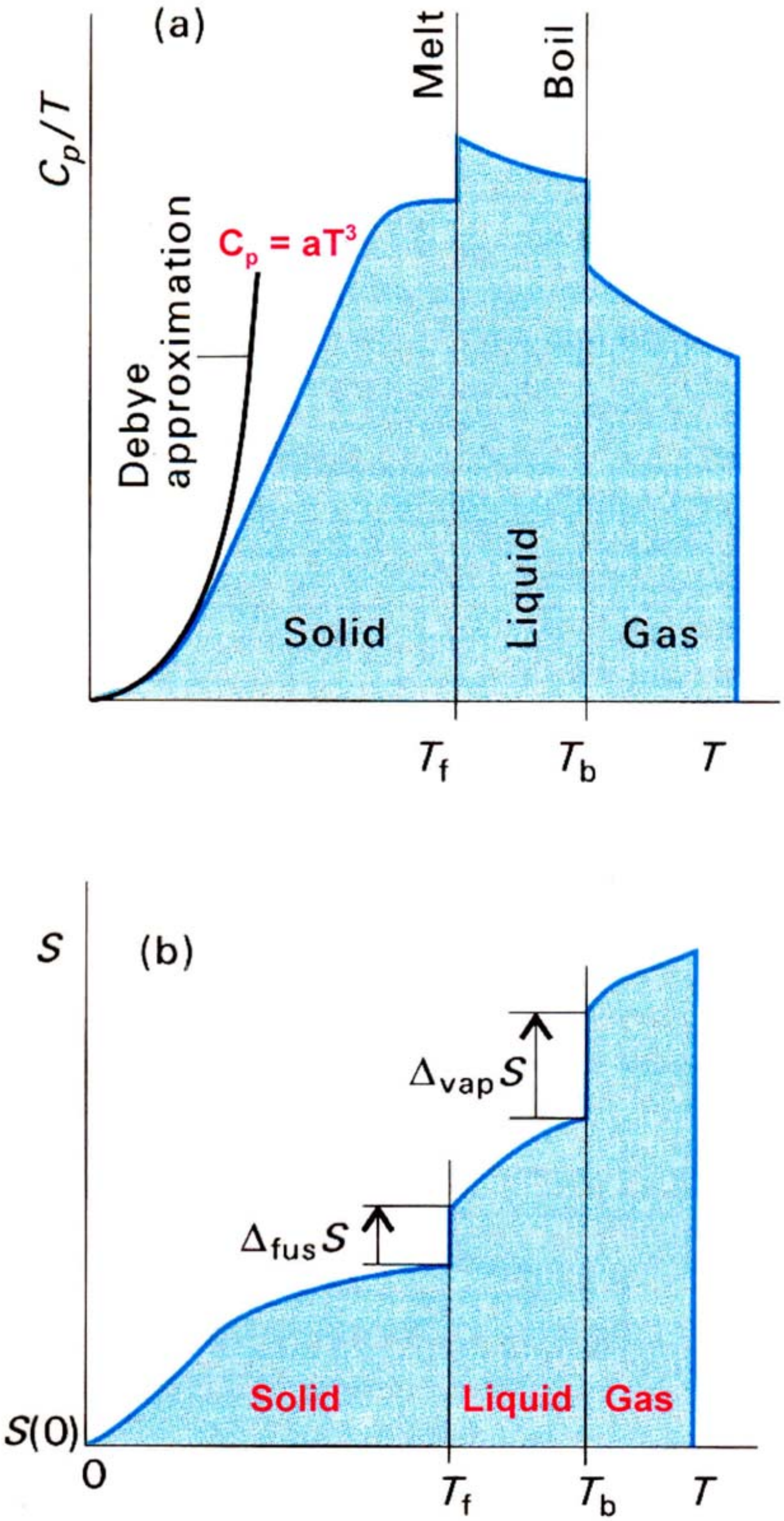
Topic 4H - Absolute Entropies



$$dS = \frac{dq_{rev}}{T} = \frac{nC_p dT}{T}$$

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

Figure E.25 The thermochemical measurement of entropy makes use of a determination of the heat capacity of a sample of the substance and then (a) making a plot of C_p/T against T (or, alternatively, a plot of C_p against $\ln T$). The entropy at a particular temperature, as depicted in (b), is then obtained by determining the area under either curve up to the temperature of interest, and adding terms corresponding to each phase transition.

