1. Two moles of $N_2$ gas at 25$^\circ$C and 1 atm pressure are expanded reversibly and isothermally to a pressure of 0.5 atm.
   a) Calculate the work done (including the sign).
   b) Calculate the heat change and the internal energy change involved in the process.
   c) Calculate the work done in expansion against a constant external pressure of 0.5 atm (final state is 0.5 atm as in a). What is your inference of the result in comparison with the result of a)?

Ans:  a) Isothermal (reversible) expansion:
Class formula: \[ w = -nRT \ln \frac{V_2}{V_1}. \]
\[ = -2 \text{ mol} \times 8.3145 \text{ JK}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \times 2.303 \log \frac{P_1}{P_2} \text{ as } PV = \text{Constant at constant temperature.} \]
\[ = -2 \times 8.3145 \times 298.15 \times 2.303 \log 2 \text{ J} \]
\[ = -3437.2 \text{ J} \]

b) Heat Change and the internal energy change.
Internal energy change is zero for an ideal gas undergoing process at constant temperature $\Delta E = 0$.

\[ \therefore \text{Heat change} = - \text{ work done by the gas.} \]
\[ = 3437.2 \text{ J.} \]
(This much heat is absorbed by the system to do the work)

c) Work done in expansion against a constant pressure of 0.5 atm.
\[ = -P\Delta V. \]
To Calculate $\Delta V$, calculate $V_1$ and $V_2$.

$V_1 = \frac{nRT}{P_1} = 2 \text{ mol} \times 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K/1 atm}$.

$= 48.09 \text{ L}$

$V_2 = 2V_1$ as $P_2 = \frac{1}{2} P_1$.

∴ $w = -P \Delta V = 0.5 \text{ atm} \times 48.90 \text{ L}$

$= 24.45 \text{ L atm}$

$= 2479.1 \text{ J}$.

Observation: Expansion against constant pressure is NOT a reversible process. Therefore, the work done by the gas is not the maximum possible work done, but less than the maximum. It is a path-dependent quantity.

2. An ideal gas expands reversibly and isothermally from 20 atm to 1 atm at 300 K. What are the values for
a) work done by the gas per mole?
b) heat absorbed by the gas per mole?
c) $\Delta E$ per mole and
d) $\Delta H$ per mole?

Ans: a) Reversible isothermal expansion from 20 atm to 1 atm at 300K.

a) $w = -nRT \ln \frac{P_1}{P_2}$.
b) $Q = -w$
c) $\Delta E = 0$
d) $\Delta H = q$ as the work done is reversible, under isothermal conditions.

Ans: $w = -7473.8 \text{ j}$.

3. The heat capacity of a gas is represented by the formula

$C_p = \alpha + \beta T + \frac{\gamma}{T}$

For $\text{O}_2$, $\alpha = 29.96 \text{ J K}^{-1}$, $\beta = 0.00418 \text{ J K}^{-2}$ and $\gamma = -1.67 \times 10^{-5} \text{ J K}$. Calculate the amount of heat required to heat the gas from 300 K to 1000K.

Ans: $\Delta H = \int_{T_1}^{T_2} C_p(T) \, dT$

$= \int_{T_1}^{T_2} (\alpha + \beta T + \frac{\gamma}{T}) \, dT$

$= \alpha (T_2 - T_1) + \beta/2 (T_2^2 - T_1^2) - \gamma (1/T_2 - 1/T_1)$
For O₂  \( \alpha = 29.96 \text{ JK}^{-1} \).
\( \beta = 0.00418 \text{ JK}^{-2} \).
\( \gamma = -1.67 \times 10^5 \text{ JK} \)
\( T_1 = 300 \text{ K} \quad T_2 = 1000 \text{ K} \).

Substitute:  Answer  \( \Delta H = 23.26 \text{ kJ} \)
\( \alpha(T_2 - T_1) = 20.97 \text{ kJ} \)
\( \beta/2 (T_2^2 - T_1^2) = 1.90 \text{ kJ} \).
\( -\gamma(1/T_2 - 1/T_1) = 0.39 \text{ kJ} \).

4. An ideal monatomic gas is expanded by a reversible adiabatic process from an initial pressure of 1 atm to a final pressure of 0.3 atm. The initial temperature of the gas is 300 K. Calculate the work done, internal energy change and the final temperature of the gas.

