Gibbs – Duhem Relations

Define homogeneous system

$$E(\lambda S, \lambda x_i, \lambda N_j) = \lambda E(S, x_i, N_j)$$

Using 2nd law: $dE = TdS + \sum_i X_i dx_i + \sum_j \mu_j N_j$

$\Rightarrow$ dE – full differential (integrations is independent of the integr. path)

dE, dS, dV, dN_j – differentials of extensive properties $\Rightarrow$ depend on N.

Coefficients of these differentials (T, P, μ) are intensive properties

$\Rightarrow$ integrating 2nd law, keeping coeffs = const

Let's assume, we move from container A to B, drop-by-drop (e.g. use z, where $0 \le z \le a$).

We can write:

$$dE = E\,dz,\ dS = S\,dz,\ dV = V\,dz,\ \text{etc.}$$

$$\Rightarrow E\,dz = TS\,dz - PV\,dz + \sum_j \mu_j N_j\,dz$$

$\Rightarrow$ divide by dz: $E = TS \underbrace{- PV}_{\sum_i X_i x_i} + \sum_j \mu_j N_j$

$\Rightarrow$ For just 1 component $X_V = -P$:

$$E = TS - PV + \mu N$$

$$\Rightarrow E - TS = A = -PV + \mu N$$

or $G = \mu N$; $\Omega_G = -PV$

(1) For such systems intensive parameters are not independent:

e.g. $E = TS - PV + \mu N$

$$\Rightarrow dE = \underline{TdS} + SdT - \underline{PdV} - VdP + \underline{\mu dN} + Nd\mu$$

(all underlined terms $\to 0$)

$$\Rightarrow SdT - VdP + Nd\mu = 0$$

(because of the 2nd law)

(2) At least one extensive variable is needed to specify completely the state of the system

Maxwell Relations

1st law

$$dE = TdS + \sum X dx + \sum \mu dN$$

$$A = E - TS$$

A - state function

$$dA = dE - TdS - SdT =$$

$$= SdT + \sum X_i dx_i + \sum \mu_j dN_j$$

$\Rightarrow$ for a single component:

$$\left(\frac{\partial A}{\partial T}\right)_{N,V} = -S; \quad \left(\frac{\partial A}{\partial V}\right)_{T,N} = -P; \quad \left(\frac{\partial A}{\partial N}\right)_{T,V} = \mu$$

From theory of PDE: derivatives are independent of the differentiation order:

$$\frac{\partial}{\partial x_i}\left(\frac{\partial \phi}{\partial x_j}\right) = \frac{\partial}{\partial x_j}\left(\frac{\partial \phi}{\partial x_i}\right)$$

Obtain Maxwell relations:

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{\partial^2 A}{\partial T \partial V} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$$

$$\left(\frac{\partial S}{\partial N}\right)_{V,T} = -\left(\frac{\partial \mu}{\partial T}\right)_{V,N}; \quad \left(\frac{\partial P}{\partial N}\right)_{V,T} = -\left(\frac{\partial \mu}{\partial V}\right)_{T,N}$$

Similar relations for the Gibbs potential:

$$dG = dE - TdS - SdT + PdV + VdP =$$
$$= -SdT + VdP + (dE - TdS + PdV) =$$
$$= -SdT + VdP + \mu N$$

$$\left(\frac{\partial G}{\partial T}\right)_{N,P} = -S; \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V; \quad \left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu$$

$\Rightarrow$ additional Maxwell relations

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}; \quad \left(\frac{\partial V}{\partial N}\right)_{P,T} = \left(\frac{\partial \mu}{\partial P}\right)_{T,N}$$

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

More: for magnetic systems

All: used to find response of the system to externally controlled parameters:

specific heats: e.g. $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$

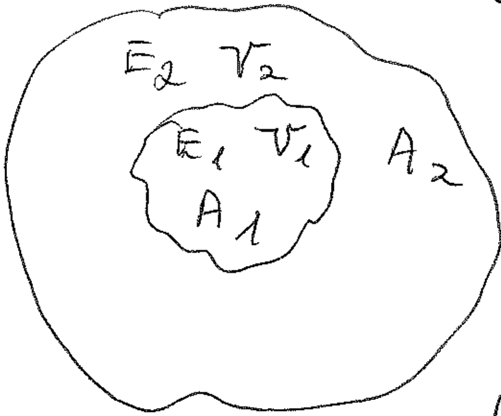
isothermal & adiabatic compressibilities:

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

coeffs. of thermal expansion:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

Stability



Suppose $E_1 + E_2$ - fixed

Consider a process in which A_1 <u>absorbs</u> some heat Q from A_2

Since $A_2 \gg A_1$, (T_2, P_2) does not change

$$\Delta S_2 = -Q/T_2$$

Since $Q = \Delta E_1 + P_2 \Delta V_1$ (1st law)