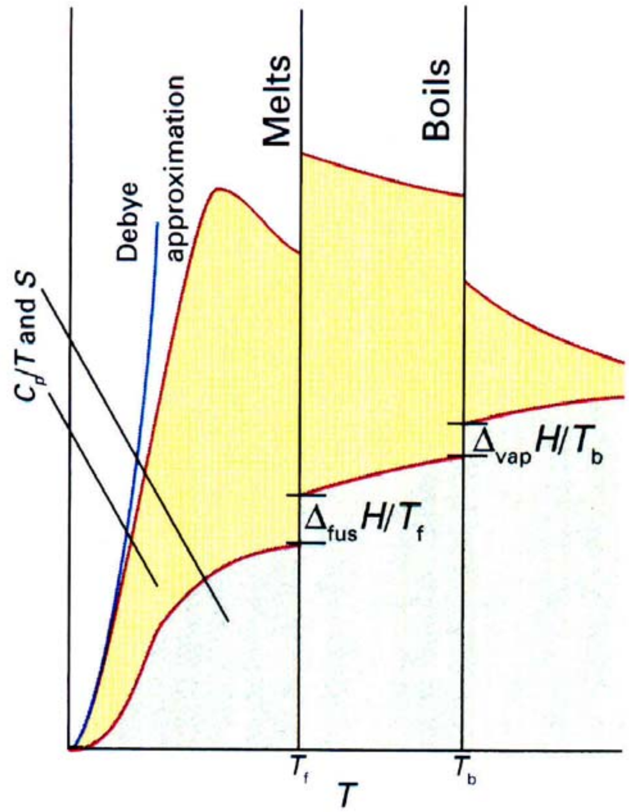
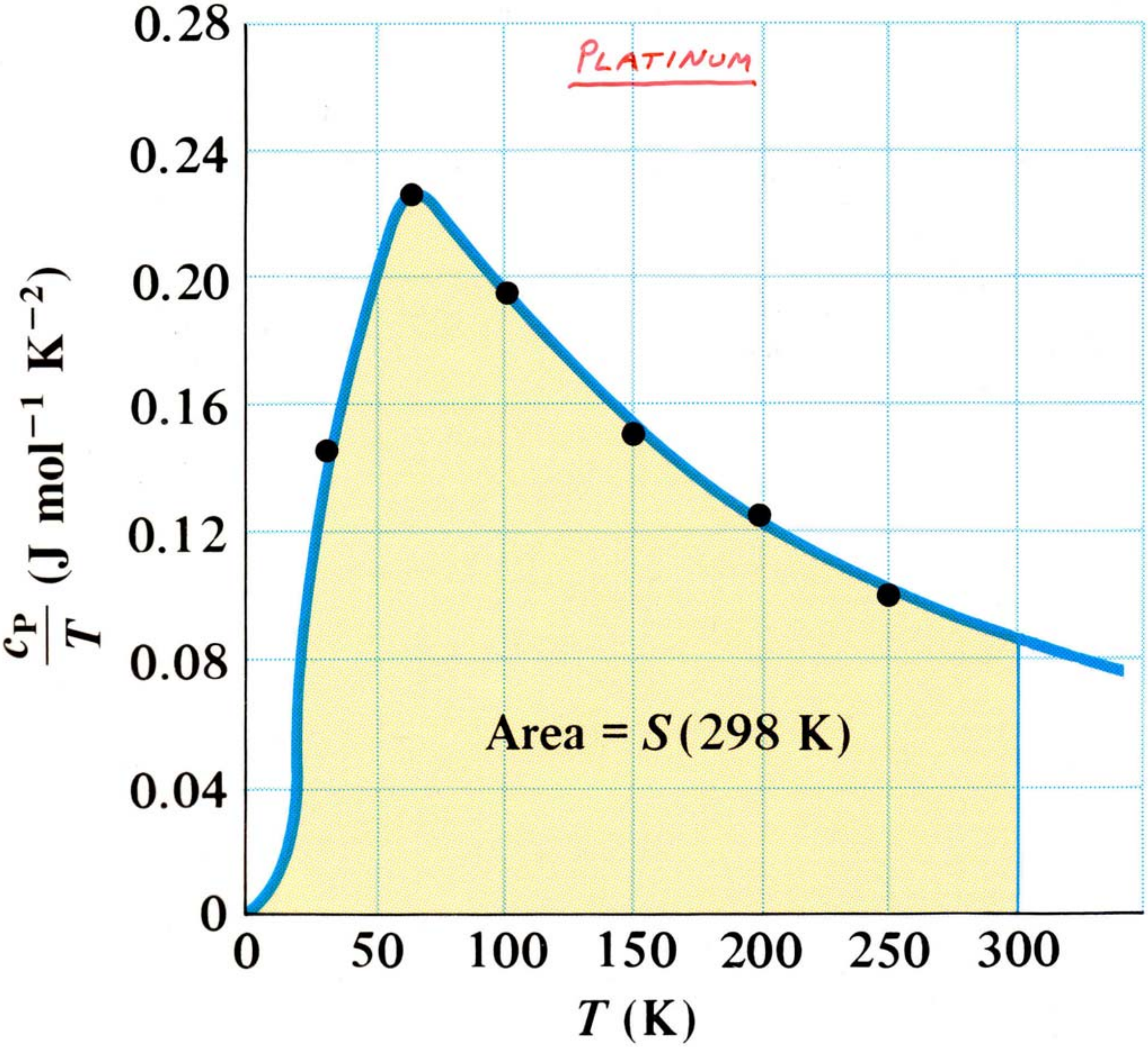


