Notes:

Homework:

- I will take volunteers for #3, 4, 5 for Thursday.

Exam: - Friday Oct. 29, 6 PM, Room 205 MPHY.

- Coverage through section 6.4. You can make one page formula sheet.
- **We covered:** • Ch 1 all; • Ch 2 all except chem. equilibrium (but I covered similar ionization-equilibrium problem); • Ch. 3, plus more expansive blackbody radiation but omitted magnetic and rubber-band cases. • Ch. 4: all except the endoreversible cycle; • Ch. 5-6 see my recent slides; • Ch. 15 all except rubber band section, but I added additional material on probabilities, and ideal gases (You should read section 13.1.)

Canvas grades & lecture links: Note that these don't update immediately, I will upload roughly every week.

Next Material: Chapter 7 then chapter 16.

Joule-Thomson process:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

Joule-Thomson coefficient:

Temperature change in constant-enthalpy process.

$$\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial P}{\partial H}\right)_T = -1$$

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}_P$$

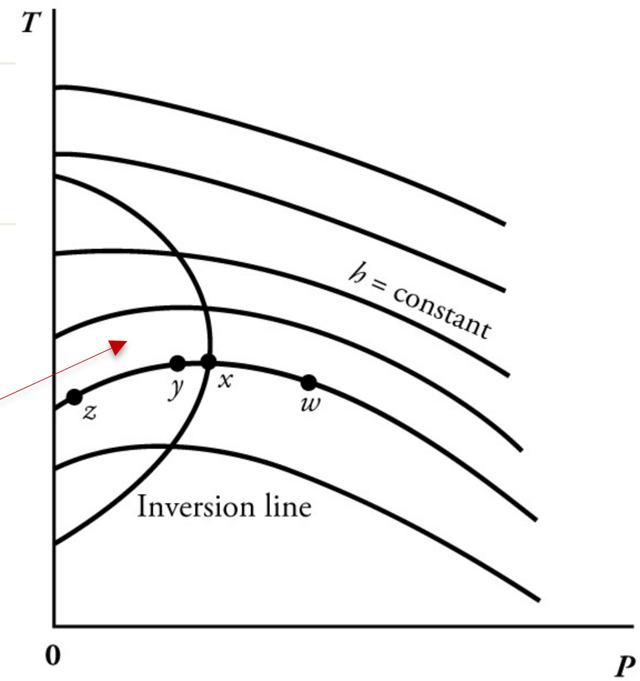
C_P

$$\left[V + T\left(\frac{\partial S}{\partial P}\right)_T\right]^{-1} = [V - TV\alpha\,]^{-1}$$

$$\mu_{JT} = \frac{V(T\alpha - 1)}{C_P}$$

Cooling with

P decrease



Recall, thermodynamic potentials:

a *Maxwell relation*

$$\frac{\partial^2 G}{\partial T \partial P} = -\frac{\partial S}{\partial P}_{TN} = \frac{\partial V}{\partial T}_{PN}$$

Helmholtz free energy: $F = U - TS$ $\qquad dF = -SdT - PdV + \mu dN$

Gibbs free energy: $G = U - TS + PV$ $(= H - TS)$ $\qquad dG = -SdT + VdP + \mu dN$

Enthalpy: $H = U + PV$ $\qquad dH = TdS + VdP + \mu dN$

$$T = \frac{\partial H}{\partial S} \qquad V = \frac{\partial H}{\partial P}$$

Equilibrium conditions: minimization for *composite systems*

- *F* minimum for constant *T, V, N* conditions $\quad F(T,V,N)$
- *G* minimum for constant *T, P, N* conditions $\quad G(T,P,N)$
- *H* minimum for constant *S, P, N* conditions $\quad H(S,P,N)$