If ΔS_1 = change of entropy of A_1

(In equilibrium $S = S_1 + S_2$)

$$\Delta S_{total} = \Delta S_2 + \Delta S_1 = \Delta S_1 - Q/T_2 =$$

$$= \Delta S_1 - \frac{1}{T_2}\Big(\underbrace{\Delta E_1 + P_2 \Delta V_1}_{\text{1st law}}\Big) =$$

$$= \frac{1}{T_2}\left(T_2 \Delta S_1 - \Delta E_1 - P_2 \Delta V_1\right)$$

$$= -\frac{\Delta G_1}{T_2}$$

where $G_1 = E_1 - T_2 S_1 + P_2 V_1$

$\Delta S_{total} \leq 0 \Rightarrow \Delta G_1 \geq 0$
(at maximum!)
i.e. at equilibrium!

Since changes of E_1, S_1, V_1 are not independent, sufficient to consider

$$G_1(S_1, V_1) \text{ or } E_1(S_1, V_1)$$

Develop ΔE_1 up to 2nd order terms:

$$\Delta G_1 = \Delta E_1 - T_2 \Delta S_1 + P_2 dV_1 =$$
$$= \underline{\left(\frac{\partial E_1}{\partial S_1}\right)\Delta S_1} + \frac{1}{2}\left(\frac{\partial^2 E_1}{\partial S_1^2}\right)(\Delta S_1)^2 + \left(\frac{\partial^2 E}{\partial S_1 \partial V_1}\right)\Delta S_1 \Delta V_1 +$$
$$+ \underline{\left(\frac{\partial E_1}{\partial V_1}\right)\Delta V_1} + \frac{1}{2}\left(\frac{\partial^2 E_1}{\partial V_1^2}\right)(\Delta V_1)^2 \underline{- T_2 \Delta S_1} + \underline{P_2 \Delta V_1} =$$
$$= \Delta S_1\left(\frac{\partial E_1}{\partial S_1} - T_2\right) + \Delta V_1\left(\frac{\partial E_1}{\partial V_1} + P_2\right) +$$
$$+ \frac{1}{2}\Big[(\Delta S_1)^2\left(\frac{\partial^2 E_1}{\partial S_1^2}\right) + 2\Delta V_1 \Delta S_1\left(\frac{\partial^2 E}{\partial V_1 \partial S_1}\right) +$$
$$+ (\Delta V_1^2)\left(\frac{\partial^2 E_1}{\partial V_1^2}\right)\Big] \geq 0 \quad \text{(at equilibr.)}$$

However, $\quad TdS = dE + PdV$

Thus, $\quad T_2 = \dfrac{\partial E_1}{\partial S_1} = T_1$

Linear terms:
(must be $=0$ at equil.!) $\quad -P_2 = \dfrac{\partial E_1}{\partial V_1} = P_1$
$\Rightarrow$ at max/min

Fluctuations of S_1 and V_1 are independent!

$$(\Delta S)^2 E''_{SS} + 2(\Delta V \Delta S) E''_{VS} + (\Delta V)^2 E''_{VV} \geq 0$$

at minimum: $\begin{cases} E''_{SS} \geq 0 \\ E''_{VV} \geq 0 \end{cases}$

multiply by E''_{SS}:

$$(\Delta S)^2 (E''_{SS})^2 + 2(\Delta V \Delta S) E''_{VS} E''_{SS} + (\Delta V)^2 E''_{VV} E''_{SS} \geq 0$$

Add terms: $(E''_{VS})^2 (\Delta V)^2 - (E''_{VS})^2 (\Delta V)^2$

$$\left[(\Delta S)^2 (E''_{SS})^2 + (E''_{VS})^2 (\Delta V)^2 + 2(\Delta V \Delta S) E''_{VS} E''_{SS}\right] +$$
$$+ (\Delta V)^2 E''_{VV} E''_{SS} - (E''_{VS})^2 (\Delta V)^2 \geq 0$$

$$\Rightarrow \underbrace{\left[(\Delta S) E''_{SS} + E''_{VS} (\Delta V)\right]^2}_{\text{always } \geq 0} + \underbrace{\left[E''_{VV} E''_{SS} - (E''_{VS})^2\right]}_{\text{must be } \geq 0} (\Delta V)^2 \geq 0$$

because ΔS, ΔV independent fluctuations

For quadratic terms to vanish, eigenvalues of matrix (i.e. at min G)

$$\begin{pmatrix} \dfrac{\partial^2 E_1}{\partial S_1^2} & \dfrac{\partial^2 E_1}{\partial S_1 \partial V_1} \\ \dfrac{\partial^2 E_1}{\partial S_1 \partial V_1} & \dfrac{\partial^2 E_1}{\partial V_1^2} \end{pmatrix}$$

where E''_{SS} E''_{VV}

must be both positive!