Quiz solns.

1. (a) Estimate the number of N_2/O_2 molecules in 1 kg of air (vapour density $= 14.5$) at room temperature.

   1

   Ans. # moles of gases in 1 kg of air $= \frac{10^3}{14.5 \times 2} \times 6.023 \times 10^{23}$. Nearly four-fifths of these are N_2 molecules and nearly a fifth of these are O_2 molecules.

 $\therefore$ A good estimate for N_2 is 2×10^{25} and for O_2, 4×10^{24}.

   (b) If a computer counts one molecule every clock cycle, then estimate the time that a 3 GHz personal computer will take to count the number of molecules in (a) above.   1

   Ans. Expressing in years, with 1 y $\approx 3.2 \times 10^7$s, the PC can count at a rate $\approx 10^{17}$per year.

   $\therefore$ it would take about 0.2 billion (N_2)/ 40 million years (O_2) to count all the molecules in one kilogram of nitrogen gas in air.

2.

   Draw a schematic plot showing the change in $[X]([Y])$ as a function of time starting from the topmost (leftmost) point and going over two cycles.

   2
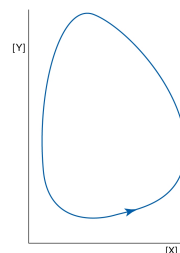
   Ans.
   Let the topmost point be at $x = x_t$ and the lowest at $x = x_l$; These are nearly the same. In each cycle, x has to decrease from x_t to a minimum value of say x_{min} and then increase back to x_l, and keep increasing to a maximum value of say, x_{max}.

   Let the leftmost point be at $y = y_l$ and the rightmost at $y = y_r$; These are nearly the same. In each cycle, y has to decrease from y_l to a minimum value of say y_{min} and then increase back to y_l, and keep increasing to a maximum value of say, y_{max}.

   For convenience, the plots shown are sinusoid, but the actual plot need not be so.
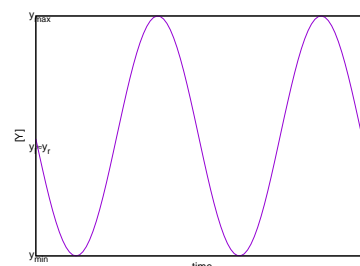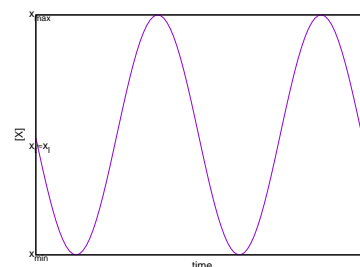

3.

   Give a molecular explanation of the variation in slopes in the graphs shown :

   Ans. The linearity of the plot indicates that the system described by the plots must be a perfect gas. Hence there are no interactions between the molecules (zero marks for any mention of interactions).

   Left plot (set A): At a given temperature, a lowering of pressure means that there are fewer molecules hitting the walls of the container per unit area. This means that the volume must have increased. The effect will be more at higher temperature, since that is when the speed of the molecules is higher.
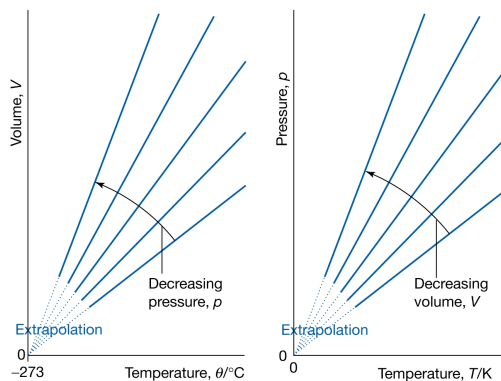
   Right plot (set B):
   At a given temperature, as the volume decreases, there are more molecules hitting the walls of the container per unit area. This means that the pressure must have increased. The effect will be more at higher temperature, since that is when the speed of the molecules is higher.

4. .
(a) The internal energy of a system at the point corresponding to the back end of the arrow in the plot, is U. What is its value at the point corresponding to the front end of the arrow? set A: If the volume was kept constant and the temperature was changed by dT,how will you express the changed internal energy? set B: If the temperature was kept constant and the volume was changed by dV, how will you express the changed internal energy?

