We now consider systems that can exchange particles, in addition to energy. This will lead to the Grand Canonical Ensemble of statistical mechanics. We saw that temperature can be used to decide how energy will flow between two systems when they are brought into thermal contact. Simply put, the system with the higher temperature will deliver energy to the system with the lower temperature when they are brought into thermal contact, according to the second law of thermodynamics. In equilibrium, the net energy transfer comes to an end, and the temperatures equalize. In analogy, we would like to define a 'potential' that determines how particles move from one system to another when they are brought into contact. We shall term the exchange of particles between systems as 'diffusive contact'. Examples include p/n junctions in semiconductors, chemical batteries, fuel cells, etc.

Consider two systems in thermal equilibrium with each other and with a reservoir at temperature τ. The Helmholtz free energy of the joint system will be minimized. If the two systems are brought into diffusive contact, there will be an exchange of particles to establish equilibrium. At that point the differential of Helmholtz free energy will be zero: $dF = 0 = \frac{\partial F}{\partial N_1}|_{\tau, V_1} dN_1 + \frac{\partial F}{\partial N_2}|_{\tau, V_2} dN_2$. Since the number of particles lost by one system must equal the particles gained by the other, it must be that: $\left(\frac{\partial F}{\partial N_1}|_{\tau, V_1} - \frac{\partial F}{\partial N_2}|_{\tau, V_2}\right) dN_1 = 0$. In equilibrium it must be these two derivatives are the same, suggesting that we define a 'chemical potential': $\mu(\tau, V, N) \equiv \frac{\partial F}{\partial N}|_{\tau, V}$, which will equilibrate after diffusive contact is established. Note that the chemical potential has the dimensions of energy per particle. Some other expressions for the chemical potential include $\frac{\mu(U, V, N)}{\tau} = -\frac{\partial \sigma}{\partial N}|_{U, V}$, and $\mu(\sigma, V, N) \equiv \frac{\partial U}{\partial N}|_{\sigma, V}$.

If two systems with different chemical potentials ($\mu_1 \ and \ \mu_2$) are brought together into diffusive contact, particles will flow, but which way? Suppose $\mu_1 > \mu_2$ before contact. From $dF = \mu_1 dN_1 + \mu_2 dN_2$, we see that the Helmholtz free energy will go down if $dN_1 < 0$. We can conclude that particles flow from systems with high chemical potential to low chemical potential.

As an example, consider the chemical potential of an ideal gas. In lecture 9 we found the Helmholtz free energy is $F = N\tau[logN - \log(n_Q V) - 1]$, where $n_Q = (\frac{M\tau}{2\pi\hbar^2})^{3/2}$ is the quantum concentration. The chemical potential is found to be $\mu = \tau\log(n/n_Q)$, where $n = N/V$ is the particle concentration. Systems with a higher concentration will have a larger chemical potential. If we consider systems in the dilute, classical limit ($n \ll n_Q$) then the chemical potential will be negative, since the logarithm is negative. The class web site has plots of μ/τ vs. $\log(n/n_Q)$, for He gas, liquid He, and for electrons at different temperatures (Note that n_Q is a function of temperature). Electrons very quickly approach the quantum limit at modest concentrations – we will attack this problem later when we consider electrons in metals.

The Thermodynamic Identity (a statement of conservation if energy) can now be expanded to include the exchange of particles: $dU = \tau d\sigma - pdV + \mu dN$. This says that energy can be added to a system by adding entropy at fixed temperature, by the system doing work, and by adding new particles.

Particles can also move between systems because of other effects. External fields (gravity, electric, magnetic) can influence the motion of particles. For example the electron has a magnetic moment $\vec{\mu}$, and in an external field $\vec{B}$ has an energy $U = -\vec{\mu} \cdot \vec{B}$. An electron also has a charge q, giving it a potential $U = qV$ in an external electric field $\vec{E} = -\vec{\nabla}V$. Mechanical effects can also induce particles to move. We propose that a total chemical potential is constructed by adding the 'internal chemical potential' that we have calculated above to the 'external' contributions such as $U_{electric}$, $U_{magnetic}$, $U_{gravity}$, etc. where each of these potential energies is per particle.

As an example, we consider a rotating centrifuge, problem 1 in Chapter 5 of K+K. The external potential is due to the 'centrifugal' force acting on a particle at a distance r from the axis of rotation: $F_{cent} = M\omega^2 r \hat{r}$, giving a potential of $U_{cent} = -\frac{M\omega^2 r^2}{2}$. The gas is at temperature τ, and we assume that the material achieves diffusive equilibrium, so that the total chemical potential is uniform. The result for the concentration as a function of radial distance r from the axis of rotation is $n(r) = n(0)Exp[\frac{M\omega^2 r^2}{2\tau}]$. A centrifuge can be used to separate isotopes, such as ^{235}U and ^{238}U, in the form of uranium hexafluoride gas, because their masses are different and they will have different concentration profiles in the spinning centrifuge.