

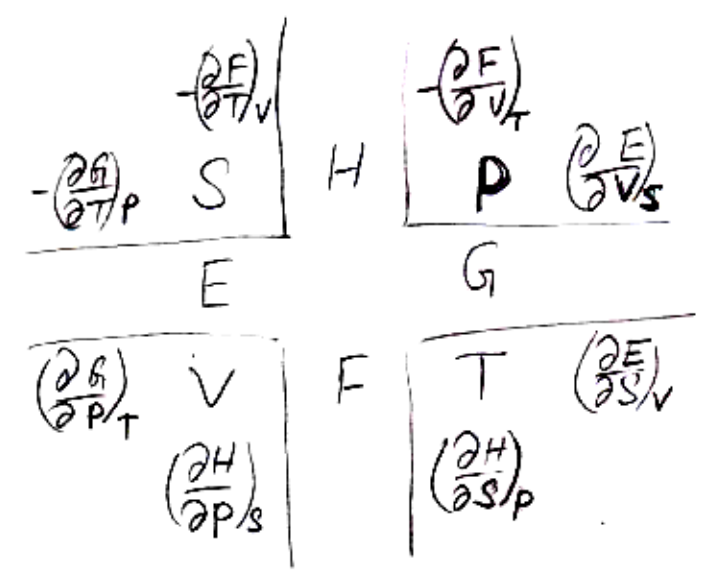
Grand potential for systems with variable number of particles

$$F = F(T, V, N) \quad dF = -SdT - pdV + \mu dN$$

$$\Omega = F - \mu N \quad d\Omega = -SdT - pdV - Nd\mu, \quad N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V}$$

$$= F - G = -PV$$

Circular diagram



$$dE = TdS - pdV$$

$$dH = TdS + vdp$$

$$dF = -SdT - pdV$$

$$dG = -SdT + vdp$$

2nd derivatives of E, H, F, G are symmetric, relate 1st derivatives of macroscopic parameters

$$dE = TdS - pdV \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 E}{\partial V \partial S}$$

$$dH = TdS + vdp \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial v}{\partial S}\right)_P = \frac{\partial^2 H}{\partial P \partial S}$$

$$dF = -SdT - pdV \quad -\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial^2 F}{\partial V \partial T}$$

$$dG = -SdT + vdp \quad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial v}{\partial T}\right)_P = \frac{\partial^2 G}{\partial P \partial T} = \alpha V \quad \boxed{\text{thermal expansion}}$$

Introduce also compressibilities (inverse bulk moduli)

$$k_T = \frac{1}{V} \left[-\left(\frac{\partial V}{\partial P}\right)_T\right] > 0 \text{ isothermal}$$

$$k_S = \frac{1}{V} \left[-\left(\frac{\partial V}{\partial P}\right)_S\right] > 0 \text{ adiabatic.}$$

Internal energy dependence on volume (fixed T)

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

Now use $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ $[-SdT - PdV = dF, \text{ exact differential}]$

And $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ ← determined by Equation of State.

Exercise (hw) show that $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$

Functions of 2 variables $df(x,y) = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$

① Exact differential
 $X dx + Y dy = df$ iff only if $\left(\frac{\partial X}{\partial y}\right)_x = \left(\frac{\partial Y}{\partial x}\right)_y$ ($= \frac{\partial^2 f}{\partial x \partial y}$)

② 1-variable trajectory
 $y = \text{const}$ $\left(\frac{\partial f}{\partial x}\right)_y = \left[\left(\frac{\partial f}{\partial x}\right)_z\right]^{-1}$ $z(x,y) = \text{const}$ $\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \cdot \left(\frac{\partial y}{\partial x}\right)_z$
Vars(x,z) ← Vars(x,y)

③ Chain rule $\left(\frac{\partial f}{\partial x}\right)_y \cdot \left(\frac{\partial x}{\partial y}\right)_f \cdot \left(\frac{\partial y}{\partial f}\right)_x = -1$ [from $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$]

④ Jacobian properties: $f(x,y), g(x,y)$

$$\frac{\partial(f,g)}{\partial(x,y)} = \det \begin{pmatrix} \left(\frac{\partial f}{\partial x}\right)_y & \left(\frac{\partial g}{\partial x}\right)_y \\ \left(\frac{\partial f}{\partial y}\right)_x & \left(\frac{\partial g}{\partial y}\right)_x \end{pmatrix} = \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial g}{\partial y}\right)_x - \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial g}{\partial x}\right)_y$$