Ans: Reversible adiabatic expansion.
\( q = 0, \Delta E = q + w = w \)
For adiabatic processes,
\( PV^\gamma = \text{constant} \)
\( \gamma = C_p/C_v = 5/3 \) for an ideal monatomic gas.
Also \( PV = nRT \) for all ideal gases.
\( \therefore (V_1/V_2) = P_2/P_1 \) and \( (V_1/V_2) = (T_1/T_2) (P_2/P_1) \)
or \( (T_1/T_2) = (P_2/P_1)^{1-\gamma/\gamma} \)
substitute the values \( T_1, P_1 \) and \( P_2 \).
\( T_2 \) is calculated as 185.3 K.
Work done = \( C_v \Delta T = -1.43 \text{ kJ} \) (\( T_2 < T_1 \), work done is done by the gas, hence negative).
Internal energy change \( \Delta E = -1.43 \text{ kJ} \).

5. An ideal monatomic gas at 1 atm pressure with a heat capacity at constant volume \( C_v = 3R/2 \) is expanded adiabatically against a constant external pressure of 0.5 atm. Calculate \( q, w, \Delta E \) and \( \Delta H \) (per mole)

Ans: For \( \Delta T \) use the same formula as above
\( T_1 = 300 \text{ k}, \quad T_2 = 227.3 \text{ k} \).
\( \Delta E = -P \Delta V = -642.5 \text{ J} \)
\( \Delta H = C_p \Delta T = 5/2R \times 72.7 \text{ J} \).
6. Determine whether the following are exact differentials.

a) \( xy^2 dx - x^2 y dy \)

b) \( \frac{dx}{y} - \frac{x}{y^2} dy \)

b). Verify that \( dq = dE + PdV = C_v dT + RT d\ln V \) is not an exact differential but that

\[
\frac{dq}{T} = C_v \, d\ln T + R \, d\ln V
\]

is an exact differential.

Ans: a). Let \( xy^2 dx - x^2 y dy = df \)

Then \( \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \) must be satisfied.

It is NOT. Therefore \( xy^2 dx - x^2 y \) is NOT an exact differential.

b) \( dq = C_v \, dT + R/T \, d\ln V \).

\[ \frac{\partial^2 q}{\partial V \partial T} = \frac{\partial}{\partial V} (C_v) = \] for an ideal gas.

\[ \frac{\partial^2 q}{\partial T \partial V} = \left[ \frac{\partial}{\partial T} (RT/V) \right]_V = R/V \neq \frac{\partial^2 q}{\partial V \partial T} . \]

Hence dq is NOT an exact differential.

\[ dq/T = C_v/T \, dT + R/V \, dV = df \]

\[ \frac{\partial^2 f}{\partial V \partial T} = \left( \frac{\partial}{\partial T} [R/V] \right)_V = 0 . \]

\[ \frac{\partial^2 f}{\partial T \partial V} = \left( \frac{\partial}{\partial V} [C_v/T] \right)_T = 0 = \frac{\partial^2 f}{\partial T \partial V} . \]

Hence \( dq/T \) is an exact differential.

7. Derive the relation

\[ C_v = -\left( \frac{\partial E}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_E \]

From the expression for the total differential of \( E (T, V) \).

Ans: \( E, V, T \) follow the cyclic relation

\[ (\partial E/\partial T)_V (\partial T/\partial V)_E (\partial V/\partial E)_T = -1 . \]

Or \( (\partial E/\partial T)_V = -1/(\partial T/\partial V)_E (\partial V/\partial E)_T = (\partial V/\partial T)_E (\partial E/\partial V)_T \)

More elaborately:

\( E = E (V,T) \)

\[ dE = (\partial E/\partial T)_V \, dT + (\partial E/\partial V)_T \, dV . \]

\[ = C_v \, dT + (\partial E/\partial V)_T \, dV . \]
Express $V$ as a function of $E$ and $T$ and substitute for $dV$ in the above expression.

$$dV = \left( \frac{\partial V}{\partial E} \right)_T dE + \left( \frac{\partial V}{\partial T} \right)_E dT.$$  

$$\Rightarrow dE = \left( \frac{\partial E}{\partial V} \right)_T \left\{ \left( \frac{\partial V}{\partial E} \right)_T dE + \left( \frac{\partial V}{\partial T} \right)_E dT \right\} + C_V dT.$$  

The equality implies the coefficients of $dE$ and $dV$ are zero, as two of the three variables $E, v, T$ are independent.

