Chapter 1.3: Derivatives of thermodynamic variables

Reminder: For exact differentials $\mathrm{d}A = a(x,y)\,dx + b(x,y)\,\mathrm{d}y$ we have $\left(\frac{\partial b}{\partial x}\right)_y = \left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial^2 A}{\partial x \partial y}\right) = \left(\frac{\partial^2 A}{\partial y \partial x}\right)$

$a = \left(\frac{\partial A}{\partial x}\right)_y \qquad b = \left(\frac{\partial A}{\partial y}\right)_x$

Def. 1.9:
Maxwell's relations

a.) From $\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V$
$a\,dx + b\,dy$

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

b.) From $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$

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

c.) From $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p$

$$\left(\frac{\partial \cancel{S}\,T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

d.) From $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$

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

1.3-2 Derivatives

General relations between 3 dependent parameters

$x(y,z), \quad y(x,z), \quad z(x,y)$

eg. $E(S,V)$

$S(E,V)$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \qquad dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

$\forall\, dx, dy, dz$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right) dz\right] + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$\forall\, dx, dz$

$dz = 0$

$$dx = \underbrace{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z}_{=1} dx$$

$dx = 0$

$$0 = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x dz + \left(\frac{\partial x}{\partial z}\right)_y dz \qquad (*)$$

Def. 1.10:

a) Reciprocal theorem

$$1=\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial x}\right)_z$$

$$\left(\frac{\partial x}{\partial y}\right)_z = 1\Big/\left(\frac{\partial y}{\partial x}\right)_z$$

b) Triple product rule

$$-1=\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y$$

$$\left(\frac{\partial x}{\partial z}\right)_y = -\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x \quad (*)$$

c) chain rule

$$\left(\frac{\partial x}{\partial y}\right)_\phi = \left(\frac{\partial x}{\partial z}\right)_\phi\left(\frac{\partial z}{\partial y}\right)_\phi$$

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

$$dS=\frac{dE}{T}+\frac{p}{T}dV$$

$$-p=\left(\frac{\partial E}{\partial V}\right)_S = -\left(\frac{\partial E}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_E = -T\left(\frac{\partial S}{\partial V}\right)_E$$

generalized Forces

$$F_\alpha = -\left(\frac{\partial E}{\partial \alpha}\right)_S = -\left(\frac{\partial F}{\partial \alpha}\right)_S \overset{\text{triple rule}}{=} T\left(\frac{\partial S}{\partial \alpha}\right)_E$$

Def. 1.11: Material constants

$$\left.\frac{\partial \ln y}{\partial x} = \frac{1}{y}\frac{\partial y}{\partial x}\right.$$

a) Thermal expansion coefficient

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial \ln V}{\partial T}\right)_p$$ isochoric

$$\alpha_V = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial \ln p}{\partial T}\right)_V$$ isobaric

b) Specific heat

$$\frac{\delta Q}{\partial T} = \frac{T dS}{\partial T}$$

$$c_v = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$ isochoric

$$dE = \delta Q - p dV$$

$$c_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$ isobaric

$$dH = \delta Q + V dp$$

c) Bulk modulus

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

$$K_s = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = -\left(\frac{\partial \ln V}{\partial p}\right)_S$$ isentropic

d) Magnetic susceptibility

$$\chi = \left(\frac{\partial M}{\partial B}\right)_{T,V} = -\left(\frac{\partial^2 F}{\partial B^2}\right)_T$$

other response functions

where $$M = -\left(\frac{\partial F}{\partial B}\right)_{T,V} = -\left(\frac{\partial E}{\partial B}\right)_{S,V}$$

General relations: Example 1

Thermal expansion coefficient

$$\alpha_V = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V = -\frac{1}{p}\overbrace{\left(\frac{\partial p}{\partial V}\right)_T}^{-\frac{1}{VK_T}}\overbrace{\left(\frac{\partial V}{\partial T}\right)_p}^{V\alpha_p} = \frac{1}{p}\frac{\alpha_p}{K_T}$$

Def.

triple product rule

General relations: Example 2

Specific heat $c_p = T\left(\frac{\partial S}{\partial T}\right)_p$ Def.

