Profesora: María Teresa Garland
Auxiliar: Gabriela Sandoval

FI22A-01: Física Estadística

Clase Auxiliar Jueves 19 de junio de 2008

$$S(T) = \int_0^T \frac{C_p(T)dT}{T}$$

$$\Delta S_{transición} = \frac{\Delta H_{transición}}{T_{transición}}$$

Debye: $\bar{S}(T_{baja}) = \frac{\overline{C_P}(T_{baja})}{3}$

Convención: a T= 0 K S=0

$$\bar{S}(T) = \frac{\overline{C_P}(T_{baja})}{3} + \int_{T_{baja}}^{T_{cambio\ fase\ 1}} \frac{\bar{C}_p^{Estado\ 1}(T)dT}{T} + \frac{\Delta H_{cambio\ fase\ 1}}{T_{cambio\ fase\ 1}} + \int_{T_{cambio\ fase\ 1}}^{T_{cambio\ fase\ 2}} \frac{\bar{C}_p^{Estado\ 2}(T)dT}{T} + \frac{\Delta H_{cambio\ fase\ 2}}{T_{cambio\ fase\ 2}} + \int_{T_{cambio\ fase\ 2}}^{T} \frac{\bar{C}_p^{Estado\ 3}(T)dT}{T}$$

Problema 1.

Calcule la entropía molar del $N_2(g)$ a 298,15K. Los datos son:

$$\frac{\overline{C_P}(sólido1)}{R} = -0{,}03165 + \left(0{,}05460K^{-1}\right)T + \left(3{,}520\times10^{-3}K^{-2}\right)T^2 - \left(2{,}064\times10^{-5}K^{-3}\right)T^3$$

$$10K \le T \le 35{,}61K$$

$$\frac{\overline{C_P}(sólido2)}{R} = -0{,}1696 + \left(0{,}2379K^{-1}\right)T - \left(4{,}214\times10^{-3}K^{-2}\right)T^2 + \left(3{,}036\times10^{-5}K^{-3}\right)T^3$$

$$35{,}61K \le T \le 63{,}15K$$

$$\frac{\overline{C_P}(líquido)}{R} = -18{,}44 + \left(1{,}053K^{-1}\right)T - \left(0{,}0148\times10^{-3}K^{-2}\right)T^2 + \left(7{,}064\times10^{-5}K^{-3}\right)T^3$$

$$63{,}15K \le T \le 77{,}36K$$

$$\frac{\overline{C_P}(gas)}{R} = 3{,}5$$

$$77{,}36K \le T \le 1000K$$

$\overline{C_P}(T = 10K) = 6{,}15\frac{J}{mol\cdot K}$ (El sólido sigue la ley de Debye bajo los 10K)

$T_{trs} = 35{,}61K$ y $\Delta H_{trs} = 0{,}2289\frac{kJ}{mol}$

$T_{fus} = 63{,}15K$ y $\Delta H_{fus} = 0{,}71\frac{kJ}{mol}$

$T_{vap} = 77{,}36K$ y $\Delta H_{vap} = 5{,}57\frac{kJ}{mol}$

Solución:

0K≤T≤10K

$$\overline{\Delta S_{0-10}} = \frac{6{,}15}{3}\frac{J}{mol\cdot K} = 2{,}05\frac{J}{mol\cdot K}$$

10K≤T≤35,61K

$$\overline{\Delta S_{10-35,61}} = \int_{10K}^{35,61K} R\frac{\left[-0{,}03165 + \left(0{,}05460K^{-1}\right)T + \left(3{,}520\times10^{-3}K^{-2}\right)T^2 - \left(2{,}064\times10^{-5}K^{-3}\right)T^3\right]}{T}dT$$

$$= 8{,}314\frac{J}{mol\cdot K}\left[\begin{array}{l}-0{,}03165Ln\dfrac{35{,}61}{10}+0{,}0546(35{,}61-10)\\ +\dfrac{3{,}520\times10^{-3}}{2}\left(35{,}61^2-10^2\right)-\dfrac{2{,}064\times10^{-5}}{3}\left(35{,}61^3-10^3\right)\end{array}\right]$$

$$= 8{,}314\frac{J}{mol\cdot K}\left[-0{,}04+1{,}4+2{,}056-0{,}304\right]$$

$$= 8{,}314\frac{J}{mol\cdot K}\times 3{,}112$$

$$= 25{,}87\frac{J}{mol\cdot K}$$

T=35,61K (Transición)

