Answer all the questions on this paper. Continue overleaf if necessary. Show all work to get full credit. Remember, if you can’t do the problem write down as much as you can that is of relevance to solving the problem.

1. Which one of the following units is not equivalent to a unit of energy? (2 points)
   (a) kg m^2/s^2  
   (b) Pa·m^2  
   (c) L atm  
   (d) m³ · bar

2. The plot to the right shows pressure-volume relationships for an ideal gas. Which one of the following statements is true? (2 points)
   (a) going from state A to C reversibly requires less work than if it is done irreversibly  
   (b) work is done during the process B → C (No change in ΔV=0)  
   (c) the path A → C represents a compression  
   (d) T₂ must be lower than T₁  
   (e) the pathway B → C represents an isothermal process

3. Using the plot from question (2), which of the following processes represents the maximum amount of work done by the gas? (2 points)
   (a) A → D  
   (b) C → D → A  
   (c) A → C  
   (d) A → D → C  

4. The shaded region in the PV plot shown to the right for the process A → B → C → D → A corresponds to the (2 points)
   (a) net work done by the system  
   (b) net work done on the system  
   (c) net heat released by the system  
   (d) net heat absorbed by the system  
   (e) total change in internal energy for the process

5. For any cyclic process (that is a process that starts and ends up in exactly the same state) the following parameters will be zero. (3 points)
   (a) q, w, ΔU, ΔH, ΔS  
   (b) q, w, ΔS  
   (c) ΔU only

6. 1.00 mol of an ideal gas at a pressure of 1.00 atm occupies 10.00 L. If the temperature is kept constant but the pressure increased to 2.50 atm, the volume occupied will be (3 points)
   (a) 20.00 L  
   (b) 7.20 L  
   (c) 10.00 L  
   (d) 4.80 L
7. An ideal gas expands isothermally and reversibly from a state \( P_1, V_1 \) to the state \( P_2, V_2 \). Which one of the following statements is not true? Give a brief explanation why you chose your answer. (3 points)
(a) \( \Delta U \) for this process is zero
(b) the temperature of the system must be the same before and after the expansion
(c) the value of the heat \( q \) must be positive
(d) the entropy of the gas after the expansion will be the same as before the expansion
(e) the work done \( (w) \) during this process will be negative

\[
\Delta S \text{ will be positive for this process (a gas expansion).}
\]

Also for this process \( \Delta S = \frac{dq}{T} \) which will be non-zero

8. The heat capacity \( C_{p,m} \) of helium is about 12.5 J mol\(^{-1}\) K\(^{-1}\). If the temperature of 150 mole of He is increased by 5.00 K at constant volume, which one of the following statements is correct? (3 points)
(a) \( q = 0, \Delta U = 93.8 \) J, \( w = 93.8 \) J
(b) \( q = 0, \Delta U = 0, w = 0 \)
(c) \( q = 93.8 \) J, \( \Delta U = 0, w = 93.8 \) J
(d) \( q = 93.8 \) J, \( \Delta U = 93.8 \) J, \( w = 0 \)
(e) \( q, w \) and \( \Delta U \) cannot be determined from the information given

9. For the reaction \( A + 2B \rightarrow 2C \), if we begin with 1 mol of A, 2 mol of B and 0.5 mol of C, the extent of reaction at the point where we have a total of 1 mol of C will be (3 points)
(a) 0
(b) 0.125
(c) 0.25
(d) 0.5
(e) 1

10. Which of the following parameters is likely to increase the mean free path of a gas molecule? Circle all that apply (there may be more than one). (2 points)
(a) an increase in temperature
(b) an increase in the volume of the gas molecula particles
(c) an increase in the volume of the gas container
(d) a decrease in pressure of the enclosed gas
(e) a decrease in the number of moles of gas

11. Which one of the following statements is false for real gases? (2 points)
(a) the compression factor of all real gases approaches 1 as the pressure approaches zero
(b) \( C_{p,m} = C_{v,m} + R \) — only approximate for ideal gas.
(c) attractive and repulsive forces cancel at the point at which the second virial coefficient equals zero
(d) the change in internal energy may be zero for a constant temperature process
(e) at the Boyle temperature real gases will behave approximately ideally

