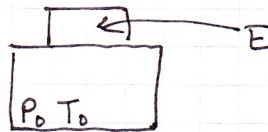


Lecture 7

Reversible Processes $\delta W = -PdV$
 $\delta Q = TdS$

System in contact with Heat Bath



Result of 2nd Law is:

$$\Delta A \leq 0$$

$$A = E + P_0 V - T_0 S$$

Consider Special Cases

① $\Delta V = 0$ for system
 $T = T_0$

$$T_{0i} = T_{0f}$$

$$\Delta A = \Delta E + P_0 \Delta V + T_0 \Delta S$$

$$\Delta A = \Delta E - T_0 \Delta S \leq 0$$

$$\therefore \Delta (E - T_0 S) \leq 0$$

$$F \equiv E - TS$$

under these conditions the Helmholtz energy must decrease at minimum it is in equilibrium

② $P_0 = P$ "too restrictive" at initial + final states
 $T_0 = T$

$$\Delta (E + PV - TS) \leq 0$$

$$G \equiv E + PV - TS$$

Gibb's free energy is a minimum at equilibrium

$$\Delta G \leq 0$$

recall $S = -\sum_r k p_r \ln p_r$

$$p_r = \frac{1}{Z} e^{-E_r/kT}$$

$$Z = \sum_r e^{-E_r/kT}$$

Helmholtz Free Energy

$$F = E - TS$$

$$dF = dE - TdS - SdT = TdS - PdV - TdS - SdT = -PdV - SdT$$

$$F = F(V, T)$$

$$dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT$$

by visual inspection :
 derive useful results :

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

Using mixed partial derivatives

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}$$

$$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$\therefore \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \quad \text{maxwell's Relations}$$

Gibb's Free Energy

$$G = E + PV - TS$$

$$dG = dE + PdV + VdP - TdS - SdT$$

$$dG = TdS - PdV + PdV + VdP - TdS - SdT = VdP - SdT$$

$$G = G(P, T)$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

by visual inspection:

$$\boxed{V = \left(\frac{\partial G}{\partial P}\right)_T}$$

$$\boxed{S = -\left(\frac{\partial G}{\partial T}\right)_P}$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P}$$

$$\boxed{-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P}$$

Maxwell's Relations

Lecture 7 continued... 'Real' Process ΔS

① Temperature Equalization
two bodies of equal size + heat capacity
 $T_1 = T_2$ @ equilibrium

$$T_f = \frac{T_{1i} + T_{2i}}{2}$$

you expect hot body to lose entropy, cold body to gain entropy

$$\Delta S = \int \frac{dQ}{T}$$

② Heat Bath T_0 and finite body T_1

$$\Delta S_{TOT} = \Delta S_{sys} + \Delta S_{HB} = \Delta S + \Delta S_0$$

$$\Delta S_0 = \frac{1}{T_0} \int dQ \quad \Delta Q = \int dQ = M_s (T_1 - T_0) \rightarrow \Delta S_0 = \frac{M_s (T_1 - T_0)}{T_0}$$

entropy change of heat bath

$$\Delta S_{SYSTEM} = \Delta S = - \int \frac{dQ}{T} \quad \text{but now } T \neq \text{constant}$$

$$\Delta S = + \int \frac{M_s dT}{T} \quad \begin{array}{l} \text{as long as heat is supplied to the system} \\ dQ = M_s dT \end{array}$$

In general, specific heat is a function of temperature, but over a small interval it can be regarded as a constant

$$\Delta S = M_s \int_{T_1}^{T_0} \frac{dT}{T} = M_s \ln\left(\frac{T_0}{T_1}\right) \quad \text{entropy change of system}$$

$$\Delta S_{TOTAL} = \Delta S_{HB} + \Delta S_{sys} = M_s \left[\ln\left(\frac{T_0}{T_1}\right) + \left(\frac{T_1 - T_0}{T_0}\right) \right]$$

