

Lecture 2

$S(U, V, N)$ A state function
 $U(S, V, N)$ " " "

Exact differential form

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

State function means

$$\oint dU = 0$$

Going around a closed path returns our system to where it was.

S, U homogeneous of order 1. Means $U(\lambda S, \lambda V, \lambda N)$
extensive $= \lambda U(S, V, N)$

Implies derivatives are zero order homogeneous

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = f(S, V, N) \quad f(\lambda S, \lambda V, \lambda N) = f(S, V, N)$$

These partials are independent of system size (same in any part of system)
intensive

Give these derivatives special names:

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \quad \text{temperature}$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -P \quad \text{pressure}$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu \quad \text{chemical potential}$$

$$dU = T dS - P dV + \sum_i \mu_i dN_i$$

$$QS \rightarrow P = P_{ext}$$

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$-PdV = dW_{as}$ quasi-static work (even when a process is not quasi-static, it still has a quasi-static component!)

$$dN_i = 0 \quad dU = TdS + dW_{as} \quad , \quad dU = dQ_{as} + dW_{as}$$

$$TdS = dQ_{as}$$

2nd Law!

Note each of these parameters is a diff eq:

$$T = T(S, V, N) = \left(\frac{\partial U}{\partial S}\right)_{V, N}$$

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

$$\mu_i = \mu_i(S, V, N) = \left(\frac{\partial U}{\partial N_i}\right)_{S, V}$$

} equations of state

Knowing any one of these tells us all only to within a function of the other two.

$$U = \int \left(\frac{\partial U}{\partial S}\right)_{V, N} dS = \int TdS + f(V, N)$$

Recall Euler relation for 1st order homogeneous fn: $f(x, y) = x \left(\frac{\partial f}{\partial x}\right) + y \left(\frac{\partial f}{\partial y}\right)$

Apply to $U(S, V, N_1, N_2, \dots, N_r)$

$$U(S, V, N) = S \left(\frac{\partial U}{\partial S}\right) + V \left(\frac{\partial U}{\partial V}\right) + \sum_i N_i \left(\frac{\partial U}{\partial N_i}\right)$$

$$U(S, V, N) = TS - PV + \sum_i \mu_i N_i$$

Knowing the $n+2$ EOS, can find the fundamental eq. $T = T(S, U, N)$, $P = P(S, U, N) \dots$

entropy representation

Could have done all this starting from $S(U, V, N)$

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

what are these partials?

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = 1 / \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} : \cancel{dU} = \left(\frac{\partial U}{\partial S}\right) dS + \left(\frac{\partial U}{\partial V}\right) dV + \left(\frac{\partial U}{\partial N}\right) \cancel{dN}$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = - \frac{(2U/2V)_{S,N}}{(2U/2S)_{V,N}} = \frac{P}{T}$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} : \cancel{dU} = \left(\frac{\partial U}{\partial S}\right) dS + \left(\frac{\partial U}{\partial V}\right) \cancel{dV} + \left(\frac{\partial U}{\partial N}\right) dN$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = - \frac{(2U/2N)}{(2U/2S)} = - \mu/T$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum_i \frac{\mu_i}{T} dN_i$$

Euler relation

Similarly in entropy representation

$$S(U, V, N) = \left(\frac{1}{T}\right) U + \left(\frac{P}{T}\right) V - \sum_i \left(\frac{\mu_i}{T}\right) N_i$$

If we have a single component system, can use homogeneity to further simplify:

$$U(S, V, N) \xrightarrow{\lambda = 1/N}$$

$$\frac{1}{N} U(S, V, N) = U\left(\frac{S}{N}, \frac{V}{N}, \frac{N}{N}\right)$$

$$= u(s, v)$$

We call these properties scaled by N "molar" properties

$$u(s, v) = T_s - Pv + \mu$$

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$$

$$= T ds - P dv$$

Similarly, in entropy representation,

$$s(u, v) = \frac{1}{T} u + \frac{P}{T} v - \frac{\mu}{T}$$

$$ds = \frac{1}{T} du + \frac{P}{T} dv$$

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Example, p 64-65 Geller

$$U = \frac{1}{2} PV \quad T^2 = \frac{AU^{3/2}}{VN^{1/2}} \quad A \text{ a positive const.}$$

What is fundamental eq? What is μ ?