From $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$ follows $\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V \underbrace{\left(\frac{\partial T}{\partial T}\right)_p}_{1} + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$

S(T,V)

Hence

$$c_p = T\left(\frac{\partial S}{\partial T}\right)_p = c_v + T\underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\text{Maxwell b)}}\left(\frac{\partial V}{\partial T}\right)_p = c_v + T\left(\frac{\partial p}{\partial T}\right)_V V\alpha_p = c_v + TpV\alpha_V\alpha_p = c_v + \underbrace{\frac{TV\alpha_p^2}{K_T}}_{>0}$$

Def. 1.11

Def. 11

general relation

$c_p > c_v$

General relations: Example 3

What is $V(p)$ for general adiabatic processes? → **adiabatic expansion**

$S = \text{const}$

$\delta Q = 0$

Goal: Calculate $\left(\frac{\partial V}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_V$

then integrate

triple product rule

Use $\left(\frac{\partial S}{\partial p}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_S = \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial T}{\partial p}\right)_V \frac{c_v}{T} = \frac{c_v}{Tp\alpha_V}$

Maxwell a   triple product rule   Maxwell b

general relation

Likewise $\left(\frac{\partial S}{\partial V}\right)_p = \frac{c_p}{TV\alpha_p}$

$$V(p) = \int_{S=\text{const}} \left(\frac{\partial V}{\partial p}\right) dp$$

Hence $\left(\frac{\partial V}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_V \overset{-}{=} \frac{c_V \alpha_p V}{c_p \alpha_V p} \overset{-}{=} \frac{c_V}{c_p} K_T V$

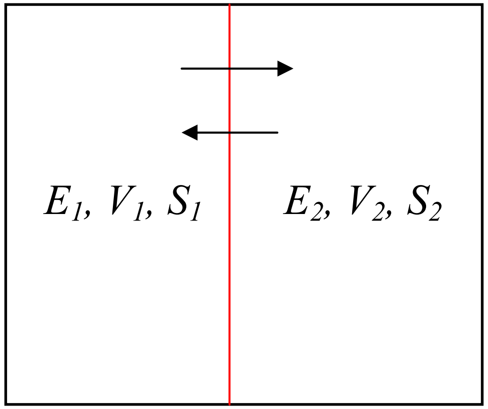
ideal gas $= \text{const}\,\frac{V}{p}$

$$\int \frac{dV}{V} = \int \frac{dp}{p}\,\text{const} \rightarrow V(p) \propto p^{\text{const}}$$

Stability conditions

S is max in equilibrium

Use minimization principle in equilibrium: Any forced change δE, δV will *lower* $S=S_1+S_2$



$S_1(E_1,V_1)$

$S_2(E_2,V_2)$

$$0 \geq \delta S = \overbrace{S_1(E_1+\delta E, V_1+\delta V) + S_2(E_2-\delta E, V_2-\delta V) - S_1(E_1,V_1)}^{\Delta S_1} - S_2(E_2,V_2)$$

$$= \left(\left(\frac{\partial S_1}{\partial E_1}\right)_V - \left(\frac{\partial S_2}{\partial E_2}\right)_V \right) \delta E + \left(\left(\frac{\partial S_1}{\partial V_1}\right)_E - \left(\frac{\partial S_2}{\partial V_2}\right)_E \right) \delta V$$

ΔS_2 must be zero

$$\underbrace{+ \left(\left(\frac{\partial^2 S_1}{\partial E_1^2}\right)_V + \left(\frac{\partial^2 S_2}{\partial E_2^2}\right)_V \right) \frac{\delta E^2}{2} + \left(\left(\frac{\partial^2 S_1}{\partial V_1^2}\right)_E + \left(\frac{\partial^2 S_2}{\partial V_2^2}\right)_V \right) \frac{\delta V^2}{2} + \left(\left(\frac{\partial^2 S_1}{\partial V_1 \, \partial E_1}\right) + \left(\frac{\partial^2 S_2}{\partial V_2 \, \partial E_2}\right)_V \right) \delta E \, \delta V}_{\leq 0}$$

$$\left(\frac{\partial S_1}{\partial E_1}\right) = \frac{1}{T_1} \Rightarrow T_1 = T_2$$

$$\frac{\partial S}{\partial V} = \frac{P}{T} \Rightarrow P_1 = P_2$$

Therefore $\left(\frac{\partial^2 S}{\partial E^2}\right)_V = -\frac{1}{T^2 c_V} \leq 0$ and $K_T \geq 0$

"stability" conditions