Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 9.7

Chemical Potential from the Partition Function

Chemical Potential Defined for *A*

Just as with the Gibbs free energy, we can take the total differential of the Helmholtz free energy with moles of substance taken as a natural variable, i.e.,

$$dA = \left(\frac{\partial A}{\partial T}\right)_{n,V} dT + \left(\frac{\partial A}{\partial V}\right)_{n,T} dV + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn$$

$$= -SdT - PdV + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn$$

Now, recalling that $G = A + PV$, we determine dG as

$$dG = dA + d\left(PV\right) = -SdT - P\cancel{d}V + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn + P\cancel{d}V + VdP$$

Equality of Chemical Potentials

$$dG = -SdT + VdP + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn$$

But, direct expansion of the total differential of *G* gives

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n}\right)_{T,P} dn$$

$$dG = -SdT + VdP + \mu dn$$

so evidently, the two chemical potentials are equal when evaluated holding the respective natural variables constant

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

What Makes *A* So Useful?

Recall the equations for *U* and *S* as functions of *Q*

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$S = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q$$

$$A = U - TS$$

$$A = -k_B T \ln Q$$

This offers a very direct way to compute the chemical potential from the partition function, based on the latter's dependence on number of particles (or moles)!

Relating Chemical Potential to q

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial A}{\partial n}\right)_{T,V} = -k_{\mathrm{B}}T\left(\frac{\partial \ln Q}{\partial n}\right)_{V,T} = -RT\left(\frac{\partial \ln Q}{\partial N}\right)_{V,T}$$

remember:

$$Q(N,V,T) = \frac{q(V,T)^{N}}{N!} \quad \text{so} \quad \ln Q = N\ln q - N\ln N + N$$

Stirling's approximation used for ln(*N*!)

Thus,

$$\mu = -RT(\ln q - \ln N - 1 + 1) = -RT\ln\frac{q(V,T)}{N}$$

Relating Chemical Potential to *q*

$$\mu = -RT \ln \frac{q(V,T)}{N}$$

Recall *q* is linear in *V* and write:

$$\mu = -RT \ln \left[\frac{q(T)}{V} \bullet \frac{V}{N} \right]$$

$$= -RT \ln \left[\frac{q(T)}{V} \bullet \frac{k_B T}{P} \right]$$

ideal gas

$$= -RT \ln \left[\frac{q(T)}{V} \bullet k_B T \right] + RT \ln P$$

Using Standard State Convention

Pressure is expressed relative to standard state (1 bar). We emphasize by writing:

$$\mu(T,P) = -RT\ln\left[\left(\frac{q}{V}\right)k_{\mathrm{B}}T\right] + RT\ln P$$

Add zero

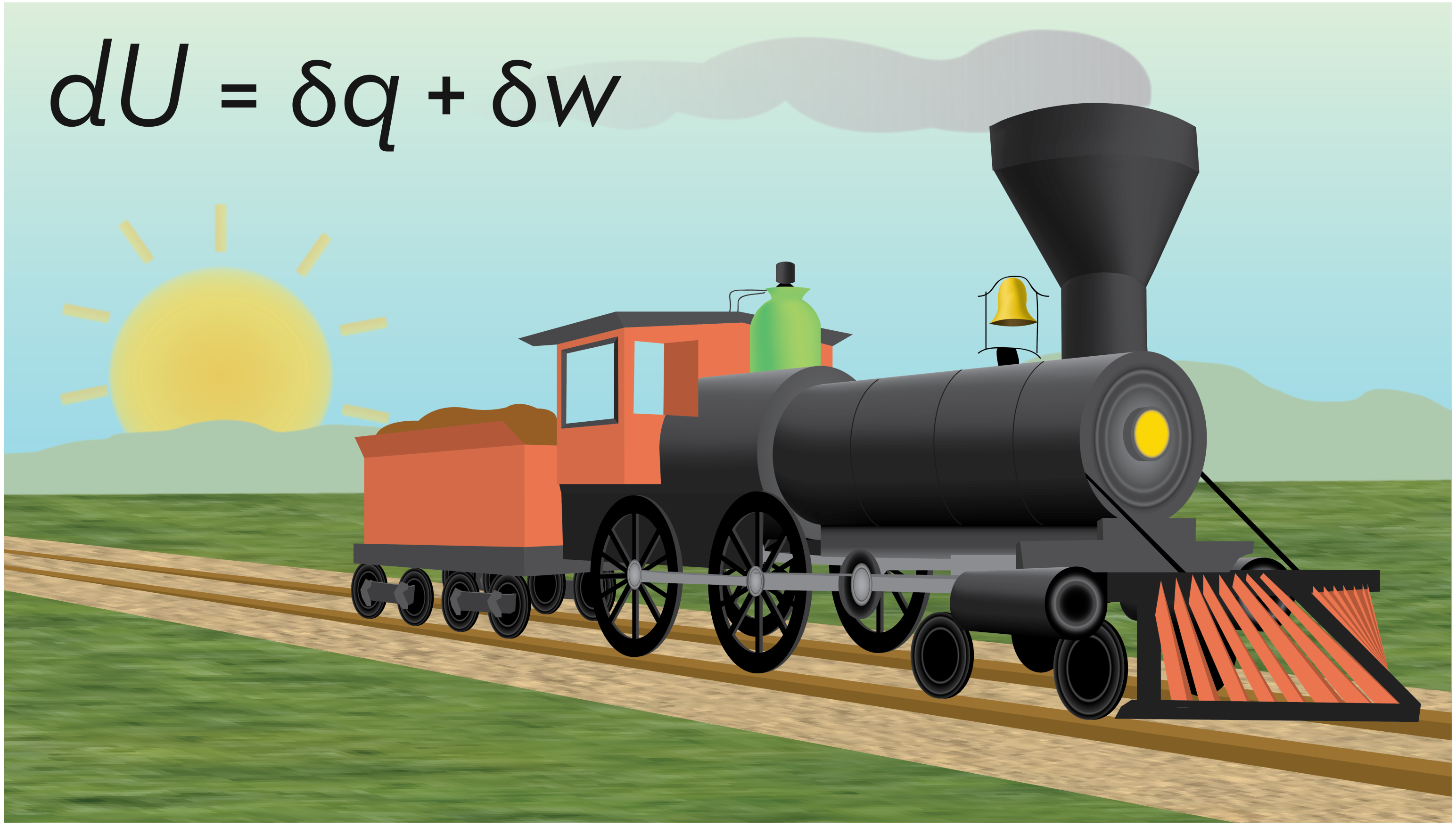
$$\left(-RT\ln P^{\circ} + RT\ln P^{\circ}\right)$$

$$\mu(T,P) = -RT\ln\left[\left(\frac{q}{V}\right)\frac{k_{\mathrm{B}}T}{P^{\circ}}\right] + RT\ln\left(\frac{P}{P^{\circ}}\right)$$

$$\mu(T,P) = \mu^{\circ}(T) + RT\ln\left(\frac{P}{P^{\circ}}\right)$$

cf. from slide 1 of video 8.7: $\overline{G}(T,P) = G^{\circ}(T) + RT\ln P$

chemical potential more general — and connects other phases to gas phase!!



Next: Review of Module 9