## Formulas:

First law $\left.\left.\quad \Delta U=Q+W \quad ; \quad C_{V}=\frac{\partial U}{\partial T}\right)_{V} \quad ; \quad H=U+P V \quad ; \quad C_{P}=\frac{\partial H}{\partial T}\right)_{P}$
$k=1.381 \times 10^{-23} \mathrm{~J} / K, N_{A}=6.02 \times 10^{23}, R=8.31 \mathrm{~J} /\left(\mathrm{mol}^{\circ} \mathrm{K}\right)$
Ideal gas: $P V=N k T \quad U=N \frac{f}{2} k T \quad W=-P \Delta V, \quad W=-\int P d V ; C_{P}=C_{V}+N k$
adiabatic process: $P V^{\gamma}=$ const.,$\quad \gamma=(f+2) / f$
$\left.S=k \ln \Omega \quad ; \quad \frac{1}{T}=\frac{\partial S}{\partial U}\right)_{V} \quad ; \quad d S=\frac{Q}{T}=\frac{C_{V} d T}{T} \quad$ (constant volume)
Stirling's approximation: $n!=n^{n} e^{-n} \sqrt{2 \pi n}$
Ideal gas (monoatomic) : $\Omega_{\mathrm{N}}=C_{N} V^{N} U^{3 N / 2} / N$ !
Einstein solid: $\Omega(N, q)=\frac{(q+N-1)!}{q!(N-1)!} \quad \sim\left(\frac{e q}{N}\right)^{N}$ for $\mathrm{q} \gg \mathrm{N}$
Two-state system: $\Omega=\frac{N!}{N_{\uparrow}!N_{\downarrow}!}$
Paramagnetism: $\mathrm{M}=\mathrm{N} \mu \tanh (\mu \mathrm{B} / \mathrm{kT}), U=-M B, \quad M=\mu\left(N_{\uparrow}-N_{\downarrow}\right)$
$d U=T d S-P d V \quad ; \quad Q=T d S, W=-P d V$ (quasistatic)
$U(S, V) \quad ; \quad F(T, V)=U-T S \quad ; \quad H(S, P)=U+P V \quad ; \quad G(T, P)=U-T S+P V$
$\left.\left.\left.\left.\left.\left.C_{V}=T \frac{\partial S}{\partial T}\right)_{V} \quad ; \quad C_{P}=T \frac{\partial S}{\partial T}\right)_{P} \quad ; \quad \beta=\frac{1}{V} \frac{\partial V}{\partial T}\right)_{P} \quad ; \quad \kappa_{\mathrm{T}, \mathrm{S}}=-\frac{1}{V} \frac{\partial V}{\partial P}\right)_{T, S} ; \quad \mu=-T \frac{\partial S}{\partial N}\right)_{U, V}=\frac{\partial U}{\partial N}\right)_{S, V}$
$\mu=-k T \ln \left(\frac{V}{N}\left(\frac{2 \pi m \mathrm{kT}}{h^{2}}\right)\right) \quad$ Ideal gas (monoatomic)
Heat engines: $e=\frac{W}{Q_{h}} \leq 1-\frac{T_{c}}{T_{h}} ; \quad$ Refrigerators: $C O P=\frac{Q_{c}}{W} \leq \frac{T_{c}}{T_{h}-T_{c}}$
Maxwell relations: $\left.\left.\left.\left.\left.\left.\left.\left.\quad \frac{\partial T}{\partial V}\right)_{\mathrm{S}}=-\frac{\partial P}{\partial S}\right)_{\mathrm{V}} \quad ; \quad \frac{\partial T}{\partial P}\right)_{\mathrm{S}}=\frac{\partial V}{\partial S}\right)_{\mathrm{P}} \quad ; \quad \frac{\partial S}{\partial V}\right)_{\mathrm{T}}=\frac{\partial P}{\partial T}\right)_{\mathrm{V}} \quad ; \quad \frac{\partial S}{\partial P}\right)_{\mathrm{T}}=-\frac{\partial V}{\partial T}\right)_{\mathrm{P}}$
Van der Waals: $\left(P+a \frac{N^{2}}{V^{2}}\right)(V-N b)=N k T ;$ Virial: $P V=N K T\left(1+\frac{N}{V} B_{2}(T)+\frac{N^{2}}{V^{2}} B_{3}(T)+\ldots\right)$
Boltzmann distribution: $P\left(E_{i}\right)=C e^{-E_{i} / k T} \quad ; \quad C=1 / \sum_{i} e^{-E_{i} / k T} \equiv 1 / Z \quad ; \quad P(E)=C \Omega(E) e^{-E / k T}$