These are 2 EOS in the entropy representation:

$$P = 2U/V = \frac{2u}{v} \quad T^2 = Au^{3/2}/v$$

(eliminate N from problem)

$$T = A^{1/2} u^{3/4} v^{-1/2}$$

$$ds = \frac{1}{T} du + \frac{P}{T} dv$$

$$\frac{1}{T} = A^{-1/2} u^{-3/4} v^{1/2} \\ = \left(\frac{\partial s}{\partial u} \right)_v$$

$$\frac{P}{T} = 2A^{-1/2} u^{1/4} v^{-1/2} \\ = \left(\frac{\partial s}{\partial v} \right)_u$$

Integrate:

$$s(u, v) = A^{-1/2} v^{1/2} 4u^{1/4} + g(v)$$

$$\begin{aligned} \left(\frac{\partial s}{\partial v} \right)_u &= 4A^{-1/2} u^{1/4} \cdot \frac{1}{2} v^{-1/2} + g'(v) \\ &= 2A^{-1/2} u^{1/4} v^{-1/2} + g'(v) \end{aligned}$$

compare

$$g'(v) = 0 \quad g(v) = \text{const} = s_0$$

$$s(u, v) = 4A^{-1/2} u^{1/4} v^{1/2} + s_0$$

$$s(u, v, N) = \left[4A^{-1/2} \left(\frac{u}{N} \right)^{1/4} \left(\frac{v}{N} \right)^{1/2} + s_0 \right] N$$

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We've now got $S(u, v, n) + 2 \text{EOS}$, for $P(u, v, n)$
 And $T(u, v, n)$. What about μ ?

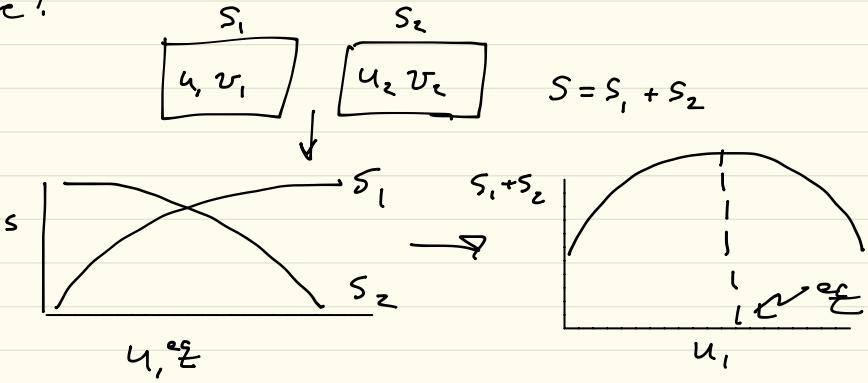
$$\begin{aligned}\mu/T &= \frac{1}{T} u + \frac{P}{T} v - s(u, v) \\ &= A^{-1/2} u^{-3/4} v^{1/4} \cdot u + 2A^{-1/2} u^{1/4} v^{-1/2} \cdot v \\ &\quad - 4A^{-1/2} u^{1/4} v^{1/4} + s_0 \\ &= -A^{-1/2} u^{1/4} v^{1/2} + s_0\end{aligned}$$

Check postulates: $(\frac{\partial s}{\partial u}) > 0 ? \quad s(\lambda u, \lambda v) = \lambda s(u, v) ?$

$$\lim_{u \rightarrow 0} \left(\frac{\partial s}{\partial u} \right) = 0 ?$$

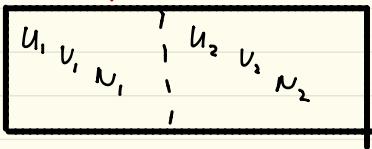
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Suppose two systems described by this fundamental eq_g are coupled to exchange U or V. How do we determine eq_g state?



