```
> restart;
```

An outline for computing G as a functon of P and T from Holland & Powell's thermodynamic data base for minerals
(the paper describing this data base is at .../chapter5/holland_jmg_98.pdf, the data has been revised several times
since the paper was published, we are using a revision made in 2002).

This script is at: .../chapter5/problem_5_1_and_2_setup.mw

The thermodynamic data base is in an Excel table at: .../chapter5/thermo_data.xls

Alternatively the data can be read in Matlab with the script

.../chapter5/load_yurak.m

from the files:

.../chapter5/yurak.dat
.../chapter5/names_yurak.dat
.../chapter5/parms.txt (a list of the variables in yurak.dat).

Problem Outline:

The reference G, S, V (i..e., the molar G, S and V at Tr=298.15 K, Pr = 1 bar) are G0, S0, V0

The heat capacity equation is: Cp := Cp_0 + Cp_T * T + Cp_Tm2 / T^2 + Cp_Tmhalf /sqrt(T);

V at 1 bar and T is: V_T := V0*(1+int(alpha,T=Tr..Tf));

with: alpha := alpha_0 + alpha_Tmhalf / sqrt(T);

V at P and T is: V_PT := V_T * (1 - Kprime*P/(KT+Kprime*P))^(1/Kprime);

with: KT := Kt_0 + Kt_T*(T-Tr)

Given these functions you need to evlauate two integrals (the first integral is a double
integral, be very careful that you obtain S_Pr(T) [and not, e.g., S_Pr(Tf)] before evaluating
the outer integral.

Note: depending on the version of maple you have it may be necessary to assume that
the integration limits are positive, or greater than some group of variables, in general this
can be done with the assuming command, e.g.,

int(c*x^n, x = 0..a) assuming n::posint, a::positive, c>x;

integrates x^n under the assumption that n is a positive integer, a is positive and c > x.

intSdT = int(S_Pr dT, T = Tr..Tf) assuming Tr > 0, Tf > 0

this is a double integral, since you must first evaluate eq 5.21 to obtain S(Pr,T)

```
> s_Pr := S0 + int(...,T=Tr..Tf) assuming Tr>0, Tf>0;
Error, (in assuming) when calling 'int'. Received: 'wrong number (or
type) of arguments: for an operator integrand a range without a
variable of integration is expected, got T = Tr .. Tf'
```

the result will be formally a function of Tr and Tf, to make this back into a function of T use the "subs" command to replace Tf with T, i.e.,

```
> S_Pr := subs(Tf=T,s_Pr);
                              S_Pr := s_Pr                          (1.1)
```

the completed integral is then

```
> intsdT := int(...;
>
Warning, premature end of input, use <Shift> + <Enter> to avoid this
message.
```

which will again be in terms of Tr and Tf, so you must again use "subs" to susbtitute T for Tf, i.e.,

```
> intSdT := subs(Tf=T,intsdT);
                            intSdT := intsdT                        (1.2)
```

it is not necessary to change names (e.g. s_Pr and S_Pr) when using the subs command, but to make maple scripts less sensitive to the order in which you exceute commands it's a wise practise.

intVdP = int(V_PT, P = Pr..Pf) assuming Kprime > 0, KT > 0, Pr > 0, Pf > 0

in contrast to the entropy integral, this is a serial integration, we need one integration to get volume at T & Pr (V_T := V0 +int(alpha,T)) which is necessary for the Murnagan equation for the volume at any pressure and temperature (V_PT as given above in the problem outline), and then a second integration to evaluate V_dP, because the second integration is independent of the first. The Maple output is simpler if you evaluate the second integral first.