Special case $\frac{\partial(f,x)}{\partial(y,x)} = \left(\frac{\partial f}{\partial y}\right)_x$

Property of determinant: $\det(A \cdot B) = \det(A) \cdot \det(B)$

Hence $\frac{\partial(f,g)}{\partial(x,y)} = \frac{\partial(f,g)}{\partial(u,v)} \cdot \frac{\partial(u,v)}{\partial(x,y)}$

Example 1
 Isothermal /
 adiabatic
 compressibility

$$\frac{\kappa_T}{\kappa_S} = \frac{[-\left(\frac{\partial V}{\partial P}\right)_T]}{[-\left(\frac{\partial V}{\partial P}\right)_S]} = \frac{\partial(V,T)}{\partial(P,T)} \leftrightarrow \frac{\partial(P,S)}{\partial(V,S)} = \frac{\partial(V,T)}{\partial(V,S)} \cdot \frac{\partial(P,S)}{\partial(P,T)}$$

$$= \frac{\partial(V,T)}{\partial(V,S)} \cdot \frac{\partial(P,S)}{\partial(P,T)} = \left(\frac{\partial T}{\partial S}\right)_V \cdot \left(\frac{\partial S}{\partial T}\right)_P = \frac{T}{C_V} \cdot \frac{C_P}{T} = \boxed{C_P/C_V = \gamma}$$

Example 2
 Change of entropy
 with volume

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{\partial(S,P)}{\partial(V,P)} = \frac{\partial(S,P)}{\partial(T,P)} \frac{\partial(T,P)}{\partial(V,P)} = \left(\frac{\partial S}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial V}\right)_P = \frac{C_P}{T} \cdot \frac{1}{\alpha V} = \boxed{\frac{C_P}{\alpha T V}}$$

More on heat capacities

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$C_p - C_v = ?$

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

$C_p = \left(\frac{\partial H}{\partial T}\right)_P \equiv \left(\frac{\partial E}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P$

change of variables: $E(T, P) = E(T, P(T, V)) \xrightarrow{EoS} E(T, V)$

$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + [T \left(\frac{\partial P}{\partial T}\right)_V - P] \left(\frac{\partial V}{\partial T}\right)_P$

Finally $C_p - C_v = \left(\frac{\partial E}{\partial T}\right)_V + [T \left(\frac{\partial P}{\partial T}\right)_V - P] \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V = T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$

Using chain rule, $\left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \frac{\alpha}{\kappa_T}$

$C_p - C_v = T \cdot \alpha V \cdot \frac{\alpha}{\kappa_T} = \frac{\alpha^2 T V}{\kappa_T}$

Express $\delta Q = T dS$ through (dT, dV) or (dT, dP) :

$\delta Q = T dS = dE + P dV = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + P dV = \left[C_v dT + \frac{\alpha T}{\kappa_T} dV \right]$
 recall $\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = \frac{T \alpha}{\kappa_T}$ "Tds" equations.

$\delta Q = T dS = dH - V dP = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP - V dP = \left[C_p dT - \alpha T V dP \right]$
 recall $\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P = -T \alpha V$

Note two useful identities:

$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$

Recall $S = - \left(\frac{\partial F}{\partial T}\right)_V = - \left(\frac{\partial G}{\partial T}\right)_P$ and get equations for thermodynamic potentials

$T \left(\frac{\partial^2 F}{\partial T^2}\right)_V = -C_v$; example: for ideal gas $C_v = \text{const}$

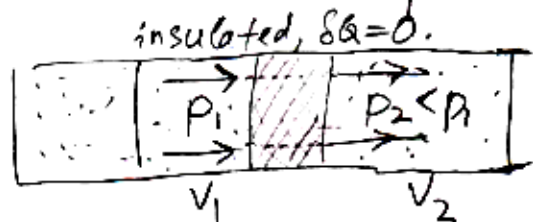
$T \left(\frac{\partial^2 G}{\partial T^2}\right)_P = -C_p$
 measurable in experiment

$F = -C_v T \log T + \underbrace{T f_1(V) + f_2(V)}_{EoS}$

$G = \dots$

Joule-Thomson process (throttling)

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Gas is forced through a porous plug
Pressure \downarrow volume \uparrow : work $\delta W \neq 0$

$$E_1 + P_1 V_1 = E_2 + P_2 V_2 = H = \text{const}$$

How does temperature change?