$$\overline{\Delta S_{trs}} = \frac{228{,}9}{35{,}61}\frac{J}{mol\cdot K}$$

$$= 6{,}43\frac{J}{mol\cdot K}$$

35,61K≤T≤63,15K

$$\overline{\Delta S_{35,61-63,15}} = \int_{35,61K}^{63,15K} R\frac{-0{,}1696+\left(0{,}2379K^{-1}\right)T-\left(4{,}214\times10^{-3}K^{-2}\right)T^2+\left(3{,}036\times10^{-5}K^{-3}\right)T^3}{T}dT$$

$$= 8{,}314\frac{J}{mol\cdot K}\left[\begin{array}{l}-0{,}1696Ln\dfrac{63{,}15}{35{,}61}+0{,}2379(63{,}15-35{,}61)\\ -\dfrac{4{,}214\times10^{-3}}{2}\left(63{,}15^2-35{,}61^2\right)+\dfrac{3{,}036\times10^{-5}}{3}\left(63{,}15^3-35{,}61^3\right)\end{array}\right]$$

$$= 8{,}314\frac{J}{mol\cdot K}\left[-0{,}097+6{,}552-5{,}731+2{,}092\right]$$

$$= 23{,}41\frac{J}{mol\cdot K}$$

T=63,15K (Fusión)

$$\overline{\Delta S_{fus}} = \frac{710}{63{,}15}\frac{J}{mol\cdot K}$$

$$= 11{,}24\frac{J}{mol\cdot K}$$

63,15K≤T≤77,36K

$$\overline{\Delta S_{63,15-77,36}} = \int_{63,15K}^{77,36K} R\frac{-18,44+\left(1,053K^{-1}\right)T-\left(0,0148\times10^{-3}K^{-2}\right)T^2+\left(7,064\times10^{-5}K^{-3}\right)T^3}{T}dT$$

$$= 8,314\frac{J}{mol\cdot K}\left[\begin{array}{l}-18,44Ln\frac{77,36}{63,15}+1,053(77,36-63,15)\\ -\frac{0,0148\times10^{-3}}{2}\left(77,36^2-63,15^2\right)+\frac{7,064\times10^{-5}}{3}\left(77,36^3-63,15^3\right)\end{array}\right]$$

$$= 11,78\frac{J}{mol\cdot K}$$

T=77,36K (Vaporización)

$$\overline{\Delta S_{vap}} = \frac{557}{77,36}\frac{J}{mol\cdot K}$$

$$= 72\frac{J}{mol\cdot K}$$

77,36K≤T≤298,15K

$$\overline{\Delta S_{77,36-298,15}} = \int_{77,36K}^{298,15K} R\frac{3,5}{T}dT$$

$$= 8,314\frac{J}{mol\cdot K}\left[3,5Ln\frac{298,15}{77,36}\right]$$

$$= 39,26\frac{J}{mol\cdot K}$$

Luego,

$$\overline{\Delta S}(298,15K) = \overline{\Delta S_{0-10}} + \overline{\Delta S_{10-35,61}} + \overline{\Delta S_{trs}} + \overline{\Delta S_{35,61-63,15}} + \overline{\Delta S_{fus}} + \overline{\Delta S_{63,15-77,36}} + \overline{\Delta S_{vap}} + \overline{\Delta S_{77,36-298,15}}$$

$$= 2,05+25,87+6,43+23,41+11,24+11,78+72+39,26$$

$$= 192,04\frac{J}{mol\cdot K}$$

$$\overline{\Delta S}(298,15K) = 192,04\frac{J}{mol\cdot K}$$

Entropía Absoluta (Tercera Ley)

Problema 3 Control 3 FI22A Primavera 2007

Calcule la temperatura de Debye Θ_D para el ciclopropano C_3H_{16}, si su entropía molar a 298,15K es igual a $237{,}26\dfrac{J}{Kmol}$ a presión Standard, y

$$\frac{\overline{C_{P[C_3H_{16}sólido]}}}{R} = -1{,}921 + \left(0{,}1508K^{-1}\right)T - \left(9{,}67\times10^{-4}K^{-2}\right)T^2 + \left(2{,}694\times10^{-6}K^{-3}\right)T^3$$

15K≤T≤145,15K

$$\frac{\overline{C_{P[C_3H_{16}liquido]}}}{R} = 5{,}624 + \left(4{,}493\times10^{-2}K^{-1}\right)T - \left(1{,}34\times10^{-4}K^{-2}\right)T^2$$

145,15K≤T≤240,3K

$$\frac{\overline{C_{P[C_3H_{16}gaseoso]}}}{R} = -1{,}793 + \left(3{,}277\times10^{-2}K^{-1}\right)T - \left(1{,}326\times10^{-5}K^{-2}\right)T^2$$