As in the SdT integration, you will have to use the subs command to replace the upper integration limits (Pf, Tf) with the original variables (P,T).

```
>
>
>
```

With these integrals we can now write G(P,T) as

```
> g := G0 - intSdT + intVdP;
                       g := G0 − intsdT + intVdP                    (1)
```

and this function can be used to evlaute derivatives, etc etc, as in V := (diff(g, P))

You can use the subs command to substitute numeric values into your function without losing the functions symbolic form, e.g., first we make a list of the molar values (here for forsterite, Mg2SiO4) as in:

```
> fo := {Pr = 1, G0 = -2052728, Tr = 298.15, S0 = 95.1, V0 = 4.366,
```

```
  Cp_0 = 233.3, Cp_T = 0.1494e-2, Cp_Tm2 = -603800, Cp_Tmhalf =
  -1869.7, alpha_0 = 0.613e-4, alpha_Tmhalf = -0.613e-3, Kt_0 =
  1305903, Kt_T = -187.5, Kprime = 4};
> Gfo := subs(fo, g);
```

$$fo := \{Cp\_0 = 233.3, Cp\_T = 0.001494, Cp\_Tm2 = -603800, G0 = -2052728, Kprime = 4, Kt\_0 = 1305903, Kt\_T = -187.5, Pr = 1, S0 = 95.1, Tr = 298.15, V0 = 4.366, alpha\_0 = 0.0000613, Cp\_Tmhalf = -1869.7, alpha\_Tmhalf = -0.000613\}$$

$$Gfo := -2052728 - intsdT + intVdP \tag{2}$$

Gfo is then your G function with the parameters for forsterite, and you can obtain Vfo simply by Vfo := diff(Gfo,P);

Note that the units of volume required for the above expressions are Joule/bar.

NOTE: if Maple does not evaluate a numeric expression that seems otherwise correct, you can use the **evalf** command to force evaluation, as in evalf(Gfo) or Gfo := evalf(subs(fo, g));

WARNING!! do not substitute numeric values for pressure and temperature into your function before integrating or differentiating in Maple. If you do so maple will no longer recognize the functional dependence, e.g.,

diff(subs(P=40000,T=1000,Gfo),P) is zero (i.e., nonsense)

but

Vfo := diff(Gfo,P);
subs(P=40000,T=1000,Vfo); or evalf(subs(P=40000,T=1000,Vfo));

will yield the volume.

To test your function calculate G, S, and V at the reference condition (T = 298.15 K and P = 1 bar), if your function
has no mathematical errors the values should be identical to the reference values (G0, S0, V0). Additionally
evalf(subs(P=40000,T=1000,Gfo)) should yield -2015940. J/mol.

Problem 5.1: Use your function for the Gibbs energy to compute the following properties at 1000 K and 40000 bar,
give the units for each property:

a) V
b) S
c) density (in kg/m3)
d) heat capacity (T*diff(entropy,T))
e) isobaric expansivity (1/volume*diff(volume,T))
f) isothermal compressibility (the inverse of the isothermal bulk modulus)

```
>
```

Problem 5.2: 5.2) Using your results from problems 5.1 and 4.5-8: **a)** Compute the isentropic and isothermal speed of sound through forsterite, whose properties are an excellent proxy for those of the upper mantle, at P = 40000 bar, T = 1000 K (the isothermal speed is computed using the isothermal bulk modulus, KT, rather than the adiabatic modulus, KS, in 4.45). **b)** The heat capacity ratio (cP/cV) of forsterite at P = 40000 bar, T = 1000 K. **c)** The adiabatic geothermal gradient in forsterite at P = 40000 bar, T = 1000 K. **d)** Use the relation derived in problem 4.8 to test whether the equation of state for forsterite from problem 5.1 is valid at 2800 K and 1400 kbar, conditions representative of the core-mantle boundary.

Be sure to indicate the units for the result.

For example, for **a)**

```
> #v_phi := ....  from problem 4.4 or 4.5, then
> #vfo := subs(G(P,T)=Gfo,N=Nfo,v_phi):
> #evalf(subs(P=40000,T=1000,vfo));
```

to get the units you may be interested in trying the Maple convert command, e.g., the commands below converts 1 J/bar to m^3 and 10000 bar to GPa:

```
> convert(1.,units,J/bar,m^3);
> convert(10000,units,bar,GPa);
                                   0.00001000000000

                                           1                                          (3)

> 
```