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial(T, H)}{\partial(P, H)} = \frac{\partial(T, H)}{\partial(T, P)} \cdot \frac{\partial(T, P)}{\partial(P, H)} = \left(\frac{\partial H}{\partial P}_T\right) \left[-\left(\frac{\partial T}{\partial H}\right)_P\right]$$

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

$$= [V - T \cdot \alpha V] \left(-\frac{1}{C_p}\right) = \frac{V}{C_p} [\alpha T - 1]. \rightarrow \text{used in hw problem}$$

How does entropy change?

$\left(\frac{\partial S}{\partial P}\right)_H = ?$ H is a function of (S, P)

$$dH = TdS + Vdp \underset{H=\text{const}}{=} 0 \Leftrightarrow \left(\frac{\partial S}{\partial P}\right)_H = -\frac{V}{T} < 0$$

Since $P_2 < P_1$, entropy always increases in throttling.

For ideal gas $PV = NT$

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

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_p} [\alpha T - 1] = \frac{V}{C_p} \left[\frac{1}{T} T - 1\right] = 0$$

Thermodynamic potentials and equilibrium

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$$\left. \begin{aligned} F &\rightarrow \min_{T, V \text{ const}} \\ G &\rightarrow \min_{T, P \text{ const}} \end{aligned} \right\} \text{at equilibrium}$$

What are the conditions for the equilibrium to be stable?



$$\begin{aligned} E &\rightarrow E + \delta E \\ V &\rightarrow V + \delta V \\ S &\rightarrow S + \delta S \end{aligned}$$

$$\delta G = \delta E + P_0 \delta V - T_0 \delta S$$

$$\delta E = \left(\frac{\partial E}{\partial S} \right)_V \delta S + \left(\frac{\partial E}{\partial V} \right)_S \delta V \Rightarrow \delta G^{1st \text{ order}} = 0$$

$T = T_0 \quad -P = -P_0 \leftarrow \text{at equilibrium}$

2nd order in $(\delta S, \delta V)$:

$$0 < \left(\frac{\partial^2 E}{\partial S^2} \right)_V \delta S^2 + \left(\frac{\partial^2 E}{\partial V^2} \right)_S \delta V^2 + 2 \frac{\partial^2 E}{\partial S \partial V} \delta S \delta V$$

for any $(\delta S, \delta V)$ must be positive

1) $\left(\frac{\partial^2 E}{\partial S^2} \right)_V = \left(\frac{\partial T}{\partial S} \right)_V = \left[\frac{T}{C_V} > 0 \right]$: heat capacity is always positive

2) $\left(\frac{\partial^2 E}{\partial V^2} \right)_S = \left[\frac{\partial (-P)}{\partial V} \right]_S = - \left(\frac{\partial P}{\partial V} \right)_S = \left[\frac{1}{\kappa_S V} > 0 \right]$: adiabatic compressibility is always positive

3) $\left(\frac{\partial^2 E}{\partial S \partial V} \right)^2 < \left(\frac{\partial^2 E}{\partial V^2} \right)_S \cdot \left(\frac{\partial^2 E}{\partial S^2} \right)_V$: (minor determinant criterion).

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

$$\left(\frac{\partial T}{\partial V} \right)_S \left(\frac{\partial P}{\partial S} \right)_V - \left(\frac{\partial P}{\partial V} \right)_S \left(\frac{\partial T}{\partial S} \right)_V = \frac{\partial(T, P)}{\partial(V, S)} > 0$$

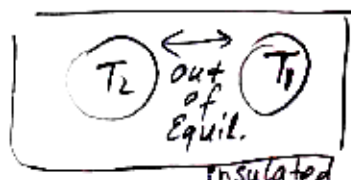
$$\frac{\partial(T, P)}{\partial(V, S)} = \frac{\partial(T, P)}{\partial(V, T)} \cdot \frac{\partial(V, T)}{\partial(V, S)} = \left[- \left(\frac{\partial P}{\partial V} \right)_T \right] \cdot \left(\frac{\partial T}{\partial S} \right)_V = \frac{1}{\kappa_T V} \cdot \frac{T}{C_V} > 0$$

Hence $\boxed{\kappa_T > 0}$ (isothermic compressibility)

Also $C_p = C_v + \frac{\alpha^2 T V}{\kappa_T} \geq C_v > 0$.

