Química Termodinámica Estadística: Potenciales termodinámicos

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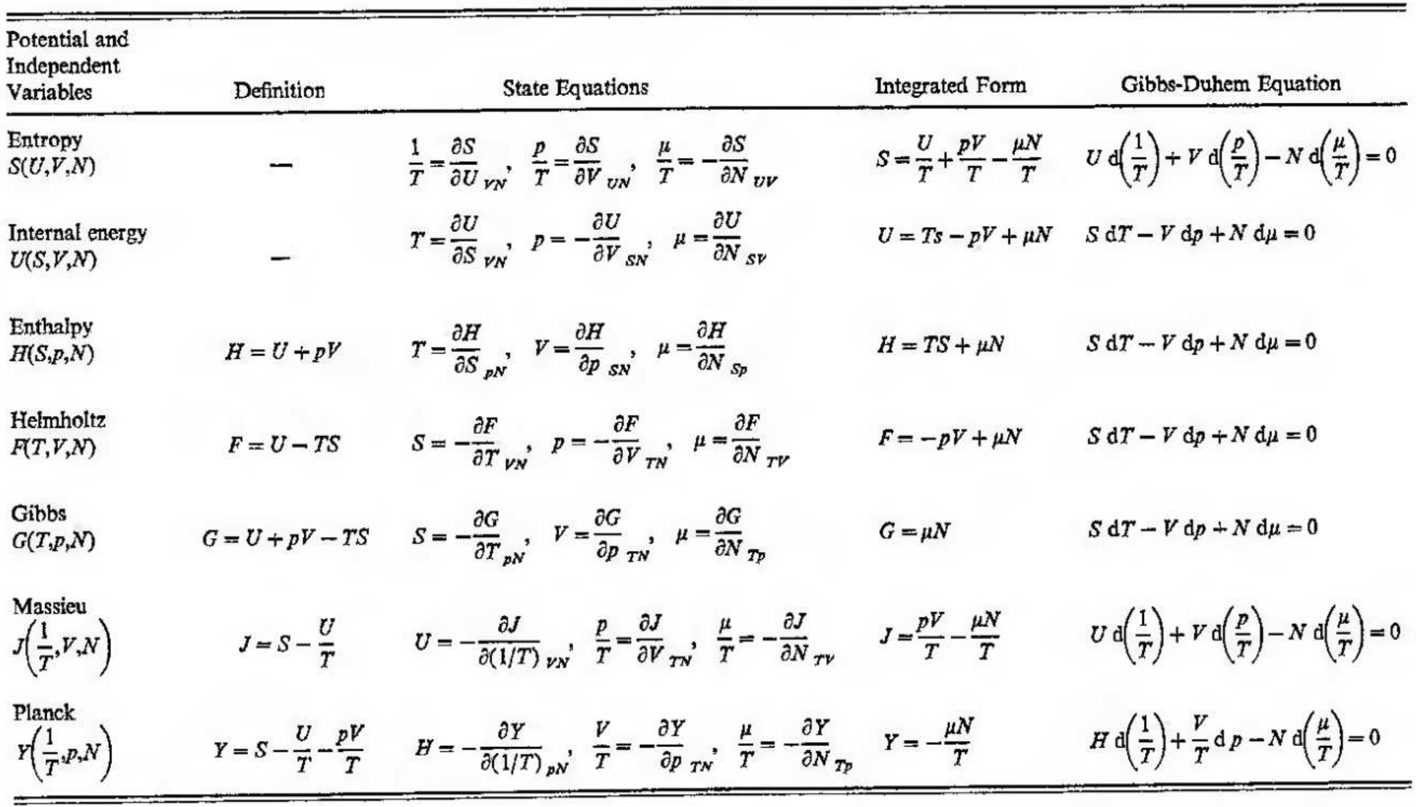
Table 1 Conjugate pairs of variables in work terms for the fundamental equation for U[a].

Type of work	Intensive variable	Extensive variable	Differential work in dU
Mechanical			
Pressure-volume	$-P$	V	$-P\mathrm{d}V$
Elastic	f	L	$f\mathrm{d}L$
Gravitational	$\psi = gh$	$m = \sum M_i n_i$	$\psi \mathrm{d}m = \sum g h M_i \mathrm{d}n_i$
Surface	γ	A_s	$\gamma \mathrm{d}A_\mathrm{s}$
Electromagnetic			
Charge transfer	ϕ_i	Q_i	$\phi_i \mathrm{d}Q_i$
Electric polarization	$\boldsymbol{E}$	$\boldsymbol{p}$	$\boldsymbol{E}\bullet\mathrm{d}\boldsymbol{p}$
Magnetic polarization	$\boldsymbol{B}$	$\boldsymbol{m}$	$\boldsymbol{B}\bullet\mathrm{d}\boldsymbol{m}$
Chemical			
Chemical: no reactions	μ_i	n_i (species)	$\mu_i \mathrm{d}n_i$
Chemical: reactions	μ_i	n_{ci} (components)	$\mu_i \mathrm{d}n_{ci}$