Justify all your answers to all (3) problems

## Problem 1

Consider a heat engine that uses a monoatomic ideal gas undergoing the cycle through points 1,2 and 3 shown in the diagram below:


The temperature at point 1 is $T_{1}=P_{1} V_{1} / \mathrm{Nk}$, with N the number of atoms, the energy is $\mathrm{U}_{1}=(3 / 2) \mathrm{NkT}_{1}$.
(a) Find $T_{2}$ and $T_{3}$ in terms of $T_{1}$.
(b) Find the work done by this engine in one cycle in terms of $\mathrm{T}_{1}$ ( and N ).
(c) Find the heat absorbed in the step 1-2 in terms of $\mathrm{T}_{1}$ (and N ).
(d) Find the heat absorbed in the step 2-3 in terms of $\mathrm{T}_{1}$ (and N ).
(e) Find the efficiency of this engine, defined as: $\mathrm{e}=($ work performed $) /$ (heat absorbed) per cycle.
(f) Find the highest and lowest temperatures in this cycle and the efficiency of a Carnot engine operating between those temperatures.

## Problem 2

A system of N particles with energy U and volume V has entropy given by

$$
S(U, V)=N k \ln (U / N)+N k \ln (V / N)
$$

(a) Find an expression for $\mathrm{U}(\mathrm{S}, \mathrm{V})$
(b) From the thermodynamic identity ( $\mathrm{dU}=\mathrm{TdS}-\mathrm{PdV}$ ) and the result in (a), derive expressions for $\mathrm{T}(\mathrm{S}, \mathrm{V})$ and $\mathrm{P}(\mathrm{S}, \mathrm{V})$.
(c) From the results in (b), find expressions for $\partial \mathrm{T} / \partial \mathrm{V})_{\mathrm{S}}$ and $\left.\partial \mathrm{P} / \partial \mathrm{S}\right)_{\mathrm{V}}$ both as functions of variables S and V , and from them verify one of the Maxwell relations.
(d) By eliminating $S$ from the expressions for $T(S, V)$ and $P(S, V)$ found in (b), find a relation between T, P and V .
(e) Find an expression for the enthalpy H , as function of S and V .
(f) Comparing the results in (e) and (a), find a relation between U, P and V.

## Problem 3

A Van der Waals gas has equation of state

$$
P=\frac{N k T}{V}-a \frac{N^{2}}{V^{2}}
$$

with $a$ a constant. Its energy as function of temperature and volume is given by

$$
U(T, V)=2 N k T-a \frac{N^{2}}{V}
$$

Find an expression that relates T and V in a process where the entropy S is constant, by:
(a) From the thermodynamic identity $d S=\frac{1}{T} d U+\frac{P}{T} d V$, find an expression for dS as function of T and V (and dT and dV ).
(b) Integrate the expression found in (a) along a line of constant $S$.
(c) For a process at constant $S$ where the initial temperature is $T_{i}$ and the final temperature is $4 \mathrm{~T}_{\mathrm{i}}$, what is the final volume $\mathrm{V}_{\mathrm{f}}$ if the initial volume is $\mathrm{V}_{\mathrm{i}}$ ?

## Justify all your answers to all problems