HB gain	-	+	if $T_0 < T_1$
HB loss	+	-	if $T_0 > T_1$

Can you show that $\Delta S_{TOT} \geq 0$ for this case?

$$\ln\left(\frac{T_0}{T_1}\right) + \left(\frac{T_1 - T_0}{T_0}\right) \geq 0$$

$$\text{let } x = T_1/T_0 \quad \Delta S_{TOT} = M_s \left(\ln\left(\frac{1}{x}\right) + (x-1) \right) = f(x)$$

$M_s > 0$ need to show that $(x-1-\ln x)$ is always positive

at $x=1$ then $\Delta S = 0$

$T_1 = T_0$

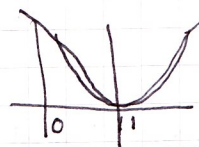
prove positive definiteness of $f(x) = x - 1 - \ln x$

$$\frac{df}{dx} = 1 - \frac{1}{x}$$

If $x > 1$ then $\frac{df}{dx} > 0$

that means f increases from $x=1$ so $f \geq 0$ if $x \geq 1$

If $x \leq 1$ then $\frac{df}{dx} \leq 0$ slope decreases to $f=0$



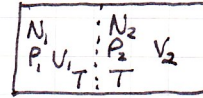
Lecture 7 cont. Third Law of Thermodynamics

Showing that the total entropy change is positive

Consider a frictionless partition

Initial P_1, P_2 — what is the final pressure?

initial $P_1 V_1 = N_1 kT$ final $P_1 = P_2 = P$



$P_2 V_2 = N_2 kT$ $P(V_1 + V_2) = (N_1 + N_2) kT$

final: $P = \frac{(N_1 + N_2) kT}{V_1 + V_2} = \frac{P_1 V_1 + P_2 V_2}{V_1 + V_2} = \frac{P_1 V_1}{V_1 + V_2} + \frac{P_2 V_2}{V_1 + V_2}$

$dQ = dE + PdV$ $dT=0 \therefore dE=0$

$PV = NkT$

$PdV + VdP = NkdT = 0 \rightarrow PdV = -VdP$

$\Delta S = \int \frac{dQ}{T} = - \int \frac{VdP}{T} = -Nk \int \frac{dP}{P}$ show positive $\Delta S_1 = -N_1 k \int_{P_1}^P \frac{dP}{P}$ $\Delta S_2 = -N_2 k \int_{P_2}^P \frac{dP}{P}$

Third Law - look at the general definition of entropy

$S = -k \sum_r p_r \ln p_r$

$\lim_{T \rightarrow 0} S = -k p_0 \ln p_0$ non-degenerate lowest state

$p_0 = 1$ 100% in this state because it is non-degenerate

$\lim_{T \rightarrow 0} S = -k p_0 \ln p_0 = -k \ln 1 = 0$ independent of any macroscopic variable
 $\left. \frac{\partial S}{\partial P} \right|_{T=0} = 0$ $\left. \frac{\partial S}{\partial V} \right|_{T=0} = 0$

Fundamental Theorem: All states of the same energy have equal probability.

States: g $P(g) = \frac{1}{g}$

$S = -k \sum_{i=1}^g \frac{1}{g} \ln \left(\frac{1}{g} \right) = -k g \frac{1}{g} \ln \left(\frac{1}{g} \right) = k \ln g$

$\left. \frac{\partial S}{\partial P} \right|_{T=0} = 0$ $\left. \frac{\partial S}{\partial V} \right|_{T=0} = 0$

When $T \rightarrow 0$ everything goes to the lowest state (ground) and everything has a definite energy.

$S \rightarrow k \ln g$ finite # $\Delta S = \int \frac{dQ}{T} = \int \frac{C_v dT}{T}$ change in entropy is independent of the process

$S(T) - S(T=0) = \int_0^T \frac{C_v dT}{T}$ to be finite

$\lim_{T \rightarrow 0} C_p = 0$ by same argument $C_p \rightarrow 0$ as $T \rightarrow 0$

