材料熱力學二 作業#1

B10704007 邱允平

V A T
U G
S H P

1 Prove the following equations:

1.1 $\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P$

1.2 $\frac{H}{RT^2} = -\left[\frac{\partial}{\partial T}\left(\frac{G}{RT}\right)\right]_P$

2 Derive $dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$

3 Several thermodynamic properties of the changes between water (l) and ice (s) are $H_{H_2O(l)}$, $H_{H_2O(s)}$, $\Delta H_{H_2O(s\to l)}$, $\Delta S_{H_2O(s\to l)}$, and $\Delta G_{H_2O(s\to l)}$. Indicate that these properties are greater than, equal to, or smaller than zero at 298 K, 273 K, and 253 K. Set that the melting temperature of water/ice is 273 K.

	$H_{H_2O(l)}$	$H_{H_2O(s)}$	$\Delta H_{H_2O(s\to l)}$	$\Delta S_{H_2O(s\to l)}$	$\Delta G_{H_2O(s\to l)}$
298 K					
273 K					
253 K					

1. (1) $\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial T}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_T = -1 \Rightarrow \left(\frac{\partial P}{\partial T}\right)_S = \frac{-\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial P}\right)_T} = \frac{-\left(\frac{C_P}{T}\right)}{-\left(\frac{\partial V}{\partial T}\right)_P} = \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P$ #

(2) $-\left[\frac{\partial}{\partial T}\left(\frac{G}{RT}\right)\right]_P = -\left[\left(\frac{\partial G}{\partial T}\right)_P \cdot \frac{1}{RT} - \frac{G}{RT^2}\right] = \frac{G}{RT^2} + \frac{S}{RT} = \frac{G+ST}{RT^2}$

(By $G = H - ST \Rightarrow H = G + ST$) $= \frac{H}{RT^2}$ #

2. $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_P dT + \left(\frac{\partial U}{\partial V}\right)_T dV$, By $dU = TdS - PdV \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$ (*)

(*)代入 $\Rightarrow dU = C_P dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right] dV = C_P dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$ Q.E.D

3.

	$H_{H_2O(l)}$	$H_{H_2O(s)}$	$\Delta H_{H_2O(s\to l)}$	$\Delta S_{H_2O(s\to l)}$	$\Delta G_{H_2O(s\to l)}$
298 K 25°C	$=0$	<0	>0	>0	<0
273 K 0°C	<0	<0	>0	>0	$=0$
253 K −20°C	<0	<0	>0	>0	>0

$H_l = 0 + \int_{298}^{T} C_{P,l}\, dT = 75.44(T-298)$

$\Delta G = \Delta H - \Delta S T$

$H_s = 0 + \int_{298}^{273} C_{P,l}\, dT - \underbrace{\Delta H_{(s\to l)}}_{at\ 273K} + \int_{273}^{T} C_{P,s}\, dT$

原本 $\Delta H_{s\to l} > 0$
現在 $\Delta H_{l\to s} < 0$

$= 75.44(273-298) - 6008 + 38(T-273)$

$= -7894 + 38(T-273)$