[a] Here $\psi = gh$ is the gravitational potential, g is the gravitational acceleration, h is height above the surface of the earth, m is mass, M_i is molar mass, ϕ_i is the electric potential of the phase containing species i, Q_i is the contribution of species i to the electric charge of a phase, z_i is the charge number, F is the Faraday constant, f is force of elongation, L is length in the direction of the force, γ is surface tension, A_s is surface area, $\boldsymbol{E}$ is electric field strength, $\boldsymbol{p}$ is the electric dipole moment of the system, $\boldsymbol{B}$ is magnetic field strength (magnetic flux density), and $\boldsymbol{m}$ is the magnetic moment of the system. In some electrochemical systems, $Q_i = Fz_i n_i$ so that $\mathrm{d}Q_i = Fz_i \mathrm{d}n_i$. The dots indicate scalar products of vectors. Some of the other work terms can be written in vector notation. Other types of work terms are possible, and some of the expressions for differential work are more complicated; for example, the force on a solid may be represented by a tensor and ψ may be a centrifugal potential. The term $\gamma \mathrm{d}A_\mathrm{s}$ applies to flat surfaces.

R. A. Alberty, Pure Appl. Chem. ***73*** *1349–1380, 2001*

Table 3.3 Thermodynamic Potentials



Potential and Independent Variables	Definition	State Equations	Integrated Form	Gibbs-Duhem Equation
Entropy $S(U,V,N)$	—	$\frac{1}{T} = \frac{\partial S}{\partial U}_{VN}, \quad \frac{p}{T} = \frac{\partial S}{\partial V}_{UN}, \quad \frac{\mu}{T} = -\frac{\partial S}{\partial N}_{UV}$	$S = \frac{U}{T} + \frac{pV}{T} - \frac{\mu N}{T}$	$U\,\mathrm{d}\left(\frac{1}{T}\right) + V\,\mathrm{d}\left(\frac{p}{T}\right) - N\,\mathrm{d}\left(\frac{\mu}{T}\right) = 0$
Internal energy $U(S,V,N)$	—	$T = \frac{\partial U}{\partial S}_{VN}, \quad p = -\frac{\partial U}{\partial V}_{SN}, \quad \mu = \frac{\partial U}{\partial N}_{SV}$	$U = Ts - pV + \mu N$	$S\,\mathrm{d}T - V\,\mathrm{d}p + N\,\mathrm{d}\mu = 0$
Enthalpy $H(S,p,N)$	$H = U + pV$	$T = \frac{\partial H}{\partial S}_{pN}, \quad V = \frac{\partial H}{\partial p}_{SN}, \quad \mu = \frac{\partial H}{\partial N}_{Sp}$	$H = TS + \mu N$	$S\,\mathrm{d}T - V\,\mathrm{d}p + N\,\mathrm{d}\mu = 0$
Helmholtz $F(T,V,N)$	$F = U - TS$	$S = -\frac{\partial F}{\partial T}_{VN}, \quad p = -\frac{\partial F}{\partial V}_{TN}, \quad \mu = \frac{\partial F}{\partial N}_{TV}$	$F = -pV + \mu N$	$S\,\mathrm{d}T - V\,\mathrm{d}p + N\,\mathrm{d}\mu = 0$
Gibbs $G(T,p,N)$	$G = U + pV - TS$	$S = -\frac{\partial G}{\partial T}_{pN}, \quad V = \frac{\partial G}{\partial p}_{TN}, \quad \mu = \frac{\partial G}{\partial N}_{Tp}$	$G = \mu N$	$S\,\mathrm{d}T - V\,\mathrm{d}p + N\,\mathrm{d}\mu = 0$
Massieu $J\left(\frac{1}{T},V,N\right)$	$J = S - \frac{U}{T}$	$U = -\frac{\partial J}{\partial(1/T)}_{VN}, \quad \frac{p}{T} = \frac{\partial J}{\partial V}_{TN}, \quad \frac{\mu}{T} = -\frac{\partial J}{\partial N}_{TV}$	$J = \frac{pV}{T} - \frac{\mu N}{T}$	$U\,\mathrm{d}\left(\frac{1}{T}\right) + V\,\mathrm{d}\left(\frac{p}{T}\right) - N\,\mathrm{d}\left(\frac{\mu}{T}\right) = 0$
Planck $Y\left(\frac{1}{T},p,N\right)$	$Y = S - \frac{U}{T} - \frac{pV}{T}$	$H = -\frac{\partial Y}{\partial(1/T)}_{pN}, \quad \frac{V}{T} = -\frac{\partial Y}{\partial p}_{TN}, \quad \frac{\mu}{T} = -\frac{\partial Y}{\partial N}_{Tp}$	$Y = -\frac{\mu N}{T}$	$H\,\mathrm{d}\left(\frac{1}{T}\right) + \frac{V}{T}\,\mathrm{d}p - N\,\mathrm{d}\left(\frac{\mu}{T}\right) = 0$

G. Emanuel, Advanced Classical Thermodynamics

AIAA Education Series, 1987