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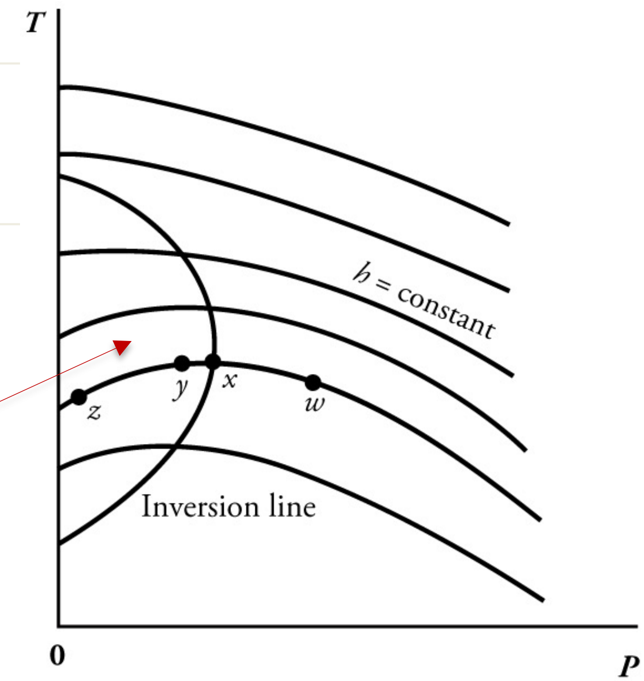
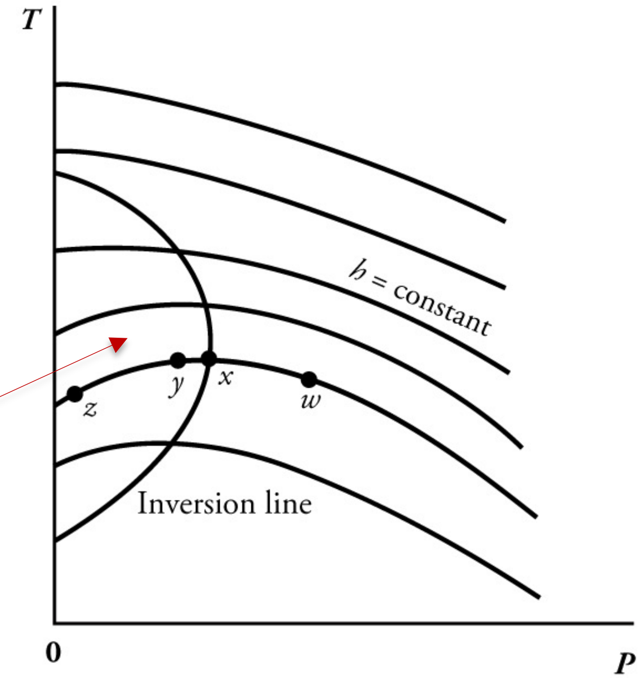


Joule-Thomson process:

Ideal gas: zero always

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V(T\alpha - 1)}{C_P}$$



Cooling with
P decrease

$$\left[P + a\left(\frac{n}{V}\right)^2\right]\left(\frac{V}{n} - b\right) = RT \quad \Rightarrow \quad \mu_{JT} \approx \frac{\left(\frac{2a}{RT} - b\right)}{C_P}$$

Rough agreement
with experiment

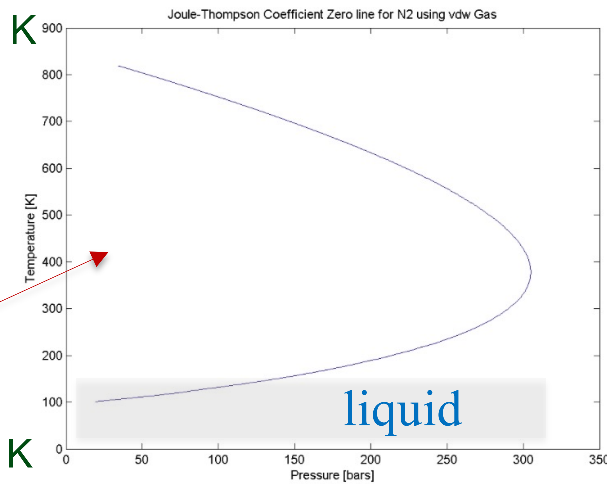
can show see text example

Joule-Thomson process:

Ideal gas: zero always

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V(T\alpha - 1)}{C_P}$$

Cooling with
P decrease



Numerical soln, inversion curve (vdW for N_2 gas)

B. Robinson UWashington

$$\left[P + a\left(\frac{n}{V}\right)^2\right]\left(\frac{V}{n} - b\right) = RT \quad \Rightarrow \quad \mu_{JT} \approx \frac{\left(\frac{2a}{RT} - b\right)}{C_P}$$