Maximal work done by an isolated system

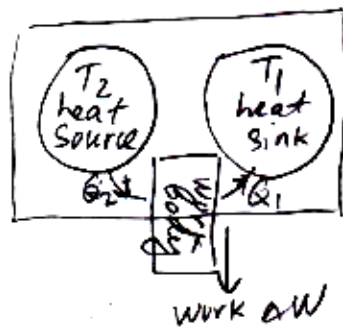
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$V_{fin} = V_{ini}$
 $V \neq \text{const}$
 $T_2 > T_1$

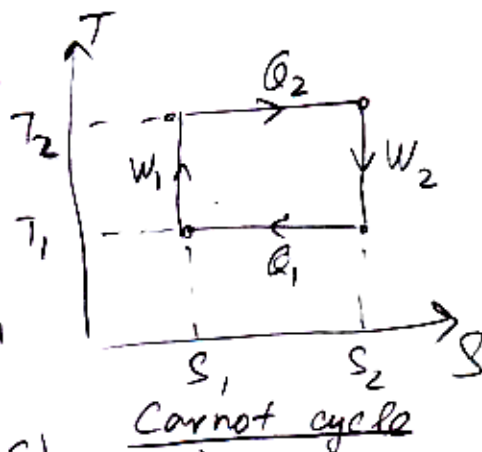
$(\Delta W)_{done\ by\ system} = E_{ini} - E_{fin}$
entropy change $S_{ini} \rightarrow S_{fin} \geq S_{ini}$ (2nd law)

$\frac{\partial \Delta W}{\partial S_{fin}} = - \left(\frac{\partial E_{fin}}{\partial S_{fin}} \right) = (-T) < 0$
 $\Delta W = \text{max}$ iff $S_{fin} = \text{min} = S_{ini}$ ie change is reversible



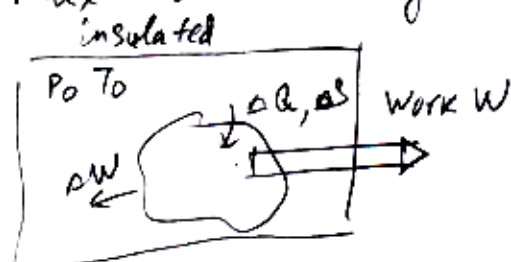
- 1) heat exchanges are reversible } between parts of isolated system
 $Q_2: T = T_2$
 $Q_1: T = T_1$

2) Work is adiabatic
 $\Delta W = W_2 - W_1 = Q_2 - Q_1$
 $= (T_2 - T_1)(S_2 - S_1)$



$\eta = \frac{\Delta W}{Q_2} = \frac{(T_2 - T_1)(S_2 - S_1)}{T_2(S_2 - S_1)} = (1 - T_1/T_2)$
 max. possible efficiency.

Max work done by a body at constant T, V



$(\Delta W)_{sys} = -\Delta E - P_0 \Delta V + \Delta Q$ (energy conserv)

$\Delta Q \leq T_0 \Delta S$ ($\Delta S + \Delta S_{env} \geq 0$)

Thus $(\Delta W)_{sys} \leq -(\Delta E + P_0 \Delta V - T_0 \Delta S)$
 $= -\Delta G$ if $T = T_0$ (at equilibrium)
 $P = P_0$

For $P = P_0$, $\text{max}(\Delta W)_{sys} = -\Delta G$
 For $V = \text{const}$, $\text{max}(\Delta W) = -\Delta F$

} reached in reversible processes, no work dissipation.