Hence: \( \left( \frac{\partial E}{\partial V} \right)_T \left( \frac{\partial V}{\partial E} \right)_T = 1, \)

\[
C_V = - \left( \frac{\partial E}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_E.
\]

8. Show that

\[
C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P
\]

Using appropriate relations between partial derivatives, show also that

\[
C_p - C_v = T \left( \frac{\partial V}{\partial T} \right)_P^2
\]

For water at 4 °C, given that the density of water is maximum, what does the above result indicate. Also evaluate \((C_p - C_v)\) for an ideal gas.

Ans: $dE = \left( \frac{\partial E}{\partial T} \right)_V dT + \left( \frac{\partial E}{\partial V} \right)_T dV = C_v dT + \pi_T dV.$

$\pi_T \rightarrow$ internal pressure.

\[
\Rightarrow \left( \frac{\partial E}{\partial T} \right)_P = \pi_T \left( \frac{\partial V}{\partial T} \right)_P + C_V.
\]

\[
\Rightarrow \left( \frac{\partial E}{\partial T} \right)_P - C_V = \pi_T \left( \frac{\partial V}{\partial T} \right)_P \] Also, $\pi_T = T(\partial P/\partial T)_V - P$

\[
\Rightarrow C_p - C_v = (\partial H/\partial T)_P - (\partial E/\partial T)_V; H = E + PV.
\]

\[
\Rightarrow P(\partial V/\partial T)_P + \pi_T (\partial V/\partial T)_P
\]

\[
= (\pi_T + P) \left( \frac{\partial V}{\partial T} \right)_P - (\partial E/\partial T)_V.
\]

Also $P_1 T_1 V$

Form cyclic partial derivatives.

\[
(\partial P/\partial T)_V = -1/(\partial T/\partial V)_P (\partial V/\partial P)_T = - (\partial V/\partial T)_P/(\partial V/\partial P)_T
\]

\[
\Rightarrow C_p - C_v = -T(\partial V/\partial T) \left[ (\partial V/\partial T)_P/(\partial V/\partial P)_T \right].
\]
For an ideal gas \( P V = nRT \)
\[ (\partial V/\partial T)_P = nR/P. \]
\[ (\partial V/\partial P)_T = -nRT/P^2 \]
\[ \therefore C_P - C_V = nR. \]

9. For \( n \) moles of a Van der Waals gas, whose equation of state is given by
\[ \left[ P + \frac{n^2a}{V^2} \right] (V - nb) = nRT \]
calculate the expression for the entropy change for the system from an initial state \( T_1, V_1 \) to the final state \( T_2, V_2 \).

Ans: Use: \( du = tDs - PdV \) \[ \text{i.e. } u \equiv u(s,v) \]
\[ = C_V dT + [T(\partial P/\partial T)_V - P] dV \]
\[ u \equiv u(T,V) \]
Also, from \( ds = (\partial S/\partial T)_V dT + (\partial S/\partial V)_T dV \)
and the first line,
\[ (\partial S/\partial T)_V = C_V/T; (\partial S/\partial V)_T = (\partial P/\partial T)_V - P/T + P/T = (\partial P/\partial T)_V. \]

Thus the equation for entropy change you need to use is \( dS = C_v dT/T + (\partial P/\partial T)_V dV. \)

For a van der Waals gas.
\[ (P + n^2a/V^2)(V - nb) = nRT, \]
\[ P = nRT/V - nb - n^2a/V^2 \]
\[ (\partial P/\partial T)_V = nR/V - nb \]
\[ \therefore \Delta S = \int_{T_1V_1}^{T_2V_2} ds \]
\[ = \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2} nR/V - nb dV \]
\[ = C_V \ln T_2/T_1 - nR \ln V_2 - nb/V_1 - nb \text{ if } C_v \text{ is independent of temperature.} \]

10. Without doing explicit calculations, predict the signs of \( \Delta P, \Delta V, \Delta T, \Delta H \text{ and } \Delta S \) for one mole of an ideal gas taken through each of the following four steps of a Carnot cycle. Assume \( C_P \) and \( C_V \) Constants.