Rough agreement with experiment

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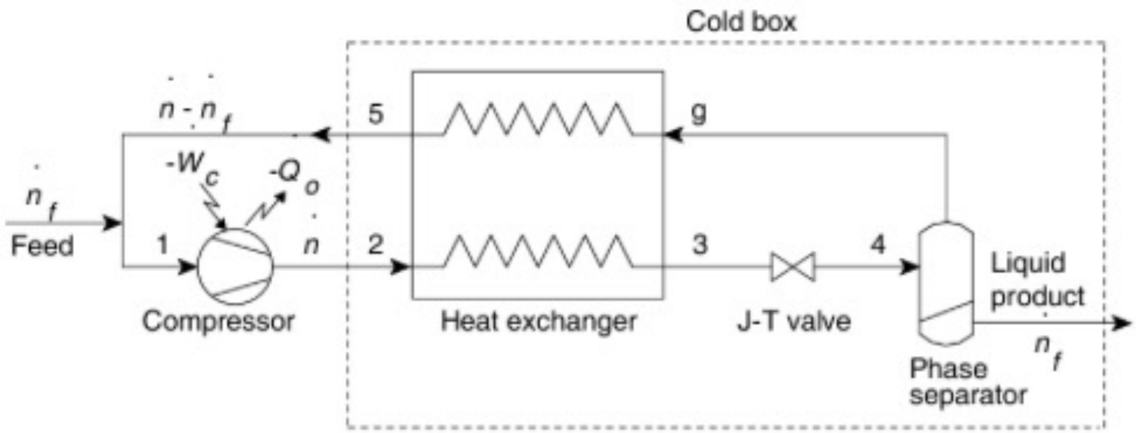
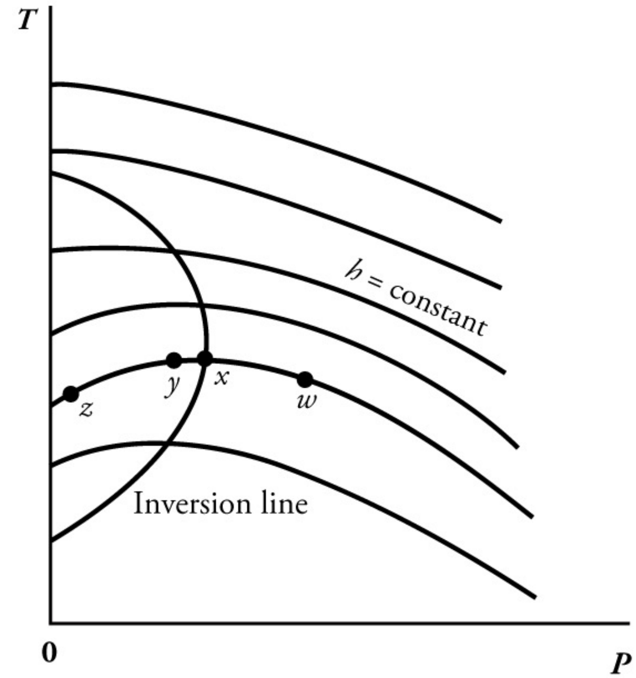
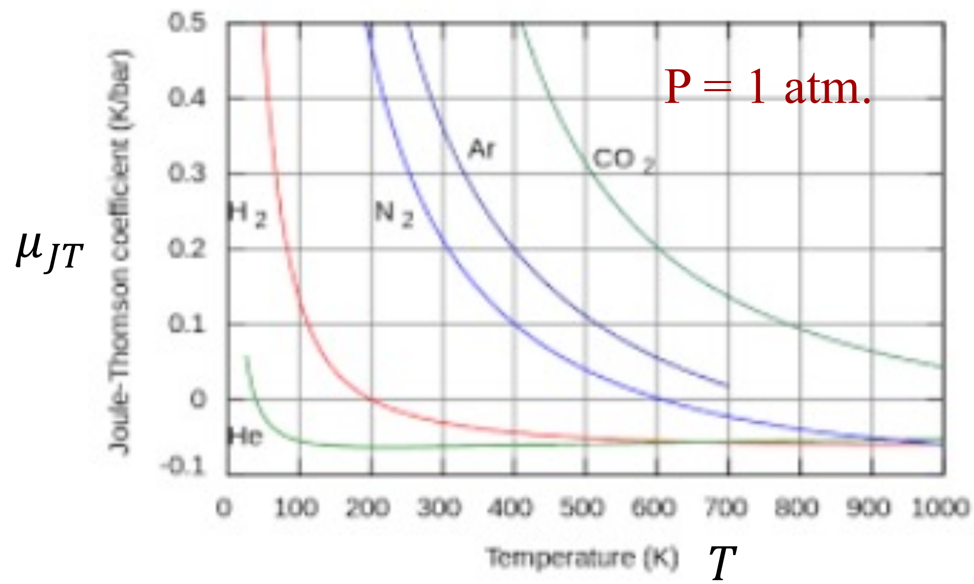
Joule-Thomson process:



Linde cycle for
condensing gases





Joule-Thomson process:

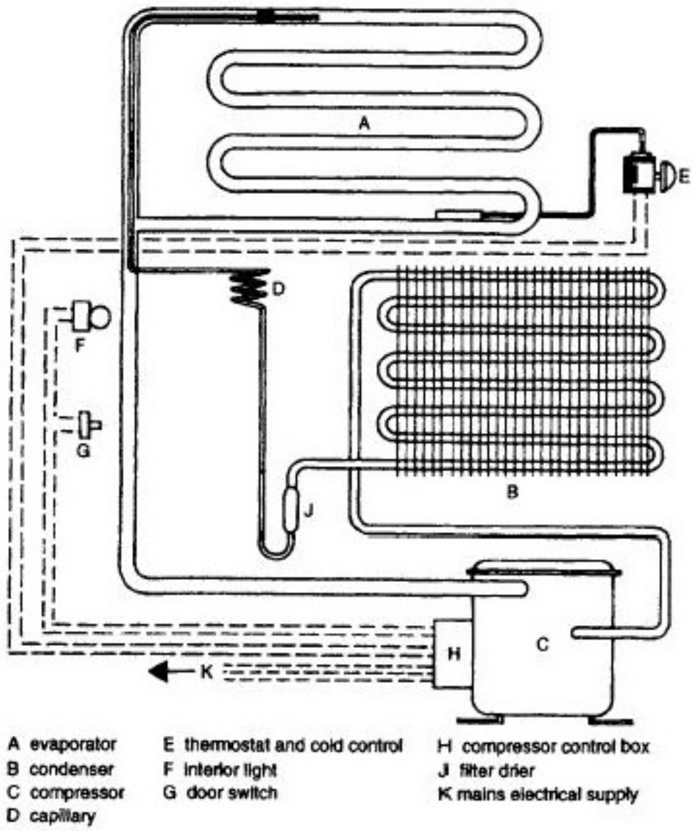
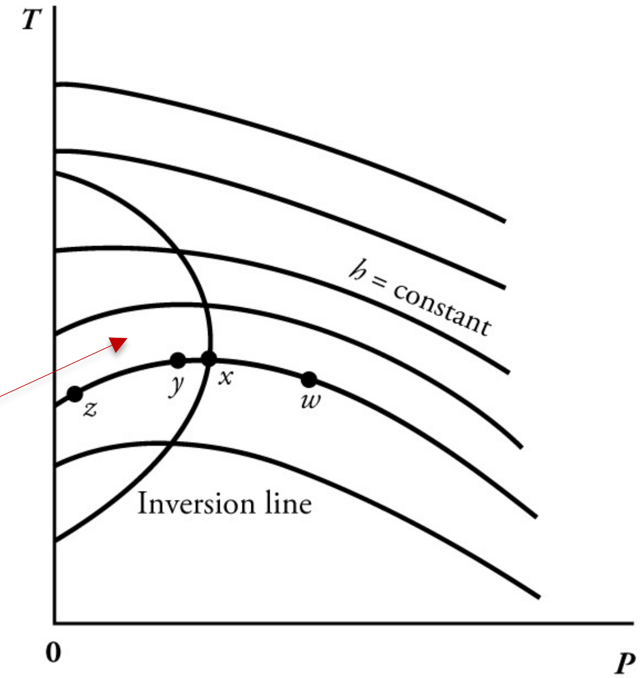


Figure 56 *Domestic refrigerator details*

Standard refrigerator also throttle valve & pressure change; different details

Cooling with
P decrease



Maxwell relations (constant *N* cases):

$dU = TdS - PdV$	S, V	$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$	$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$
$dH = TdS + VdP$	S, P	…	…
$dF = -SdT - PdV$	T, V	$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$	… etc.
$dG = -SdT + VdP$	T, P	$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$	…

Recall, thermodynamic potentials:

Internal energy: U $dU = TdS - PdV + \mu dN$

Helmholtz free energy: $F = U - TS$ $dF = -SdT - PdV + \mu dN$

Gibbs free energy: $G = U - TS + PV$ $dG = -SdT + VdP + \mu dN$

Enthalpy: $H = U + PV$ $dH = TdS + VdP + \mu dN$

Thermodynamic potentials (constant *N* cases):

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$dH = TdS + VdP$	S, P	…	…
$dF = -SdT - PdV$	T, V	$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$	… etc.
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Maxwell relation: $\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$ etc.