12. Given the following average bond enthalpies (all in kJ mol\(^{-1}\)) [\( N≡N \) = 297, \( N≡N \) = 950, \( H≡H \) = 436, \( N≡H \) = 460], the estimated \( \Delta H_{rx} \) for the process \( N_2(g) + 2H_2(g) \rightarrow N_2H_4(g) \) is (3 points)
(a) -629 kJ mol\(^{-1}\)
(b) -605 kJ mol\(^{-1}\)
(c) -315 kJ mol\(^{-1}\)
(d) +950 kJ mol\(^{-1}\)
(e) +1822 kJ mol\(^{-1}\)
13. The difference between $C_{p,m}$ and $C_{v,m}$ for an ideal gas may be principally explained by (2 points)
   (a) assumptions made in the kinetic molecular theory which neglect volumes of the gas particles
   (b) the additional PP work done by the gas expansion at constant pressure
   (c) the neglect of intermolecular interactions in an ideal gas
   (d) the differences in mean free path when the pressure is restricted to remain constant
   (e) additional ways of storing energy in molecules at constant pressure

14. The Carnot cycle is shown to the right. Which one of the following statements is false? (2 points)
   (a) the heat ($q$) for the isothermal steps 1 and 3 is zero
   (b) $\Delta U$ for step 1 is equal and opposite in sign to $\Delta U$ for step 3
   (c) The total change in internal energy for the cyclic process is zero
   (d) heat is absorbed by the system in step 1
   (e) the net work done by the system cannot exceed the heat absorbed

15. The units of $C_{v,m}$ will be (1 point)
   (a) J
   (b) K
   (c) J K$^{-1}$
   (d) J mol$^{-1}$
   (e) J mol K$^{-1}$

Section II: Longer answer questions (40 points)
16. Why do real gases begin to behave ideally as their pressure approaches zero? Give an explanation, making sure you specifically address the 3 main postulates of kinetic molecular theory. (6 points)

At low $P \Rightarrow$ fewer collisions $\Rightarrow$ molecules tend to be far apart

Ideal gas behavior comes from a lack of intermolecular interaction
(KMT #1) $\Rightarrow$ if molecules are far apart this is a good approx.

KMT #2 assumes particlelike no volume (so, again if the molecules are spaced far apart, the assumption of the particles occupying no volume is a good one).

KMT #3 states that the molecules will be in contact when any collisions are elastic $\Rightarrow$ if the molecules are far apart then, as stated above, collisions will be less regular and the opportunity for them to interact (via internal interactions) is much reduced.
17. Set up the appropriate equation that would enable you to calculate the work done during the isothermal expansion of 1.00 mol of ethane at a temperature $T$ from an initial volume of $V_{m1}$ to a final volume of $V_{m2}$. Hint: use the form of virial equation given on your equation sheet to describe the pressure during this expansion. The second and third virial coefficients for ethane at the temperature $T$ are represented simply by $B$ and $C$. (8 points)

Work, $W = -\int P \, dV$

Can write virial equation in terms of $P$

$$P = \frac{RT}{V_m} + \frac{BRT}{V_m^2} + \frac{CRT}{V_m^3} + ...$$

Plug this expression for $P$ into our work expression $W = -\int P \, dV$

$$\Rightarrow W = -RT \left[ \int \frac{1}{V_m} \, dV_m + \int \frac{B}{V_m^2} \, dV_m + \int \frac{C}{V_m^3} \, dV_m \right]$$

$$= -RT \left[ \ln \left( \frac{V_{m2}}{V_{m1}} \right) + B \left( \frac{1}{V_{m1}} - \frac{1}{V_{m2}} \right) + \frac{C}{2} \left( \frac{1}{V_{m1}^2} - \frac{1}{V_{m2}^2} \right) \right]$$

$$W = -RT \left[ \ln \left( \frac{V_{m2}}{V_{m1}} \right) + B \left( \frac{1}{V_{m1}} - \frac{1}{V_{m2}} \right) + \frac{C}{2} \left( \frac{1}{V_{m1}^2} - \frac{1}{V_{m2}^2} \right) \right]$$
18. 1.00 mol of an ideal gas (at an initial pressure of 1.00 atm and temperature of 300.00 K) undergoes a reversible heating process at a constant volume, until the final temperature is 500.00 K. The temperature dependence of \( C_v \) has been approximated in this temperature range by a simple power series expression of the form

\[
\begin{align*}
C_v \approx (3.5 \text{ mol}^{-1} \text{ K}^{-1}) &= 29.30 + (6.14 \times 10^{-3})T - (1.59 \times 10^{-5})T^2 \\
&= nR_N C_v, n 
\end{align*}
\]

