<u>Thermodynamic Functions from Partition Functions</u>

$$U-U(0) = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V \qquad S = k \ln Q + \frac{U-U(0)}{T}$$

$H = U + PV$ at $T = 0$, $H(0) = U(0)$

<u>for ideal gases:</u> $PV = nRT$

$H - H(0) = U - U(0) + nRT$

$A = U - TS$ at $T = 0$, $A(0) = U(0)$

$A - A(0) = U - U(0) - TS$

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

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

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

$G = A + PV$ at $T=0$, $G(0) = A(0)$

$G - G(0) = A - A(0) + PV$

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

<u>for ideal gases:</u> $PV=nRT$ $\qquad G - G(0) = -kT \ln Q + nRT$

$Q = \frac{q^N}{N!}$ $\qquad G - G(0) = -kT \ln q^N + kT \ln N! + nRT$

$\ln N! = N \ln N - N$ $\qquad G - G(0) = -NkT \ln q + NkT \ln N - NkT + nRT$

$Nk = nR$ $\qquad G - G(0) = -nRT \ln q + nRT \ln N - nRT + nRT$

$$G - G(0) = -nRT \ln\left(\frac{q}{N}\right)$$

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separate out translational and internal degrees of freedom:

$$G - G(0) = -nRT \ln\left(\frac{q_t}{N}\right) - nRT \ln\left(q_r q_v q_e\right)$$