Temp dependence of vapour pressure.

pressure exerted by a vapour in thermodynamic eq with it's condensed phase at a given temp & closed system

v_l & v_g are molar volume of liquid & gas

$$v_g >> v_l$$

From Clapeyron eq. $\left(\frac{dp}{dT}\right)_{vap} = \frac{L_{vap}}{T\,\Delta v}$

$$p v_g = RT$$

$$\frac{dp}{dT} = \frac{Lp}{T^2 R}$$

$$\Rightarrow \frac{dp}{p} = \frac{L\,dT}{RT^2}$$

$$\ln p = -\frac{L}{RT} + C.$$

$$\Rightarrow p = C_0 \exp\left[-\frac{L}{RT}\right]$$

Heat capacity of saturated vapour.

$$L = T(S_g - S_l)$$

$$\Rightarrow \frac{L}{T} = (S_g - S_l)$$

$$\Rightarrow \frac{d}{dT}\left(\frac{L}{T}\right) = \frac{\partial}{\partial T}\left(\frac{L}{T}\right) + \frac{dp}{dT}\frac{\partial}{\partial p}\left(\frac{L}{T}\right)$$

$$= \frac{\partial}{\partial T}(S_g - S_l) + \left[\frac{\partial}{\partial p}(S_g - S_l)\right]\left(\frac{dp}{dT}\right)$$

$$= \cancel{-\left(\frac{\partial V_g}{\partial T}\right)_p + \left(\frac{dp}{dT}\right)\left[\right.}$$

$$= \frac{1}{T}(C_p^g - C_p^l) + \left(\frac{dp}{dT}\right)\left[\left(\frac{\partial S_g}{\partial p}\right)_T - \left(\frac{\partial S_l}{\partial p}\right)_T\right]$$

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

$$\Rightarrow \left(\frac{dp}{dT}\right)\left(\frac{\partial V_g}{\partial T}\right)_p = \frac{1}{T}(C_p^g - C_p^l) - \frac{d}{dT}\left(\frac{L}{T}\right)$$

$$\Rightarrow \boxed{\frac{dp}{dT} = \frac{(C_p^g - C_p^l) - T\frac{d}{dT}(L/T)}{T\left(\frac{\partial V_g}{\partial T}\right)_p}}$$

Do Adiabatic expansion of saturated vapour.

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp = 0.$$

$$= \frac{C_p^g}{T} dT - \left(\frac{\partial v_g}{\partial T}\right)_p dp = 0.$$

$$\Rightarrow \boxed{\frac{dp}{dT} = \frac{C_p^g}{T\left(\frac{\partial v_g}{\partial T}\right)_p}}$$

Liquid condenses if

$$\frac{C_p^g}{T\left(\frac{\partial v_g}{\partial T}\right)_p} < \frac{(C_p^g - C_p^l) - T\frac{d}{dT}(L/T)}{T\left(\frac{\partial v_g}{\partial T}\right)_p}$$

$$0 < -C_p^l - T\frac{d}{dT}\left(\frac{L}{T}\right)$$

$$\Rightarrow \boxed{C_p^l + T\frac{d}{dT}\left(\frac{L}{T}\right) < 0}$$

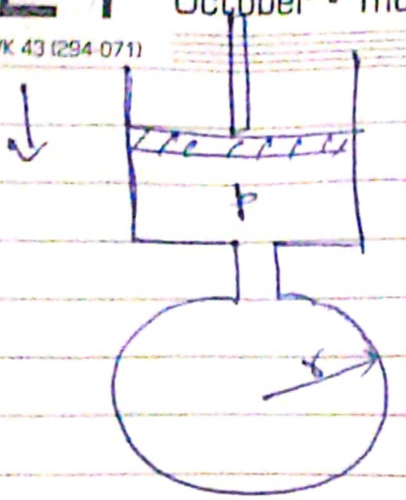
$dU = TdS - pdV$

$dW = -pdV = Xdx.$

X = some intensive generalized force.

x = some extensive generalized displacem

	X	x
Fluid	$-p$	V
elastic road	f	L
liquid film	γ	A
dielectric	$\vec{E}$	$\vec{p}_1$
magnetic	$\vec{B}$	$\vec{m}$



$$\bar{d}W = \gamma\, dA$$

Liquid surface of surface area A

$$dA = 4\pi(r+dr)^2 - 4\pi r^2 = \;= 8\pi r\, dr$$

Piston moves down → work done on the system

$$\bar{d}W = p\,dV = p\,4\pi r^2 dr$$

$$\bar{d}W = \gamma\, dA = 8\pi\gamma\, r\, dr$$

$$\rightarrow \quad p = \frac{2\gamma}{r}$$

$$dU = TdS + \gamma\, dA$$

$$\left(\frac{\partial U}{\partial A}\right)_T = T\left(\frac{\partial S}{\partial A}\right)_T + \gamma$$

$$dF = -SdT - pdV$$

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

$$F = -SdT + \gamma\, dA$$

$$\left(\frac{\partial S}{\partial A}\right)_T = -\left(\frac{\partial \gamma}{\partial T}\right)_A$$

$$\left(\frac{\partial U}{\partial A}\right)_T = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_A$$

$$\left(\frac{\partial U}{\partial A}\right)_T = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_A$$

Usually $\left(\frac{\partial \gamma}{\partial T}\right)_A < 0$.

Increase in heat

$$\Delta Q = T\,dS = T\left(\frac{\partial S}{\partial A}\right)_T \Delta A$$

$$= -T\Delta A\left(\frac{\partial \gamma}{\partial T}\right)_A > 0.$$

$$\Rightarrow \left(\frac{\partial S}{\partial A}\right)_T > 0$$

Entropy has two term

One from bulk

One from surface.