Fig. 3.14 The variation of C_p/T with the temperature for a sample is used to evaluate the entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

$$S_T = \int_0^T \frac{C_p}{T}\, dT$$



The standard molar entropy of nitrogen gas at 25°C has been calculated from the following data:

		$S^{\ominus}_{m}/(J\ K^{-1}\ mol^{-1})$	
Debye extrapolation	($C_p = aT^3$)	1.92	
Integration, from 10 K to 35.61 K		25.25	
Phase transition at 35.61 K		6.43	
Integration, from 35.61 K to 63.14 K		23.38	
Fusion at 63.14 K	($\Delta H_{fus}/T_{MP}$)	11.42	(720 J / 63.14 K)
Integration, from 63.14 K to 77.32 K		11.41	
Vaporization at 77.32 K	($\Delta H_{vap}/T_{BP}$)	72.13	(5,577 J / 77.32 K)
Integration, from 77.32 K to 298.15 K		39.20	
Correction for gas imperfection		0.92	
Total		192.06	

Therefore,

$$S_m(298.15\ K) = S_m(0) + 192.1\ J\ K^{-1}\ mol^{-1}$$

Determining Entropy of HCl at 298.15 K from Its Heat-Capacity Measurements[a]

Contribution		$\bar{S}^{\circ}_{T}/J \cdot K^{-1} \cdot mol^{-1}$
1. Extrapolation from 0 to 16 K (Equation 5.25)	($C_p = aT^3$)	1.3
2. $\int C_P d\ln T$ for solid I from 16 K to 98.36 K		29.5
3. Phase transition at 98.36 K, solid I → solid II, $\Delta H/T = 1190\ J\ mol^{-1}/98.36\ K$		12.1
4. $\int C_P d\ln T$ for solid II from 98.36 K to 158.91 K		21.1
5. Fusion, $1992\ J\ mol^{-1}/158.91\ K$	($\Delta H_{fus}/T_{MP}$)	12.6
6. $\int C_P d\ln T$ for liquid from 158.91 K to 188.07 K		9.9
7. Vaporization, $\frac{16,150\ J\ mol^{-1}}{188.07\ K}$	($\Delta H_{vap}/T_{BP}$)	85.9
8. $\int C_P d\ln T$ for gas from 188.07 K to 298.15 K		13.5
		$\bar{S}^{\circ}_{298.15} = 185.9$[b]

