

# Thermodynamics lecture 6.

## W.A.L.T.

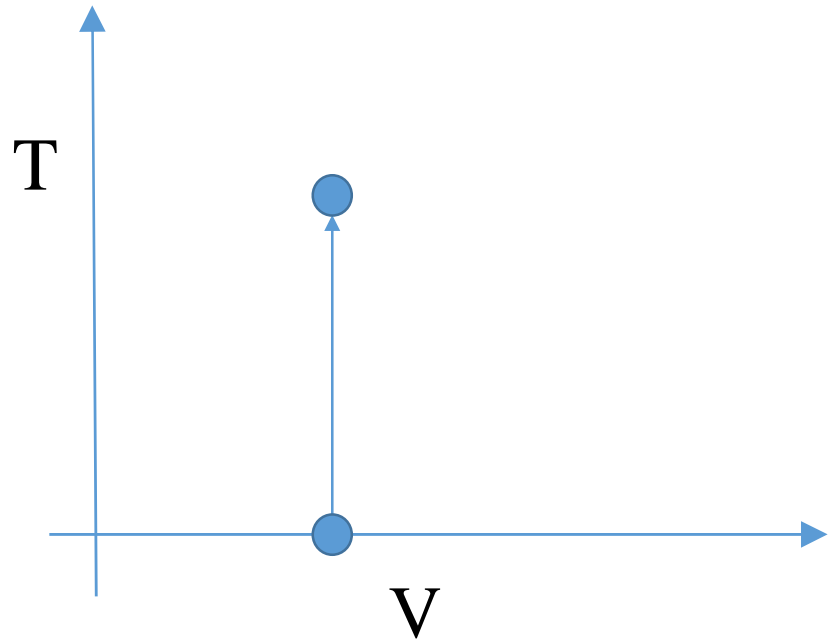
- Introduce chemical potential
- Euler relation, Gibbs-Duhem relation
- Thermodynamic potentials
- Maxwell relations
- Applications
- Natural variables

Total (also called absolute) entropy

$$S(T_f) - S(0) = \int_0^{T_f} \frac{\bar{d}Q_{\text{rev}}}{T}$$

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$$S(V, T_f) = \int_0^{T_f} \frac{C_V(V, T)}{T} dT + \sum_i \frac{L_i}{T_i}$$

(assuming  $S(V, 0) = 0$ )

internal energy  $U$

$$dU = TdS - pdV + \mu dN$$

enthalpy  $H = U + pV$

$$dH = TdS + Vdp + \mu dN$$

Helmholtz function  $F = U - TS$

$$dF = -SdT - pdV + \mu dN$$

Gibbs function  $G = U + pV - TS$

$$dG = -SdT + Vdp + \mu dN$$

$$\tilde{U} = U - \mu N$$

$$d\tilde{U} = TdS - pdV - Nd\mu$$

$$\tilde{H} = H - \mu N$$

$$d\tilde{H} = TdS + Vdp - Nd\mu$$

Grand potential  $\Omega = F - \mu N$

$$d\Omega = -SdT - pdV - Nd\mu$$

$$G - \mu N = 0$$

Function	Significance	Natural variables	Maxwell relation
$U$	Energy content	$S, V, N$	$\left. \frac{\partial T}{\partial V} \right _S = - \left. \frac{\partial p}{\partial S} \right _V$
$F$	Effective potential energy for system at fixed $T$	$T, V, N$	$\left. \frac{\partial S}{\partial V} \right _T = \left. \frac{\partial p}{\partial T} \right _V$
$H$	Related to energy changes at fixed pressure $\Delta H =$ process energy, latent heat, heat of reaction	$S, p, N$	$\left. \frac{\partial T}{\partial p} \right _S = \left. \frac{\partial V}{\partial S} \right _p$
$G$	Determines direction of phase and chemical changes	$T, p, N$	$-\left. \frac{\partial S}{\partial p} \right _T = \left. \frac{\partial V}{\partial T} \right _p$
$\Omega$	Useful in general study of open systems	$T, V, \mu$	