240,3K≤T≤298,15K

$$T_{fus} = 145{,}5K\,,\ T_{vap} = 240{,}3K\,,\ \overline{\Delta H}_{fus} = 5{,}44\frac{kJ}{mol}\,,\ \overline{\Delta H}_{vap} = 20{,}05\frac{kJ}{mol}$$

$$\overline{C_P}(T) = \frac{12\pi^4 R}{5}\left(\frac{T}{\Theta_D}\right)^3 \quad 0<T<T_{baja}$$

Solución:

0K≤T≤15K

$$\overline{\Delta S}_{Debye} = \frac{\overline{C_P}}{3}\frac{J}{mol\cdot K}$$

15K≤T≤145,15K

$$\overline{\Delta S_{15-145,5}} = \int_{15K}^{145,15K} R\frac{\left[-1,921+\left(0,1508K^{-1}\right)T-\left(9,67\times10^{-4}K^{-2}\right)T^2+\left(2,694\times10^{-6}K^{-3}\right)T^3\right]}{T}dT$$

$$= 8,314\frac{J}{mol\cdot K}\begin{bmatrix} -1,921Ln\frac{145,15}{15}+0,1508(145,15-15) \\ -\frac{9,67\times10^{-4}}{2}\left(145,15^2-15^2\right)+\frac{2,694\times10^{-6}}{3}\left(145,15^3-15^3\right)\end{bmatrix}$$

$$= 8,314\frac{J}{mol\cdot K}[-4,36+19,68-10,13+2,76]$$

$$= 8,314\frac{J}{mol\cdot K}\times7,95$$

$$= 66,1\frac{J}{mol\cdot K}$$

T=145,15K (Fusión)

$$\overline{\Delta S_{fus}} = \frac{5440}{145,15}\frac{J}{mol\cdot K}$$

$$= 37,39\frac{J}{mol\cdot K}$$

145,15K≤T≤240,3K

$$\overline{\Delta S_{145,15-240,3}} = 8,314\frac{J}{mol\cdot K}\begin{bmatrix} 5,624Ln\frac{240,3}{145,15}+4,493\times10^{-2}(240,3-145,15) \\ -\frac{1,34\times10^{-4}}{2}\left(240,3^2-145,15^2\right)\end{bmatrix}$$

$$= 8,314\frac{J}{mol\cdot K}[2,82+4,26-2,45]$$

$$= 8,314\frac{J}{mol\cdot K}\times4,63$$

$$= 38,5\frac{J}{mol\cdot K}$$

T=240,3K (Vaporización)

$$\overline{\Delta S_{vap}} = \frac{20050}{240,3}\frac{J}{mol\cdot K}$$

$$= 83,44\frac{J}{mol\cdot K}$$

240,3K≤T≤298,15K

$$\overline{\Delta S_{240,3-298,15}} = 8,314\frac{J}{mol\cdot K}\begin{bmatrix} -1,793Ln\dfrac{298,15}{240,3}+3,277\times 10^{-2}(298,15-240,3) \\ -\dfrac{1,326\times 10^{-5}}{2}\left(298,15^2-240,3^2\right) \end{bmatrix}$$

$$= 8,314\frac{J}{mol\cdot K}[-0,39+1,9-0,21]$$

$$= 8,314\frac{J}{mol\cdot K}\times 1,3$$

$$= 10,83\frac{J}{mol\cdot K}$$

Luego,

$$\overline{\Delta S}(298,15K) = \overline{\Delta S_{Debye}} + \overline{\Delta S_{15-145,15}} + \overline{\Delta S_{fus}} + \overline{\Delta S_{145,15-240,3}} + \overline{\Delta S_{vap}} + \overline{\Delta S_{240,3-298,15}}$$

$$237,26\frac{J}{mol\cdot K} = \frac{\overline{C_P}}{3} + 66,1 + 37,39 + 38,5 + 83,44 + 10,83$$

$$= \frac{\overline{C_P}}{3} + 236,25\frac{J}{mol\cdot K}$$

$$\Rightarrow \begin{aligned} \overline{C_P} &= 3\times[237,26-236,25]\frac{J}{mol\cdot K} \\ &= 3\times 1,01\frac{J}{mol\cdot K} \end{aligned}$$

$$\overline{C_P} = 3,03\frac{J}{mol\cdot K} = \frac{12\pi^4 R}{5}\times\left(\frac{T}{\Theta_D}\right)^3 \quad \text{con} \quad \begin{aligned} R &= 8,314\frac{J}{mol\cdot K} \\ T &= 15K \end{aligned}$$

Finalmente, reemplazando los datos y despejando se tiene que:

$$\boxed{\Theta_D = 129,37K}$$