Solution 7:

3 Anorthite = Grossular + 2 Kyanite + Quartz
3 $CaAl_2Si_2O_8$ = $Ca_3Al_2Si_3O_{12}$ + 2 Al_2SiO_5 + SiO_2

1). ΔV^o_{rx} at STP
$\Delta V^o_{rx} = \sum V^o_{\text{products}} - \sum V^o_{\text{reactants}}$
= 125.3 + 2*44.090 + 22.688 – 3*100.79 cm^3
= -66.2 cm^3 = -6.62 * 10^{-5} m^3 = -6.62 J/bar
So, the products are denser.

2). ΔH^o_{rx} at STP
$\Delta H^o_{rx} = \sum H_f^o{}_{\text{products}} - \sum H_f^o{}_{\text{reactants}}$
= -6643.14 + 2*(-2591.73) + (-910.70) – 3*(-4229.10) kJ
= -50.000 kJ = -50 000 J
So, the reaction is exothermic.

3). ΔE_{rx} at STP
$\Delta E_{rx} = q - W = \Delta H^o_{rx} - P*\Delta V^o_{rx}$
= -50 000 J – 1 bar * (-6.62 * 10^{-5} m^3)
= -49 993 J ≈ -50 kJ
So, under these conditions, the q is the large term (Forget the signs of q and W here, because they are given by the conversion.).

ATTENTION:
At constant P, q = ΔH_{rx}.
Also at the initial state of the reaction, the system is not reversible, so, q < T*ΔS^o_{rx}. Only when the reaction reaches an equilibrium state, the system is reversible. Then q = T*ΔS^o_{rx}.

4). ΔS^o_{rx} at STP
$\Delta S^o_{rx} = \sum S^o_{\text{products}} - \sum S^o_{\text{reactants}}$
= 255.5 + 2*83.76 + 41.46 – 3*199.3 J/K
= -133.4 J/K
So, the reactants are more disordered.

5). ΔG^o_{rx} at STP
$\Delta G^o_{rx} = \Delta H^o_{rx} - T*\Delta S^o_{rx}$
= -50 000 J – 298 K * (-133.4 J K)
= -10247 J
So, the products are stable at STP.

6).

$dG = VdP - SdT$

$\Delta G^o_{rx(P, T)} - \Delta G^o_{rx(P1, T1)} = \Delta V_{rx} (P - P_1) - \Delta S_{rx} (T - T_1)$

At equilibrium, K=1 i.e. all the reactants and products are pure substances.

Then, we have $G^o_{rx\ (P, T)} = 0$ (or as mentioned in this problem).

$\Delta G^o_{rx(P1, T1)} = \Delta S_{rx} (T - T_1) - \Delta V_{rx} (P-P_1)$

In this problem, $P = P_1$, so

$\Delta G^o_{rx(P1, T1)} = \Delta S_{rx} (T - T_1)$

$T = \Delta G^o_{rx(P1, T1)} / \Delta S_{rx} + T_1$

$T = -10247 / (-133.4) + 298\ K = 375\ K$

There are two methods to calculate the change in enthalpy for the reaction.

Method 1:

$\Delta H_{rx(P, T)} = \Delta G_{rx(P, T)} + \Delta S_{rx(P, T)} * T$

Because we assume that ΔS_{rx} is constant with P and T, $\Delta S_{rx(P, T)} = \Delta S_{rx(P1, T1)}$,

i.e. $\Delta S_{rx(P, T)} = \Delta S_{rx}^o$.