Ans. For A, plot $U(V + dV) = U(V) + \left(\frac{\partial U}{\partial V}\right)_T dV$;
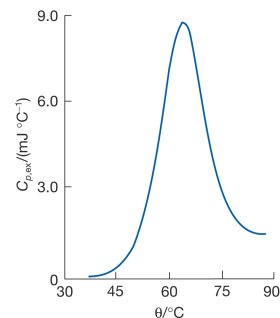$U(T + dT) = U(T) + \left(\frac{\partial U}{\partial T}\right)_V dT$
For B, the equations are the same but written in reverse order.
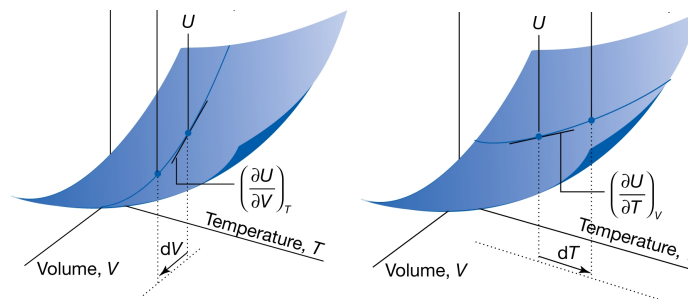
(b) What does the singularity in the DSC thermogram for protein ubiquitin shown here imply?

Ans. The singularity indicates that there is a structural transformation, similar to a phase transition, happening in the protein at that temperature.

5. Given $z = f(x, y)$, Prove : set A : $\left(\frac{\partial z}{\partial y}\right)_x = -\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z$; set B : $\left(\frac{\partial z}{\partial x}\right)_y = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial x}{\partial y}\right)_z}$

Ans. $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

For constant z, $\left(\frac{\partial z}{\partial x}\right)_y dx_z + \left(\frac{\partial z}{\partial y}\right)_x dy_z = 0 \implies \left(\frac{\partial z}{\partial y}\right)_x = -\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z$; $\therefore \left(\frac{\partial z}{\partial x}\right)_y = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial x}{\partial y}\right)_z}$

6. Under what conditions gases have compression factor, (set A) $Z = \frac{pV_m}{RT} > 1$ (set B) , $Z = \frac{pV_m}{RT} < 1$ with the symbols having usual meaning? Give a brief molecular level explanation. What sign will the Joule Thomson coefficient have under these conditions? $1+1$

Ans. set A - $\frac{pV_m}{RT} > 1 \implies$ the gas has volume larger than when the molecules have no interactions, This means that the repulsions must be dominant. Under these circumstances, the molecules will run away from each other with higher speed and hence the temperature will rise as the pressure is decreased, i.e., Joule Thomson coefficient $\mu = \left(\frac{\partial T}{\partial p}\right)_H < 0$.

set B - $\frac{pV_m}{RT} < 1 \implies$ the gas has volume smaller than when the molecules have no interactions, This means that the attractions must be dominant. Under these circumstances, the molecules will slow down as the pressure is decreased and hence the temperature will decrease, i.e., J T coefficient $\mu = \left(\frac{\partial T}{\partial p}\right)_H > 0$.

7. $C_{p, m}(H_2O,g)$= 33.58 J K^{-1}mol^{-1}; $C_{p, m}(H_2,g)$= 28.84 JK^{-1} mol^{-1}; $C_{p, m}(O_2,g)$= 29.37JK^{-1} mol^{-1}
set A : Given $\Delta_f H^{\ominus}(H_2O(g);298\ K)$= -241.82 kJ mol^{-1}; Estimate $\Delta_f H^{\ominus}$ at 100°C. set B : Given $\Delta_f H^{\ominus}(H_2O(g);100°C)$= -242.6 kJ mol^{-1}
Ans. $\Delta_r C_p^{\ominus} = C_{p, m}(H_2O,g) - \{C_{p, m}(H_2,g) + \frac{1}{2}C_{p, m}(O_2,g)\}$= -9.94JK^{-1} mol^{-1}
set A : $\therefore \Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + (T_2 - T_1)\Delta_r C_p^{\ominus}$
$= -241.82 - 75 \times 9.94 \times 10^{-3} = -242.6$kJ mol^{-1}
set B : $\therefore \Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + (T_2 - T_1)\Delta_r C_p^{\ominus}$
$= -242.6 + 75 \times 9.94 \times 10^{-3} = -241.82$kJ mol^{-1}

8. What is the maximum possible efficiency of an engine operating between two thermal reservoirs, one at $-100°$ C (set A)$/ -200°$ C (set B), and the other at $0°$ C? 1
Ans. set A: $\eta = \frac{T_h - T_c}{T_h} = \frac{273 - 173}{273} = \frac{100}{273} = 0.37$
set B : Ans.$\eta = \frac{T_h - T_c}{T_h} = \frac{273 - 73}{273} = \frac{200}{273} = 0.733$