Illustrates the essential core of thermodynamics
Know / infer a fundamental equation, seek a minimum w.r.t. whatever variables you like to find equilibrium. Do we always have to find / know final eq?

thermal equilibrium - temperature
closed composite system



Allow energy exchange
 $dU_1 = dU_2 = 0$
 $dN_1 = dN_2 = 0$

$$dU_1 = -dU_2$$

$$S = S_1 + S_2$$

What are U_1, U_2 @ equilibrium?

$$\text{At equilibrium } dS = dS_1 + dS_2 = 0$$

$$= \left(\frac{\partial S_1}{\partial U_1}\right)_{V, N_1} dU_1 + \left(\frac{\partial S_2}{\partial U_2}\right)_{V, N_2} dU_2$$

$$dS = \frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU,$$

In general $dU_i \neq 0$, \therefore At equilibrium must have

$$\frac{1}{T_1} = \frac{1}{T_2} \quad \text{or} \quad T_1 = T_2$$

~~Just as we saw in the 2 state example, the total S~~ is maximized when the two subsystems have the same T .

Note that this is the condition necessary for S to be an extremum. To prove it is a maximum, also need $d^2S > 0$. More later.

Does this make sense? Intuitively?

Suppose we are not at thermal equilibrium, so e.g.

$$T_1 > T_2 \quad \therefore \frac{1}{T_1} < \frac{1}{T_2}$$

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 > 0 \quad \text{spontaneously}$$

$\underbrace{< 0}_{\text{in}} \quad \underbrace{< 0}_{\text{in}}$

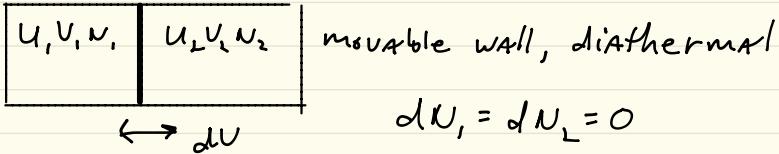
$U_1 \downarrow, U_2 \uparrow$ when $T_1 > T_2$. Makes sense!!

Nice discussion in book about T units. We now understand that S is basically just a number, A degeneracy S could be unitless + T an energy (J, eV, \dots)
By convention we make S an energy / temperature unit

$$k_B = 1.381 \times 10^{-23} \text{ J/K} \quad \text{"really" a conversion factor between E scales}$$

$$= 8.6173 \times 10^{-5} \text{ eV/K}$$

mechanical equilibrium - pressure



$$dU_1 + dU_2 = 0 \quad dV_1 + dV_2 = 0 \quad S = S_1 + S_2$$

$$dS = dS_1 + dS_2 = 0$$

$$\begin{aligned} &= \left(\frac{\partial S_1}{\partial U_1} \right) dU_1 + \left(\frac{\partial S_1}{\partial V_1} \right) dV_1 + \left(\frac{\partial S_2}{\partial U_2} \right) dU_2 + \left(\frac{\partial S_2}{\partial V_2} \right) dV_2 \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 \end{aligned}$$

For arbitrary dU_1, dV_1 , must have

$$\frac{1}{T_1} = \frac{1}{T_2} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{or} \quad T_1 = T_2 \quad P_1 = P_2$$

Recover the intuitive result

Pressure units - $\frac{\text{energy}}{\text{volume}} = \frac{\text{force}}{\text{area}}$

$$1 \text{ Pa} = 1 \text{ J/m}^3 = 1 \text{ N/m}^2 \quad \text{hydrostatic energy}$$

The adiabatic case is less simple; T indeterminate. See problem 2.7-3.

$$(dU = dU_1 + dU_2 = -P_1 dV_1 + P_2 dV_1 = 0) \Rightarrow P_1 = P_2$$

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) (-P_1 dV_1) + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 = 0 \cdot dV_1 = 0$$

chemical equilibrium - matter flow



$$dU_1 + dU_L = 0 \quad dN_1 + dN_2 = 0$$

$$\begin{aligned} dS &= \left(\frac{\partial S_1}{\partial U_1}\right) dU_1 + \left(\frac{\partial S_1}{\partial N_1}\right) dN_1 + \left(\frac{\partial S_2}{\partial U_2}\right) dU_2 + \left(\frac{\partial S_2}{\partial N_2}\right) dN_2 \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 - \left(\frac{M_1}{T_1} - \frac{M_2}{T_2}\right) dN_1 = 0 \end{aligned}$$

$$\frac{1}{T_1} = \frac{1}{T_2} \quad \frac{M_1}{T_1} = \frac{M_2}{T_2} \quad \dots \quad T_1 = T_2 \quad M_1 = M_2$$

At equilibrium, chemical potentials are equalized

Units: $\frac{\text{energy}}{\#}$ $\frac{\text{kJ}}{\text{mol}}$, $\frac{\text{eV}}{\text{particle}}$

Does this make sense? Intuitively?

