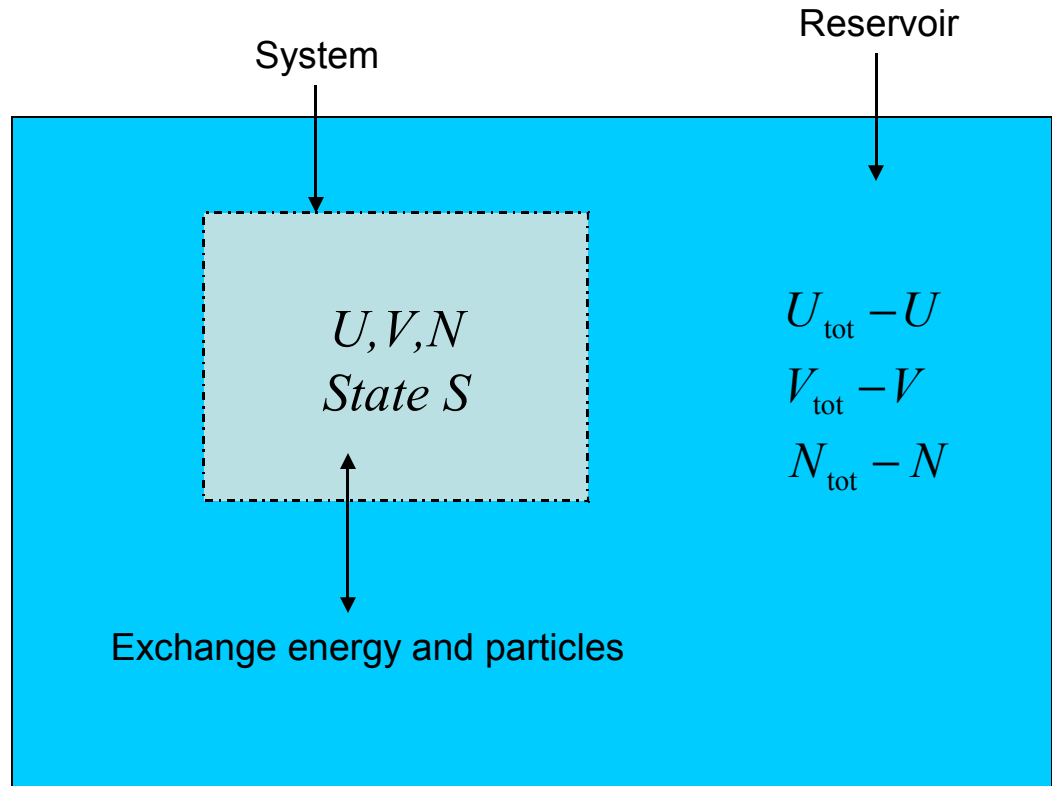
Gibbs factor

Gibbs sum
(Grand Canonical partition function)

Grand potential

Gibbs Factor

What is the probability of finding the system in a microstate S with some given values of U and N ?



U and N fluctuate, V is fixed

- Derivation follows exactly along the lines of the canonical case. The probability is proportional to the multiplicity!

$$P(S_{U,N}) \propto g(\text{reservoir} + \text{system})$$

$$= \underset{\text{no boundary effects}}{=} g(\text{reservoir}) \cdot \underset{\substack{\text{system is in fixed microstate} \\ \text{system is in fixed microstate}}}{g(\text{system})}$$

$$= g(\text{reservoir}) \cdot 1$$

$$= g_r(U_{\text{tot}} - U, N_{\text{tot}} - N)$$

$$= \exp\{\sigma_r(U_{\text{tot}} - U, N_{\text{tot}} - N)\}$$

$$= \underset{\text{Taylor}}{\exp} \left\{ \sigma_r(U_{\text{tot}}, N_{\text{tot}}) - \frac{\partial \sigma_r}{\partial U_{\text{tot}}} U - \frac{\partial \sigma_r}{\partial N_{\text{tot}}} N \right\}$$

$$= \exp \left\{ \sigma_r(U_{\text{tot}}, N_{\text{tot}}) - \frac{1}{\tau} U + \frac{\mu}{\tau} N \right\}$$

$$= \text{constant} \cdot \exp \left\{ -\frac{(U - \mu N)}{\tau} \right\}.$$

Hence: The probability of finding the system in a particular state S , in which it has energy U and particle number N is proportional to the