(a) Calculate the final pressure (\( P_f \)), the heat (\( q \)), the work (\( w \)), the enthalpy change (\( \Delta H \)) and the change in internal energy (\( \Delta U \)) for this process. (4 points)

(b) Set up (but do not solve) the appropriate equation to calculate the entropy change (\( \Delta S \)) for this process. (4 points)

\[
\begin{align*}
\rho_i &= 1.00 \text{ atm} & \rho_f &= ? \\
T_i &= 300.00 \text{ K} & T_f &= 500.00 \text{ K}
\end{align*}
\]

\[
\begin{align*}
\rho_i &= \frac{P_i}{RT_i} & \rho_f &= \frac{P_f}{RT_f} \\
\frac{\rho_f}{\rho_i} &= \frac{P_f}{P_i} \Rightarrow \frac{P_f}{760.00} &= \frac{P_i}{300.00} \\
\Rightarrow P_f &= \frac{1.67 \text{ atm}}{760.00}
\end{align*}
\]

\[
\begin{align*}
\Delta H &= \int_{T_i}^{T_f} nC_v \, dT = n \int_{T_i}^{T_f} \left( 29.30 + \frac{6.14 \times 10^{-3}}{T} - \frac{1.59 \times 10^{-5}}{T^2} \right) \, dT
\end{align*}
\]

\[
\begin{align*}
\Delta H &= 1.00 \text{ mol} \left[ 29.30 \left( \frac{500.00 - 300.00}{300.00} \right) + \frac{6.14 \times 10^{-3}}{300.00} \left( \frac{-50.00 - 300.00}{300.00} \right) \right] \\
\Delta H &= 1.00 \left( 5832 \right)
\end{align*}
\]

\[
\Delta H = 5832 \text{ J} = \frac{5832 \times 10^3 \text{ J}}{\Delta H}
\]

\[
\begin{align*}
\Delta U &= q = 4.169 \text{ J} \\
\Delta S &= \frac{\Delta U}{T} = \frac{4.169 \text{ J}}{500.00 \text{ K}} \\
\Delta S &= 4.169 \times 10^{-3} \text{ J/K}
\end{align*}
\]
19. 1.00 mol of an ideal gas at a constant pressure of 1 bar is compressed adiabatically and reversibly from an initial temperature of 25.00°C to a volume of 0.1000 m³ to a volume of 0.0100 m³. Cp,m = 12.5 J mol⁻¹ K⁻¹. Calculate T₁, V₁, the final temperature, T₂, and ΔH. Cp,m may be assumed constant. (8 points)

\[
C_p,m = 12.5 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{and} \quad Cp,m = Cv,m + R
\]

\[
\text{at } T_0 = 298.15 \text{ K} \quad \text{and} \quad V_0 = 0.1000 \text{ m}^3
\]

\[
\text{and } \frac{V_0}{V_1} = \frac{T_1}{T_0} = \frac{V_1}{V_0} \Rightarrow T_1 = \frac{(V_0/V_1)T_0}{(V_1/V_0)}
\]

\[
\Delta U = nC_p,m\Delta T = n(1.00 \text{ mol})(12.5 \text{ J mol}^{-1} \text{ K}^{-1})(342.8 \text{ K} - 298.15 \text{ K})
\]

\[
\Delta H = \Delta U + nRT = \frac{(1000 \text{ mol})(298.15 \text{ K})}{12.5 \text{ J mol}^{-1} \text{ K}^{-1}}
\]

\[
\Delta H = 22134.77 \text{ J}
\]

20. Answer EITHER part (a) OR part (b) of this question (if you answer both, I'll only grade part (a) unless you cross out the question you don't want me to grade):

(a) Prove that evaluation of the integral \( w = -\int PdV \) gives the result \( w = -nRT \ln(V_f/V_i) \) for an ideal gas expansion at constant temperature (4 points)

\[
w = -nRT \int \ln\left(\frac{V_f}{V_i}\right) dV = -nRT \ln\left(\frac{V_f}{V_i}\right)
\]