Thermodynamic potentials (constant *N* cases):

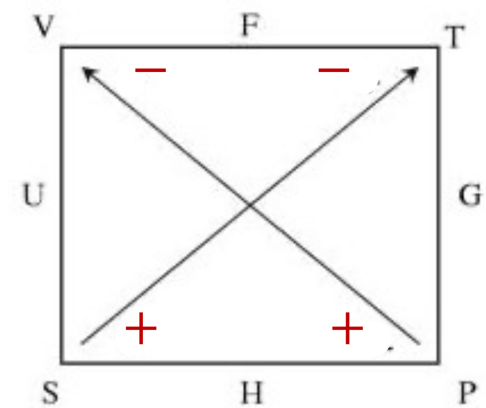
$dU = TdS - PdV \quad S, V \quad T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$

$dH = TdS + VdP \quad S, P \quad \ldots \quad \ldots$

$dF = -SdT - PdV \quad T, V \quad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad \ldots$ etc.

$dG = -SdT + VdP \quad T, P \quad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \quad \ldots$

Born thermodynamic square



Maxwell relation: $\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$ etc.

Thermodynamic potentials (constant *N* cases):

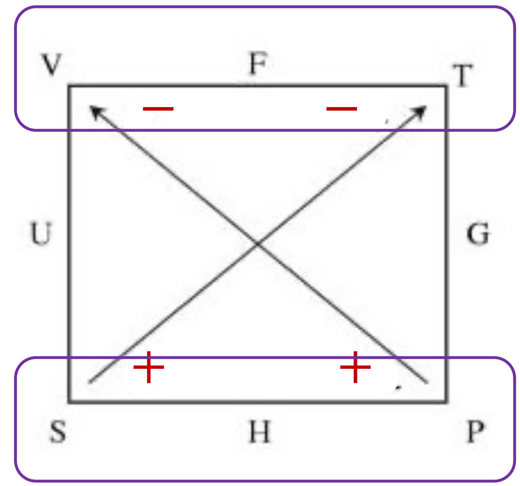
$dU = TdS - PdV$ S, V $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ $P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$

$dH = TdS + VdP$ S, P … …

$dF = -SdT - PdV$ T, V $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$ … etc.

$dG = -SdT + VdP$ T, P $S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$ …

Born thermodynamic square



Differentials

Maxwell relation: $\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$ etc.

Thermodynamic potentials (constant *N* cases):

$$dU = TdS - PdV \qquad S, V \qquad T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

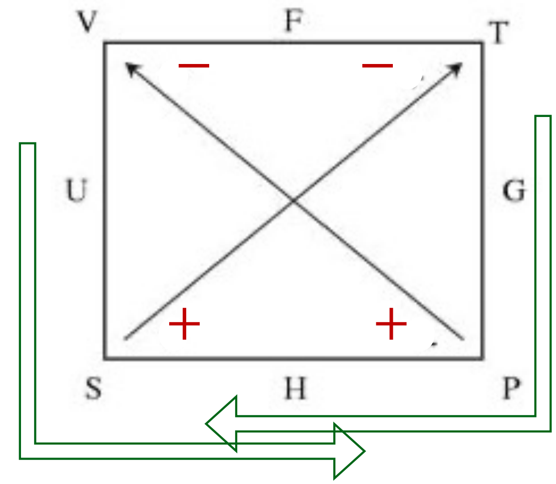
$$dH = TdS + VdP \qquad S, P \qquad \cdots \qquad \cdots$$

$$dF = -SdT - PdV \qquad T, V \qquad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad \cdots \qquad \text{etc.}$$

$$dG = -SdT + VdP \qquad T, P \qquad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \qquad \cdots$$

Maxwell relation: $\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$ etc.

Born thermodynamic square



Maxwell relations (corners)

Thermodynamic potentials:

$$dU = TdS - PdV + \mu dN \quad S, V, N \quad T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \quad \ldots$$

$$dH = TdS + VdP + \mu dN \quad S, P, N \quad \ldots \quad \ldots \quad \ldots$$

$$dF = -SdT - PdV + \mu dN \quad T, V, N \quad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad \ldots \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

$$dG = -SdT + VdP + \mu dN \quad T, P, N \quad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \quad \ldots \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

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

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

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

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

$$\left(\frac{\partial \ln V}{\partial T}\right)_P$$

Thermal expansion coeff

More Maxwell relations:

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