$\Delta H_{rx(P, T)} = 0 + (-133.4) * 375\ J = -50025\ J \approx -50\ kJ$

Method 2:

ΔH_{rx} at 375 K and 1 bar

$\Delta\ C_{p\ rx} = \sum C_{p\ products} - \sum C_{p\ reactants}$
$= [1.5293*10^3 - 0.699(T) + 2.53*10^{-4}(T^2) - 1.8943*10^4(T^{-0.5}) + 7.4426*10^6(T^{-2})] + 2*[4.3612*10^2 - 0.13576(T) + 4.7236*10^{-5}(T^2) - 4.8027*10^3(T^{-0.5})] + [44.603 + 3.7754*10^{-2}(T) - 1.0018*10^6(T^{-2})] - 3*[5.1683*10^2 - 9.2492*10^{-2}(T) + 4.1883*10^{-5}(T^2) - 4.5885*10^3(T^{-0.5}) - 1.4085*10^6(T^{-2})]$ J K
$= 895.653 - 0.65529(T) + 2.21823*10^{-4}(T^2) - 1.47829*10^4(T^{-0.5}) + 9.8529*10^6(T^{-2})$ J K

$\Delta H_{rx,\ 375\ K} = \Delta H^o_{rx,\ 298\ K} + \int_{298}^{375} \Delta C_p\ dT$
$= -50\ 000 + \int_{298}^{375} [895.653 - 0.65529(T) + 2.21823*10^{-4}(T^2) - 1.47829*10^4(T^{-0.5}) + 10.6663*10^6(T^{-2})]\ dT$ J

$= -50\ 000 + 895.653*(375-298) - 1/2*0.65529*(375^2-298^2) + 1/3*2.21823*10^{-4}*(375^3-298^3) - 2*1.47829*10^4*(375^{0.5}-298^{0.5}) + (-1)*10.6663*10^6*(375^{-1}-298^{-1})$ J

$= -50\ 000 + 68965.3 - 16978.9 + 1942.5 - 62154.4 + 7349.5$ J
$= -50876\ J = \approx -51\ kJ$

You will find both methods give us similar values. The second is more precise. The first is only applicable when we assume that ΔS_{rx} is constant with P and T. In addition, the reaction is still exothermic at 375K.

7).

$\Delta G^o_{rx(P,\,T)} - \Delta G^o_{rx(P1,\,T1)} = \Delta V_{rx}\,(P - P_1) - \Delta S_{rx}\,(T - T_1)$

If $G^o_{rx\ (P,\,T)} = 0$ (as mentioned in this problem).

$\Delta G^o_{rx(P1,\,T1)} = \Delta S_{rx}\,(T - T_1) - \Delta V_{rx}\,(P\text{-}P_1)$

$P = \Delta S_{rx} * T/\Delta V_{rx} - \Delta S_{rx} * T_1/\Delta V_{rx} + P_1 - \Delta G^o_{rx(P1,\,T1)}/\Delta V_{rx}$

Attention: ΔV^o_{rx} = -66.2 cm^3 = -6.62 * 10^{-5} m^3 = -6.62 J/bar

P = (-133.4) * (700-298) /(-6.62) + 1 - (-10247) / (-6.62) bar

P = 6554 bar ≈ 6.6 kbar

8).

The Clapeyron slope:

$dP/dT = \Delta S_{rx}/\Delta V_{rx}$ = (-133.4)/(-6.62) bar/K = 20.2 bar/K

9).

You can plot the P-T phase diagram by using:

a), two points (375K, 1bar) and (700K, 6554bar)