(b) Starting from the relationship \( H = U + PV \), prove that \( C_v,m = C_p,m - R \) for an ideal gas. (4 points)

\[
\text{(a) Since } PV = nRT \text{ we can rewrite } w = \int U dV = \int V dP \Rightarrow -nRT \ln\left(\frac{V_f}{V_i}\right)
\]

\[
\text{(b) } H = U + PV \Rightarrow \Delta H = \Delta U + \Delta (PV)
\]

\[
\text{Taking partials, we get }\]

\[
\frac{\partial M}{\partial T} = \frac{\partial U}{\partial T} + nR \Rightarrow \Delta (PV) = \Delta U + nR
\]

\[
\text{If } n = 1 \text{ at } V_i \text{ then we get } \\
\text{definition of } C_v,m \Rightarrow \text{definition of } C_v,m = C_p,m - R
\]
Section III: True/False questions (26 points) For each of the following questions state whether the statement is TRUE or FALSE. In each case, explain your choice of answer and show the relevant logic behind your answer.

21. For a fixed amount of an ideal gas, the product PV will always remain constant during any process. (4 points)

F] PV = nRT but T is still a variable & can vary so if we have a process where T changes, product PV cannot be constant. [If T remains constant, PV is a cont.]

22. For a reversible, adiabatic expansion of a gas, the change in internal energy (ΔU) will be identical to the work (w) done. (4 points)

□ Since q = 0 (adiabatic) & ΔU = q + w
ΔU = w

23. Chlorine gas (Cl₂) will effuse at twice the rate that fluorine (F₂) will since Cl₂ is about twice as heavy as F₂. Mass (Cl) = 35.453 g mol⁻¹, mass (F) = 18.998 g mol⁻¹. (4 points)

□ From equation sheet:
\[
\frac{\text{rate Cl}_2}{\text{rate F}_2} = \sqrt{\frac{M_{\text{F}}}{M_{\text{Cl}}}} = \sqrt{\frac{35.453}{18.998}} = 0.7
\]

24. A change from state 1 to state 2 will produce a greater change in entropy if the process is carried out reversibly in going from state 1 to state 2, than if the same process is done irreversibly. (4 points)

□ S is a state function so as long as you go from the same state, ΔS will be identical, regardless of the nature of the process.

Don’t confuse this with the example where we showed the entropy change for an irreversible isolated process will differ from a reversible, non-isolated process (heat will play a key role here).
25. Given the critical constant information below, 1 mol of \( \text{O}_2 \) at 231.45 K and 100.8 bar and 1 mol of \( \text{Cl}_2 \) at 625.5 K and 154.2 bar can be said to be in corresponding states. (4 points)

(Critical constant data: \( P_c(\text{O}_2) = 50.4 \) bar, \( T_c(\text{O}_2) = 154.3 \) K; \( P_c(\text{Cl}_2) = 77.1 \) bar, \( T_c(\text{Cl}_2) = 417 \) K.)

\[
\frac{P_c(\text{O}_2)}{T_c(\text{O}_2)} = \frac{50.4 \text{ bar}}{154.3 \text{ K}} = 0.321 \text{ bar K}^{-1} \\
\frac{P_c(\text{Cl}_2)}{T_c(\text{Cl}_2)} = \frac{77.1 \text{ bar}}{417 \text{ K}} = 0.185 \text{ bar K}^{-1}
\]

26. The expression to account for the temperature dependence of the heat capacity at constant volume for a gas is given by \( C_v = 25.62 + 0.0837T \). The expression for \( C_v \) is therefore given by \( C_v = 33.935 + 0.0837T \). (3 points)

27. The value of \( \Delta H_f(\text{H}_2\text{O}(l)) \) will be half of the value for the reaction \( 2\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \). (2 points)

\[
\Delta H_f(\text{H}_2\text{O}(l)) \text{ corresponds to } \Delta H_f \text{ for the reaction:} \\
\Delta H_f: \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \\text{so } \Delta H_f = -2 \Delta H_f \text{ for } 2\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l)
\]

BONUS question (3 points)

28. In your own words, describe what you understand as the physical interpretation of entropy (don’t just attempt to regurgitate your lecture notes for this question, I’m interested to see what ideas you have so be creative).