Step (a): Isothermal reversible expansion \( P_1 V_1 T_1 \to P_2 V_2 T_1 \)
Step (b): Adiabatic reversible expansion \( P_2 V_2 T_1 \to P_3 V_3 T_2 \)
Step (c): Isothermal reversible compression \( P_3 V_3 T_2 \to P_4 V_4 T_2 \)
Step (d): Adiabatic reversible compression \( P_4 V_4 T_2 \to P_1 V_1 T_1 \)

Text book material.
11. On a single entropy versus temperature diagram, draw the curves for the following reversible processes for an ideal gas (the initial state is the same for all processes).
(a) isothermal expansion,
(b) adiabatic expansion and
(c) isochoric process in which heat is added.

Ans:

\[ \Delta S = C_v \ln \frac{T_2}{T_1} \]

12. Sketch diagrams for the reversible Carnot cycle of an ideal gas with constant \( C \) and \( C' \): \( P \) vs. \( S \); \( E \) vs. \( P \); \( T \) vs. \( P \); \( H \) vs. \( P \); \( V \) vs. \( T \); \( S \) vs. \( V \); \( V \) vs. \( E \); \( V \) vs. \( H \); \( E \) vs. \( T \); \( H \) vs. \( T \); \( T \) vs. \( S \), \( E \) vs. \( H \) and \( H \) vs. \( S \).

Ans: discuss three cases. The others are similar.
I $\rightarrow$ Isothermal expansion.
II $\rightarrow$ adiabatic exp.
III $\rightarrow$ Isothermal compression.
IV $\rightarrow$ adiabatic compression.

b) Others can be constructed similarly.

c) Others can be constructed similarly.

13. One mole of water at $0^0C$ is brought into contact with a large heat reservoir at $100^0C$. When the water reaches $100^0C$ calculate the entropy change of water, the reservoir and the universe (which consists of water and the reservoir). If the water was brought into contact with a heat reservoir at $75^0C$ first and then water at $75^0C$ is brought into contact with the reservoir at $100^0C$ so that the final state of the water is $100^0C$, calculate the net entropy change of water, the reservoir and the universe. Assume that the heat capacity of water to be constant at 1.0 cal g$^{-1}$K$^{-1}$.

Ans: For a body at temp $T_1$ in contact with a reservoir at $T_2$ with $T_1 < T_2$.

$\Delta S$ for the body
(for a suitable reversible path by which $T_1 \rightarrow T_2$) = $nC_v \ln T_2/T_1$.

$\Delta S$ for the reservoir: heat is supplied at $T_2$ to heat a body from $T_1$ to $T_2$ with a constant heat capacity $C_v$. 
\[ \Delta s = -nC_V \frac{(T_2 - T_1)}{T_2}. \]
\[
\Delta S_{\text{universe}} = nC_V \ln \frac{T_2}{T_1} - nC_V \frac{(T_2 - T_1)}{T_2}.
\]
\[
> 0 \quad \text{if } T_2 > T_1.
\]
\[
= 0 \quad \text{if } T_2 = T_1. \text{ (obvious)}.
\]
Apply this for each of the cases mentioned in the problem.
\[
T_1 = 273 \text{ k}, \quad T_2 = 373 \text{ k}. \quad C_V = 18.0 \text{ cal mol}^{-1} \text{ k}^{-1}
\]
\[ \Delta S = 18[2.303 \log 373/273 - 100/373] = 0.7938 \text{ cal}. \]
Please understand the underlying assumption. Reservoir is so huge that the process of heat transfer is assumed to be reversible! Otherwise \( \Delta S \neq \text{heat}/T. \)

Process 2:

\( \Delta S_{\text{universe}} \) is calculated for two processes.
\[
T_1 = 273 \text{ k}. \quad T_2 = 348 \text{ k}
\]
And \( T_1 = 348 \text{ k}, \quad T_2 = 373 \text{ k}. \)
\[ \Delta S = 18 [2.303 \log 348/273 - 75/348] + [2.303 \log 373/348 - 25/373]
\]
\[ = 0.5346 \text{ cal}. \]
What does this tell you?
If you divide this further and further, (i.e. infinitely many such intermediate temperatures and attain equilibrium at each stage, what will be the value of \( \Delta S_{\text{universe}} \)? [zero, in the end!!].

