Discussion 9

Name and section: ______________________________

$$\begin{aligned} U(S,V,N) &= TS - pV + \mu N \\ S(U,V,N) &= \frac{U}{T} + \frac{p}{T}V - \frac{\mu}{T}N \\ F(V,T) &= U - TS \\ G(p,T) &= U + pV - TS \\ H(S,p) &= U + pV \end{aligned}$$

1. Differential forms of energies

   In the past we have worked with the expression $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$ (for a single component system).

   (a) Write an expression for $\mathrm{d}F$.

   Solution:

   $$\begin{aligned} \mathrm{d}F &= \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T \\ &= T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N - T\,\mathrm{d}S - S\,\mathrm{d}T \\ \mathrm{d}F &= -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N \end{aligned}$$

   (b) Write an expression for $\mathrm{d}G$.

   Solution:

   $$\begin{aligned} \mathrm{d}G &= T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N \\ &\quad + p\,\mathrm{d}V + V\,\mathrm{d}p - S\,\mathrm{d}T - T\,\mathrm{d}S \\ \mathrm{d}G &= -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N \end{aligned}$$

   (c) Write an expression for $\mathrm{d}H$.

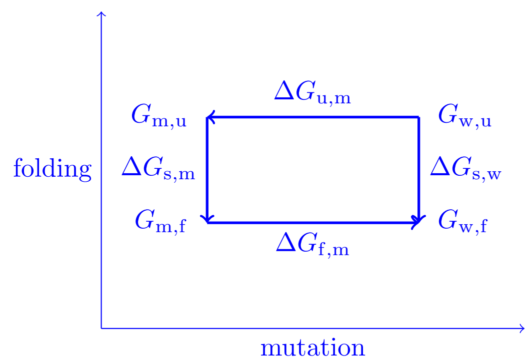
   Solution:

   $$\begin{aligned} \mathrm{d}H &= T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N \\ &\quad + p\,\mathrm{d}V + V\,\mathrm{d}p \\ \mathrm{d}H &= T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N \end{aligned}$$

2. A thermodynamic cycle for mutations in protein folding

   Suppose you can measure the stability of a protein, $\Delta G_{\mathrm{s}} = G_{\mathrm{folded}} - G_{\mathrm{unfolded}}$ (the free energy difference between folded and unfolded states) and $\Delta G_{\mathrm{f,m}} = G_{\mathrm{folded,type\ a}} - G_{\mathrm{folded,type\ b}}$ (the free energy difference between two types of a protein in their folded states). A mutant of a protein has a single amino acid replacement. Design a thermodynamic cycle that will help you find the free energy difference $\Delta G_{\mathrm{u,m}} = G_{\mathrm{unfolded,mutant}} - G_{\mathrm{unfolded,wild-type}}$, the effect of the mutation on the unfolded state.

Solution:



where $\Delta G_{\mathrm{f,m}} = G_{\mathrm{folded,wild-type}} - G_{\mathrm{folded,mutant}}$.

$$
\begin{aligned}
0 &= \Delta G_{\mathrm{f,m}} - \Delta G_{\mathrm{s,w}} + \Delta G_{\mathrm{u,m}} + \Delta G_{\mathrm{s,m}} \\
\Delta G_{\mathrm{u,m}} &= -\Delta G_{\mathrm{f,m}} + \Delta G_{\mathrm{s,w}} - \Delta G_{\mathrm{s,m}}
\end{aligned}
$$

3. Free energy of an ideal gas

   (a) For an ideal gas, calculate $F(V)$, the free energy versus volume at constant temperature. Hint: start from the differential form of $F(T, V, N)$.

   Solution:

   $$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$$

   Then, assuming constant number,

   $$
   \begin{aligned}
   &= -p\,\mathrm{d}V \\
   &= -\frac{nk_BT}{V}\,\mathrm{d}V \\
   F(V) &= -nk_BT\ln V + C
   \end{aligned}
   $$

   where C is some constant.

   (b) Compute $G(V)$. Note that V is not a natural variable of $G = G(T, P, N)$.

Solution:

$$\begin{aligned} G &= F + pV \\ &= pV - nk_BT\ln V + C \\ G(V) &= nk_BT\,(1 - \ln V) + C \end{aligned}$$

4. Heat capacity of an ideal gas

   (a) The energy of an ideal gas does not depend on volume: $\left(\frac{\partial U}{\partial V}\right)_T = 0$. Use this fact to prove that the constant-volume heat capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ for an ideal gas is independent of volume.

Solution: We want to prove that

$$\frac{\partial C_V}{\partial V} = 0.$$

$$\begin{aligned} &= \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V \\ &= \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)\right)_V \\ &= \left(\frac{\partial\, 0}{\partial T}\right)_V \\ &\boxed{\frac{\partial C_V}{\partial V} = 0} \end{aligned}$$

   (b) Show that the constant-pressure heat capacity $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ for an ideal gas is also independent of volume.

Solution:

$$\begin{aligned} \frac{\partial}{\partial V}\left(\frac{\partial H}{\partial T}\right)_p &= \left(\frac{\partial}{\partial T}\frac{\partial H}{\partial V}\right)_p \\ &= \frac{\partial}{\partial V}\left[\frac{\partial}{\partial T}\left(U + pV\right)\right]_p \\ &= \frac{\partial}{\partial V}\left[\frac{\partial}{\partial T}\left(U + nk_BT\right)\right]_p \end{aligned}$$

$$= \frac{\partial}{\partial V} (C_V + nk_B)_p$$

$$\boxed{\frac{\partial C_p}{\partial V} = 0}$$

This shows that C_p is also independent of volume for an ideal gas.