b), one point (375K, 1bar) or (700K, 6554bar), and slope 20.2 bar/K

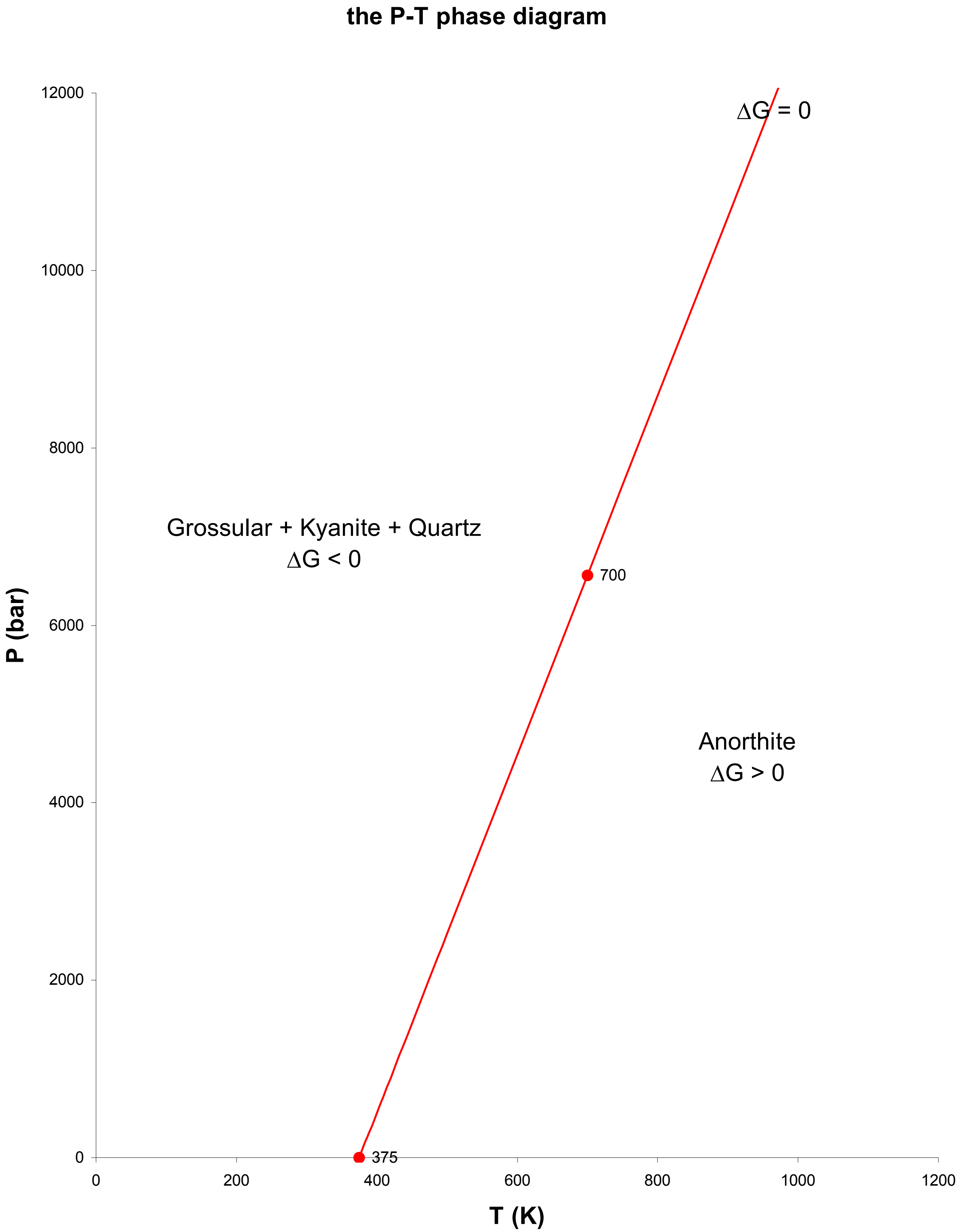
or

c), slope 20.2 bar/K and intercept $-(\Delta G^o_{rx(P1,\,T1)} + \Delta S_{rx} * T_1)/\Delta V_{rx} + P_1$,

i.e. $-\ \Delta H_{rx(P1,\,T1)}/\Delta V_{rx} + P_1$ in this problem, which has value -7552 bar/K.

See the figure attached at the end.

10). Grossular has a higher coordination number for Al, because it is more stable than Anorthite at higher pressure state.


the P-T phase diagram
ΔG = 0
Grossular + Kyanite + Quartz
ΔG < 0
700
Anorthite
ΔG > 0
375
P (bar)
T (K)
0
2000
4000
6000
8000
10000
12000
0
200
400
600
800
1000
1200