Phys 112 : Lecture 25

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel
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1 Work for different processes

Suppose that we have a reversible process at constant temperature. Then we have the conditions:

$$d\tau = 0; \qquad dQ = \tau d\sigma = d(\tau\sigma)$$

$$dW = dU - dQ = dU - d(\tau\sigma) = d(U - \tau\sigma) = dF$$

where F is the Helmholtz free energy. Now for an ideal gas, if the temperature is constant then the internal energy is constant, so we have that:

$$dU = 0; \qquad dW = -dQ = dF$$

Now, we can imagine an isobaric process, where the pressure in constant. Then we know that the work done on the system is given:

$$-pdV = -d(pV)$$

Now we can consider the "effective work done on system":

$$dW' = dW - (-d(pV)) = dW + pdV = dU - dQ + d(pV) = d(U + pV) - dQ$$

Now notice that if we define the enthalpy $H = U + PV$, which plays the role of the Helmholtz free energy in the isobaric case. So now we have that the Heat capacity at constant pressure is given by

$$C_p = \frac{\partial H}{\partial \tau} = \frac{\partial U}{\partial \tau} + \frac{\partial}{\partial \tau}(pV) = \frac{\partial U}{\partial \tau} + \frac{\partial}{\partial \tau}(N\tau) = \frac{\partial U}{\partial \tau} + N = C_v + N$$
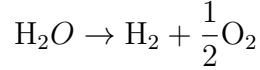
Note that say if we are vaporizing water, we have $dQ = dH = $ heat of vaporization. Note also that e have:

$$dW = dU - \tau d\sigma + pdV = dF + pdV = dG$$

where G is the Gibbs free energy. We can play with the equations to get relations:

$$G = F + pV = U + pV - \tau\sigma = H - \tau\sigma$$

As an example of when we would use the Gibbs free energy, consider the chemical equation

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

Now the amount of work you need to do is the change in Gibbs free energy (in this case, roughly 237kJ/mol). Now, notice that we have

$$dW = dQV_0; \qquad dQ = ZeN_A$$

where Q represents charge here, Z is presumably the charge of the particles, N_A is the Avogadro's number. With this, we can calculate the voltage needed (roughly 1.23 Volts for this system). Note that we have:

$$\Delta G = \Delta U + p\Delta V - \tau\Delta\sigma$$

where ΔU is the change in internal energy for the chemical reaction, $p\Delta V$ is the amount of 'expansion' that occurs in the reaction, and $\tau d\sigma$ is the change in entropy in the chemical reaction. We can also define the efficiency as $\Delta G/\Delta H$.

Now, consider a reversible process where particles can be exchanged:

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

$$\tau d\sigma = dQ = \text{heat transfer}$$

$$-pdV = dW_m = \text{mechanical work on system}$$

$$\mu dN = dW_c = \text{chemical work}$$

Now, the total chemical work is:

$$dW_c = dW_{c1} + dW_{c2} = \mu_1 dN_1 + \mu_2 dN_2 = (\mu_2 - \mu_1)dN$$

where $dN_1 = -dN_2 = dN$ from system 1 to system 2. Now, in the case of ideal gases, where system one is at state n_1, V_1, and system two is at n_2, V_2, we have:

$$\mu_2 - \mu_1 = \tau\left[\ln\left(\frac{n_2}{n_Q}\right) - \ln\left(\frac{n_1}{n_Q}\right)\right] = \tau\ln\left(\frac{n_2}{n_1}\right)$$

i.e. moving a particle from system 1 to system 2 is equivalent (particle by particle) to compressing system 1 to the density of system 2.