Gibbs factor

$$P(S_{U,N}) \propto \exp \left\{ -\frac{(U - \mu N)}{\tau} \right\}.$$

In order to get an equality, and not just a proportionality, we need to find the normalization factor. It is called the “Gibbs sum” or “grand canonical partition function”:

$$Z(\tau, V, \mu) := \sum_{N=0}^{\infty} \sum_{S_N} \exp\left(-\frac{(H_N(S_N) - \mu N)}{\tau}\right)$$

So that we have

$$P(S_{U,N}) = \frac{\exp\left(-\frac{(U - \mu N)}{\tau}\right)}{Z(\tau, V, \mu)}$$

The logarithm of Z is again a thermodynamic potential:

$$\Omega(\tau, V, \mu) := -\tau \ln Z(\tau, V, \mu)$$

It is called **Grand Potential**.

Relation of the grand potential with other thermodynamic potential:

$$\begin{aligned}\exp\left(-\Omega/\tau\right) &= Z = \sum_N \sum_{S_N} \exp\left(-\left(H(S_N) - \mu N\right)/\tau\right) \\ &= \sum_N \sum_U g_N(U) \exp\left(-\left(U - \mu N\right)/\tau\right) \\ &= \sum_{N,U} \exp(\sigma(U, N)) \exp\left(-\left(U - \mu N\right)/\tau\right) \\ &= \sum_{N,U} \exp\left(-\left(U - \tau\sigma - \mu N\right)/\tau\right)\end{aligned}$$

For large systems only the largest term in the sum will contribute significantly

$$\underset{\text{large system}}{\approx} \exp\left(-\min_{N,U}\left(U - \tau\sigma - \frac{\mu N}{\tau}\right)\right)$$

Taking the logarithm, we find

$$\Omega \approx \min_{N,U}\{U - \tau\sigma - \mu N\}$$

$$= \min_N\{F - \mu N\}.$$

Example: What is the average number of particles in our system

Consider

$$\begin{aligned}\langle N \rangle &= \sum_{N=0}^{\infty} \sum_{S_N} N P(S_N) \\ &= \frac{\sum_{N=0}^{\infty} \sum_{S_N} N \exp\left(-\frac{(H_N(S_N) - \mu N)}{\tau}\right)}{\sum_{N=0}^{\infty} \sum_{S_N} \exp\left(-\frac{(H_N(S_N) - \mu N)}{\tau}\right)} \\ &= \frac{\sum_{N=0}^{\infty} \sum_{S_N} \left(\tau \frac{\partial}{\partial \mu}\right) \exp\left(-\frac{(H_N(S_N) - \mu N)}{\tau}\right)}{\sum_{N=0}^{\infty} \sum_{S_N} \exp\left(-\frac{(H_N(S_N) - \mu N)}{\tau}\right)}\end{aligned}$$

$$= \frac{\tau \frac{\partial}{\partial \mu} Z(\tau, V, \mu)}{Z(\tau, V, \mu)} = \tau \frac{\partial}{\partial \mu} \ln Z(\tau, V, \mu)$$

$$= -\frac{\partial}{\partial \mu} (-\tau \ln Z(\tau, V, \mu)) = -\frac{\partial \Omega(\tau, V, \mu)}{\partial \mu}$$

$$\Rightarrow \langle N \rangle = \tau \frac{1}{Z} \frac{\partial Z}{\partial \mu}$$

Also

$$\lambda \equiv \exp\left(\frac{\mu}{\tau}\right)$$

$$\Rightarrow Z = \sum_N \sum_S \lambda^N \exp\left(-\frac{\epsilon_s}{\tau}\right), \quad \text{since } \frac{\partial}{\partial \mu} = \frac{\partial \lambda}{\partial \mu} \frac{\partial}{\partial \lambda}$$

$$\Rightarrow \langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \log Z.$$