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

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internal energy U $\qquad$ $dU = T\,dS - p\,dV + \mu\,dN$

Helmholtz function $F = U - TS$ $\qquad$ $dF = -S\,dT - p\,dV + \mu\,dN$

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 $G = U + pV - TS$	$dG = -SdT + Vdp + \mu dN$

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Gibbs function $G = U + pV - TS$ $\quad dG = -SdT + Vdp + \mu dN$

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

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

Grand potential $\Omega = F - \mu N$ $\quad d\Omega = -SdT - pdV - Nd\mu$

$G - \mu N = 0$

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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	

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F. Some applications: energy, $C_p - C_V$, γ , $C_V(\mathrm{T}, \mathrm{V})$

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

$$S(T_{\mathrm{f}}) - S(0) = \int_0^{T_{\mathrm{f}}} \frac{đQ_{\mathrm{rev}}}{T}$$

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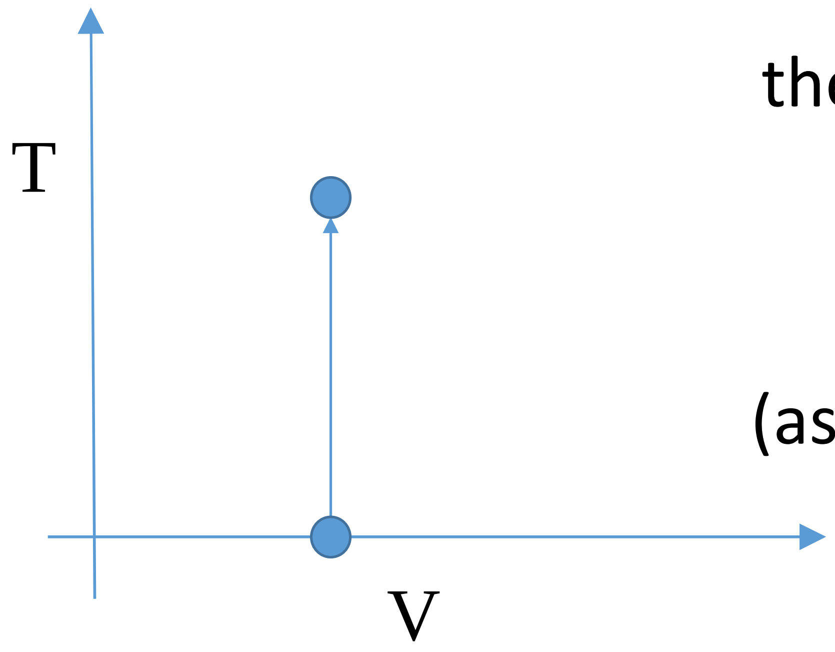

therefore

$$S(V, T_\mathrm{f}) = \int_0^{T_\mathrm{f}} \frac{C_V(V,T)}{T}\mathrm{d}T + \sum_i \frac{L_i}{T_i}$$

Latent heat

Temperature of *i*'th phase change

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