Chemical potential and grand potential

Gibbs potential $G(p,T)$ - function of intensive variables.

chemical potential $\mu(p,T) = \frac{G(p,T)}{N}$ = intensive thermal function of state.

describe systems with variable particle number N

$d\mu = -s dT + v dp$ $s = \frac{S'}{N}$, $v = \frac{V}{N}$

for changing N ,

$$\left. \begin{aligned} dG &= -S' dT + \bar{V} dp + \mu dN \\ dF &= -S' dT - p dV + \mu dN \\ dE &= T dS' - p dV + \mu dN \\ dH &= T dS' + \bar{V} dp + \mu dN \end{aligned} \right\} \mu = \left(\frac{\partial G}{\partial N} \right)_{p,T} = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \left(\frac{\partial E}{\partial N} \right)_{S',V} = \left(\frac{\partial H}{\partial N} \right)_{S,p}$$



$dF = -S' dT + \mu dN$

$d(F - \mu N) = -S' dT - N d\mu$

Ω grand potential, $\Omega = F - \mu N = F - G = -P \cdot V$

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

$\frac{1}{v} = n = \frac{N}{V} = \left(\frac{\partial P}{\partial \mu} \right)_{T,V}$	$n = \text{concentration}$
	$v = \text{per-particle volume}$

Equilibrium of substance components in a mix

$P_1 = P_2, T_1 = T_2$

$G = \mu_1 N_1 + \mu_2 N_2 \rightarrow \min_{N_1+N_2=\text{const}} : \mu_1 = \mu_2$

$\mu_1(p,T) = \mu_2(p,T)$	equation of equilibrium
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Equilibrium of phases

Saturated
vapor
 N_2
liquid

$$p = \text{const} \quad \left. \begin{array}{l} \\ T = \text{const} \end{array} \right\} \text{vapor and liquid at equilibrium}$$

$$\mu_1(p, T) = \mu_2(p, T)$$

$$V = V_1 + V_2 \text{ change}$$

$$N = N_1 + N_2 \text{ constant (or } m_1 + m_2)$$

$$G = \mu_1 N_1 + \mu_2 N_2 = \mu_1 N + (\mu_2 - \mu_1) N_2$$

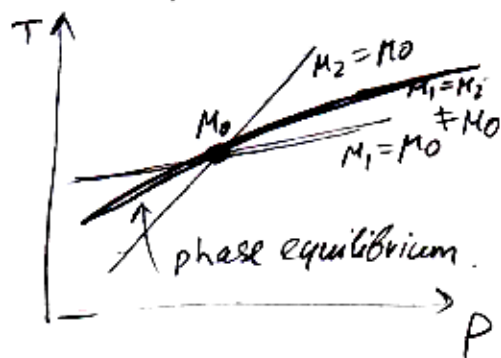
$\Delta G \leq 0$:
Spontaneously with time

$\mu_2 < \mu_1$: $N_2 \rightarrow N$, $N_1 \rightarrow 0$ all vapor
 $\mu_2 > \mu_1$: $N_2 \rightarrow 0$, $N_1 \rightarrow N$ all liquid.
 $\mu_2 = \mu_1$: phase equilibrium, coexistence.

Now suppose (p, T) change, but $\mu_2 = \mu_1$, phases stay in equilibrium.

$$\mu_2(p, T) = \mu_1(p, T) \Rightarrow \boxed{p = p_{\text{vapor}}(T)}$$

2 variables
1 equation



$$d\mu_1 = -s_1 dT + v_1 dp \quad \left| \begin{array}{l} v = \frac{V}{N} \\ s = \frac{S}{N} \end{array} \right.$$

$$d\mu_2 = -s_2 dT + v_2 dp$$

$$\underline{d\mu_1 = d\mu_2} \quad (s_1 - s_2) dT = (v_1 - v_2) dp$$

$$\left(\frac{\partial p}{\partial T} \right)_{\mu_1 = \mu_2} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{\Delta s_{12}}{\Delta v_{12}}$$

$$\Delta Q = T \Delta S = \text{latent heat of transition} = l$$

$$\Delta v = v_1 - v_2 = \left(\frac{m}{\rho_1} - \frac{m}{\rho_2} \right) \leftrightarrow \text{change of density}$$

$$\left(\frac{\partial p}{\partial T} \right)_{\text{phase equilibrium}} = \frac{l}{T \Delta v} \quad \text{Clapeyron-Clausius equation}$$

Water \rightarrow vapor $l > 0, \Delta v > 0 \quad \left(\frac{\partial p}{\partial T} \right)_{\text{sat. vapor}} > 0 \quad p(100^\circ\text{C}) = p_{\text{atm}}$

ice \rightarrow water $l > 0, \Delta v < 0 \quad \left(\frac{\partial p}{\partial T} \right)_{\text{melting}} < 0. \quad \text{compressed ice will melt.}$