

**Table 20.1** Statistical thermodynamic relations

In terms of the canonical partition function  $Q$

internal energy

$$U - U(0) = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_V$$

$$\beta = 1/kT$$

entropy

$$S = \frac{U - U(0)}{T} + k \ln Q$$

Helmholtz

$$A - A(0) = -kT \ln Q$$

$$A = U - TS$$

pressure

$$p = kT \left( \frac{\partial \ln Q}{\partial V} \right)_T$$

enthalpy

$$H - H(0) = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_V + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T$$

$$H = U + PV$$

Gibbs F.  $\bar{G}$

$$G - G(0) = -kT \ln Q + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_T$$

$$G = H - TS = A + PV$$

For indistinguishable, independent particles  $Q = q^N / N!$

$$* U - U(0) = -N \left( \frac{\partial \ln q}{\partial \beta} \right)_V$$

$$* S = \frac{U - U(0)}{T} + nR (\ln q - \ln N + 1)$$

$$* G - G(0) = -nRT \ln \left( \frac{q_m}{N_A} \right)$$

where  $q_m$  is the molar partition function. For distinguishable, independent particles  $Q = q^N$

$$U - U(0) = -N \left( \frac{\partial \ln q}{\partial \beta} \right)_V$$

$$\rightarrow S = \frac{U - U(0)}{T} + nR \ln q$$

$$G - G(0) = -nRT \ln q$$

$U, G, H, A$  }  $\lim_{T \rightarrow 0} = U(0)$