5

5.1 (also available as a Mathcad worksheet)

(a) $\hat{G} = \hat{H} - TS$ at $P = 2.5$ MPa and $T = 223.99°\text{C} = 497.14$ K

$$\left.\begin{array}{l}\hat{G}^{\text{V}} = \hat{H}^{\text{V}} - T\hat{S}^{\text{V}} = 2803.1 - 497.14 \times 6.2575 = -307.8 \text{ J/g} \\ \hat{G}^{\text{L}} = \hat{H}^{\text{L}} - T\hat{S}^{\text{L}} = 962.11 - 497.14 \times 2.5547 = -307.9 \text{ J/g}\end{array}\right\} \text{equal with the accuracy of tables}$$

(b)

$T(°\text{C})$	$T(\text{K})$	$\hat{H}^{\text{V}}$	$-$	$T\hat{S}^{\text{V}}$	$\hat{G}^{\text{L}}$
225	498.15	2806.3	$-$	$498.15 \times 6.2639 =$	-314.1 J/g
250	523.15	2880.1	$-$	$523.15 \times 6.4085 =$	-472.5
300	573.15	3008.8	$-$	$573.15 \times 6.6438 =$	-799.1
350	623.15	3126.3	$-$	$623.15 \times 6.8403 =$	-1136.2
400	673.15	3239.3	$-$	$673.15 \times 7.0148 =$	-1482.7

(Note: All Gibbs free energies are relative to the internal energy and entropy of the liquid phase being zero at the triple point. Since $\hat{H}^{\text{L}} \sim \hat{U}^{\text{L}}$, and $\hat{G}^{\text{L}} = \hat{H}^{\text{L}} - T\hat{S}^{\text{L}}$, we have that $\hat{G}^{\text{L}} = 0$ at the triple point.)

(c)

$T(°\text{C})$	$T(\text{K})$	$\hat{H}^{\text{L}}$	$-$	$T\hat{S}^{\text{L}}$	$\hat{G}^{\text{V}}$
160	433.15	675.55	$-$	$433.15 \times 1.9427 =$	-165.9 J/g
170	443.15	719.21	$-$	$443.15 \times 2.0419 =$	-185.7
180	453.15	763.22	$-$	$453.15 \times 2.1396 =$	-206.3
190	463.15	807.62	$-$	$463.15 \times 2.2359 =$	-227.9
200	473.15	852.45	$-$	$473.15 \times 2.3309 =$	-250.4
210	483.15	897.76	$-$	$483.15 \times 2.4248 =$	-273.8

RESULTS

(d)

$T(°\text{C})$	150	160	180	200	220	224
$\hat{V}(\text{m}^3/\text{kg})$	0.001091	0.001102	0.001127	0.001157	0.001190	0.001197 to 0.07998

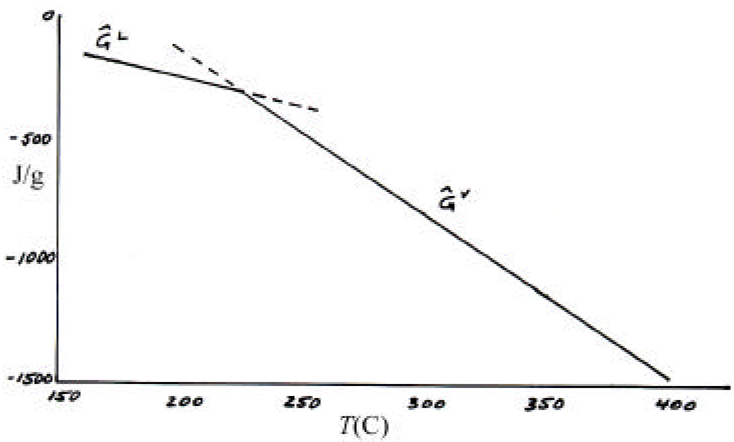
$T(°\text{C})$	225	250	300	350	400
$\hat{V}(\text{m}^3/\text{kg})$	0.08027	0.08700	0.09890	0.10976	0.12010

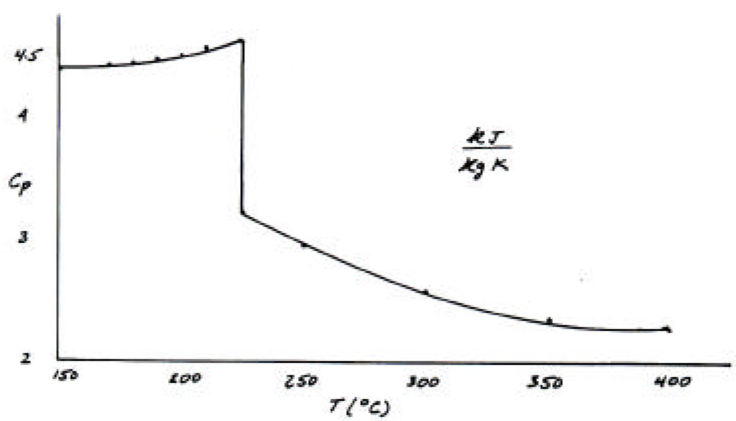
(e) Will compute C_{P} from $C_{\text{P}} \sim \left(\frac{\Delta \hat{H}}{\Delta T}\right)_P = \frac{\hat{H}(T + \Delta T) - \hat{H}(T)}{\Delta T}$

T(° C)	150	170	180	190	200	210	224
C_P(kJ/kg K)	4.328	4.392	4.430	4.472	4.518	4.572	4.6225 to 3.200

T(° C)	250	300	350	400
C_P(kJ/kg K)	2.952	2.574	2.350	2.260

These results are plotted below.





5.2 Closed system energy balance: $\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt}$

Closed system entropy balance: $\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}}$

(a) System at constant volume and constant entropy

$$\frac{dV}{dt} = 0 \text{ and } \frac{dS}{dt} = 0$$

$$\Rightarrow \frac{dU}{dt} = \dot{Q} \text{ and } 0 = \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}} \Rightarrow \dot{Q} = -T\dot{S}_{\text{gen}}$$

$$\text{and } \frac{dU}{dt} = -T\dot{S}_{\text{gen}}\,;\ T > 0\,;\ \dot{S}_{\text{gen}} \geq 0$$

$$\Rightarrow \frac{dU}{dt} \leq 0 \text{ or } U = \text{minimum at equilibrium at constant } V \text{ and } S.$$

(b) System at constant entropy and pressure again $\dot{Q} = -T\dot{S}_{\text{gen}}$.

Now $\frac{dP}{dt} = 0 \Rightarrow P\frac{dV}{dt} = \frac{d}{dt}(PV)$. Thus

$$\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt} = -T\dot{S}_{\text{gen}} - \frac{d}{dt}(PV)$$

and

$$\frac{dU}{dt} + \frac{d}{dt}(PV) = \frac{d}{dt}(U + PV) = \frac{dH}{dt} = -T\dot{S}_{\text{gen}} \leq 0$$

Therefore, enthalpy is a minimum at equilibrium at constant S and P.