

Thermodynamics lecture 6.

W.A.L.T.

- A. Introduce chemical potential
- B. Euler relation, Gibbs-Duhem relation
- C. Thermodynamic potentials
- D. Obtaining one potential from another
- E. Maxwell relations
- F. Some applications

Total entropy (also called *absolute entropy*) of a given physical entity:

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

Total entropy (also called *absolute entropy*) of a given physical entity:

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

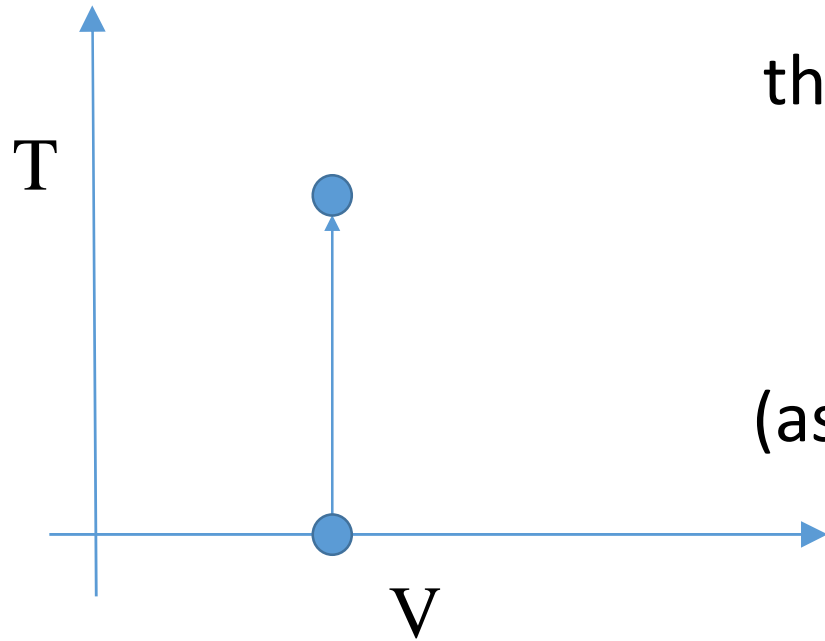
therefore

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

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

Latent heat

Temperature
of i 'th phase
change



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internal energy U

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

Helmholtz function $F = U - TS$

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

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 $\Omega = F - \mu N$

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

$$G - \mu N = 0$$

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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	$-\left. \frac{\partial S}{\partial p} \right _T = \left. \frac{\partial V}{\partial T} \right _p$
Ω	Useful in general study of open systems	T, V, μ	