Suppose we are not at chemical equilibrium, so e.g.

$$M_1 > M_2$$

$$dS = \left(\frac{-M_1}{T} - \frac{-M_2}{T}\right) dN_1 > 0 \quad \text{spontaneously}$$

$\underbrace{-}_{<0} \quad \underbrace{-}_{<0}$

$N_1 \downarrow, N_2 \uparrow$ when $M_1 > M_2$. Makes sense!!

Critical when dealing with phase + chemical equilibrium.

Suppose T, P, μ all come to equilibrium in a single component system. Can all 3 of these really take independent values? Seems like not.

By homogeneity property,

$$S(u, v, N) \xrightarrow{x_i = \frac{N_i}{N}} s(u, v) \quad \text{Only 2 independent D.O.F.s}$$

The intensive variables are also fns of the same variables:

0th order homo.

$$\begin{array}{l} T \rightsquigarrow T(u, v) \\ P \rightsquigarrow P(u, v) \\ \mu \rightsquigarrow \mu(u, v) \end{array} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \mu \text{ must be expressable in terms of } T, P \text{ or any other combo}$$

We'll find the relationship in a minute

That's why we don't have an intuitive sense for μ independent of $T + P$

More about chemical pot'l when we talk about phase equilibria, mixtures, & reactions

Said the intensive parameters are not all independent.

From Euler relation, can write complete differential of U :

$$dU = TdS + SdT - PdV - VdP + \sum_i \mu_i dN_i + \sum_i n_i d\mu_i$$

U is a state function of S, V, N :

$$dU = TdS - PdV + \sum_i \mu_i dN_i$$

By difference:

$$\boxed{0 = SdT - VdP + \sum_i n_i d\mu_i}$$

Gibbs-Duhem relation

Eg for 1 component system,

$$d\mu = \frac{1}{N} [-SdT + VdP]$$

$$\boxed{d\mu = -SdT + VdP}$$

knowing $r+1$ intensive variables gives the $r+2$ nd to w/i & constant

Variations in μ coupled to variations in T, P . Integration gives the relationship to within a constant.

In entropy representation:

$$\boxed{0 = U d\left(\frac{1}{T}\right) + V d\left(\frac{P}{T}\right) - \sum_i \mu_i d\left(\frac{\mu_i}{T}\right)}$$

Variations in intensive variables not independent

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Return to old example:

$$\frac{1}{T} = A^{-1/2} u^{-3/4} v^{1/2} \quad \frac{P}{T} = 2A^{-1/2} u^{1/4} v^{-1/2}$$

Gibbs-Duhem:

$$d\left(\frac{M}{T}\right) = u d\left(\frac{1}{T}\right) + v d\left(\frac{P}{T}\right)$$

$$d\left(\frac{1}{T}\right) = A^{-1/2} \left[\frac{1}{2} u^{-3/4} v^{-1/2} dv - \frac{3}{4} u^{-7/4} v^{-1/2} du \right]$$

$$d\left(\frac{P}{T}\right) = 2A^{-1/2} \left[-\frac{1}{2} u^{1/4} v^{-3/2} dv + \frac{1}{4} u^{-3/4} v^{-1/2} du \right]$$

$$u d\left(\frac{1}{T}\right) + v d\left(\frac{P}{T}\right) = A^{-1/2} \left[-\frac{1}{2} u^{1/4} v^{-1/2} dv - \frac{1}{4} u^{-3/4} v^{1/2} du \right] \\ = d\left(\frac{M}{T}\right)$$

$$d\left(\frac{M}{T}\right) = -A^{-1/2} d(u^{1/4} v^{1/2}) \quad \text{by inspection}$$

$$\boxed{\frac{M}{T} = -A^{-1/2} u^{1/4} v^{1/2} + \text{const}}$$

$$\text{const} = \left(\frac{M}{T}\right)_0.$$

Could substitute into Euler relation to recover the same S as above.