14. A mass \( m \) of liquid at temp \( T_1 \) is mixed with an equal mass of the same liquid at a temperature \( T_2 \). If the system is isolated show that the entropy change of the universe is

\[ 2mC_p \ln \left[ \frac{(T_1 + T_2)/2}{\sqrt{T_1T_2}} \right] \]

Where \( C_p \) is the specific heat capacity of the liquid and is assumed to be constant over the temperature range.

Ans: Heat capacity of the liquid is \( mC_p \).
Let \( T_1 > T_2 \), \( T \) be an intermediate temp. (equilibrium).
Then:
\[
mC_p (T_1 - T) = mC_p (T - T_2).
\]
Heat lost by the hot liquid. \quad Heat gained by the hot liquid.
\[ T_1 - T = T - T_2 \quad \text{or} \quad T = T_1 + T_2. \] It is also trivially true.

Entropy change in the liquid.

\[ (\text{hot}) = m C_P \ln \left( \frac{T_1 + T_2}{2} / T_1 \right) \]

Entropy change in the cold liquid = \( m C_P \ln \left( \frac{T_1 + T_2}{2} / T_2 \right) \).

\[ \therefore \text{Total entropy change} = 2m C_P \ln \left[ \left( \frac{T_1 + T_2}{2} \right) / \sqrt{T_1 T_2} \right] \]

Always positive. So long as \( T_1 \) and \( T_2 \) are different.

15. Two moles of an ideal gas are expanded isothermally at 298 K from a volume \( V \) to a final volume of 2.5 \( V \). Find the value of \( \Delta S_{\text{gas}} \) and \( \Delta S_{\text{total}} \) for the following:
   a) Reversible expansion
   b) Irreversible expansion in which the heat absorbed is 400 J mol\(^{-1}\) less than the reversible expansion and
   c) Free expansion.

Ans: Reversible expansion.

\[ \Delta S_{\text{gas}} = nR \ln \left( \frac{V_2}{V_1} \right) = 2 \times 8.314 \ln 2.5 \]

\[ = 15.24 \text{ JK}^{-1}. \]

\[ \Delta S_{\text{surr}} = -15.24 \text{ JK}^{-1} \] as the heat transfer takes places reversibly from surroundings at the same temperature.

\[ \therefore \Delta S_{\text{tot}} = 0. \]

b) \( \Delta S_{\text{gas}} = 15.24 \text{ JK}^{-1} \). Remember the initial and final states of the gas are exactly the same as in the previous case, therefore \( \Delta S_{\text{gas}} = 15.24 \) only still.

\[ \Delta S_{\text{surr}} = -(nRT \ln \left( \frac{V_2}{V_1} - 400 \right)/T! \]

\[ = -13.90 \text{ JK}^{-1}. \]

\[ \therefore \Delta S_{\text{tot}} = 1.34 \text{ JK}^{-1} > 0. \] (irreversible path).

c) Free expansion: system does not draw any heat from the surroundings.

\[ \therefore \Delta S_{\text{surr}} = 0. \]

\[ \Delta S_{\text{tot}} = 15.24 \text{ JK}^{-1}. \]

16. The molar entropy of an ideal gas at 298 K is 146 J K\(^{-1}\) Mol\(^{-1}\). Find the value of entropy of the gas at 500 K when its pressure is kept constant.

Ans: Missing statement: (\( C_P \) of the gas is a constant and is 20.97 JK\(^{-1}\) mol\(^{-1}\).) use this to calculate.

\[ S_{500} = S_{298} + C_P \ln \left( \frac{T_2}{T_1} \right) \]
\[ = 146 + 20.97 \times 2.303 \times \log 500/298. \]
\[ = 156.85 \text{ JK}^{-1} \text{ mol}^{-1}. \]

17. How much does the entropy of an ideal gas increase when one mole is heated from 298 K to 1000 K at a constant pressure and then expanded to five times the volume at the higher temperature?

\[ C = 20.9 \text{ J} \text{ K}^{-1} \text{ mol}^{-1} \]

Ans: \( \Delta S = C P \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}. \)
\[ = 2.9 \times 2.303 \times \log 1000/298 + 8.314 \times 2.303 \times \log 5 \]
\[ = 25.3 + 13.4 = 38.7 \text{ JK}^{-1} \text{ mol}^{-1}. \]