TABLE 11.1

Standard absolute entropies S°_{298} of some common elements and their compounds

Element or compund	S°_{298} cal/mol K	S°_{298} J/mol K	Element or compound	S°_{298} cal/mol K	S°_{298} J/mol K
$H_2(g)$	31.208	130.57	$NO(g)$	50.347	210.65
$O_{2(g)}$	49.003	205.03	$NO_2(g)$	57.35	240.0
$H_2O(l)$	16.71	69.91	$O_3(g)$	57.08	238.8
$H_2O(g)$	45.104	188.72	$S(s)$	7.60	31.8
$C(s,gr)$	1.372	5.74	$H_2S(g)$	49.16	205.7
$CO(g)$	47.219	197.56	$SO_2(g)$	59.30	248.1
$CO_2(g)$	51.06	213.6	$Cl_2(g)$	53.288	222.96
$CH_4(g)$	44.492	186.15	$HCl(g)$	44.646	186.80
$C_2H_2(g)$	48.00	200.8	$Na(s)$	12.24	51.2
$C_2H_4(g)$	52.45	219.5	$NaCl(s)$	17.24	72.1
$C_2H_6(g)$	54.85	229.5	$NH_4Cl(s)$	22.6	94.6
$CH_3OH(l)$	30.3	127.	$NaHCO_3(s)$	24.3	102.
$C_2H_5OH(l)$	38.4	161.	$Na_2CO_3(s)$	32.26	135.0
$C_6H_6(l)$	41.30	172.8	$Ca(s)$	9.90	41.4
$C_6H_6(g)$	64.34	269.2	$CaO(s)$	9.50	39.7
$C_6H_{12}O_6(g)$	69.0	289.	$CaCO_3(s)$	22.2	92.9
$i\text{-}C_8H_{18}(l)$	101.1	423.	$Fe(s)$	6.52	27.3
$Si(s)$	4.50	18.8	$Fe_2O_3(s)$	20.89	87.4
$SiO_2(s,quartz)$	10.00	41.8	$Al(s)$	6.77	28.3
$N_2(g)$	45.77	191.5	$Al_2O_3(s)$	12.17	50.9
$NH_3(g)$	45.97	192.3			

TABLE 11.2

Standard entropies for common molecules and ions in aqueous solution

	S°_{298}			S°_{298}	
Species	**cal/mol K**	**J/mol K**	**Species**	**cal/mol K**	**J/mol K**
$Li^{+}(aq)$	3.2	13.4	$OH^{-}(aq)$	−2.57	−10.75
$Na^{+}(aq)$	14.1	59.0	$Cl^{-}(aq)$	13.5	56.5
$K(aq)$	24.5	102.5	$Br^{-}(aq)$	19.7	82.4
$Mg^{2+}(aq)$	−33.0	−138.	$I^{-}(aq)$	26.6	111.
$Ca^{2+}(aq)$	−12.7	−53.1	$HCO_3^{-}(aq)$	21.8	9.2
$Ba^{2+}(aq)$	2.3	10.	$CO_3^{2-}(aq)$	−13.6	−57.
$Mn^{2+}(aq)$	−17.6	−74.	$CH_3COOH(aq)$	42.7	179.
$Fe^{2+}(aq)$	−32.9	−138.	$CH_3COO^{-}(aq)$	20.7	86.6
$Fe^{3+}(aq)$	−75.5	−316.	$NO_2^{-}(aq)$	29.4	123.
$Cu^{2+}(aq)$	−23.8	−99.6	$NO_3^{-}(aq)$	35.0	146.
$Zn^{2+}(aq)$	−26.8	−112.1	$PO_4^{3-}(aq)$	−52.	−218.
$Al^{3+}(aq)$	−76.9	−322.	$SO_3^{2-}(aq)$	−7.	−29.
$NH_4^{+}(aq)$	27.1	113.	$SO_4^{2-}(aq)$	4.8	20.
$CO_2(aq)$	28.1	118.	$ClO^{-}(aq)$	10	42.
$NH_3(aq)$	26.6	111.	$ClO_3^{-}(aq)$	38.8	162.
$Br_2(aq)$	31.2	131.	$Cr_2O_7^{2-}(aq)$	62.6	262.
$I_2(aq)$	32.8	137.	$MnO_4^{-}(aq)$	45.7	191.

Reaction Entropies

$$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

$$\Delta S_r^\circ = S_m^\circ(CO_2, g) + 2\,S_m^\circ(H_2O, g) - S_m^\circ(CH_4, g) - 2\,S_m^\circ(O_2, g)$$
$$= 213.74 + 2(188.83) - 186.26 - 2(205.14) = -5.14\ J/K$$

$$\Delta H_r^\circ = \Delta H_f^\circ(CO_2, g) + 2\,\Delta H_f^\circ(H_2O, g) - \Delta H_f^\circ(CH_4, g) - 2\Delta H_f^\circ\,(O_2, g)$$
$$= (-393.51) + 2(-241.82) - (-74.81) - 0 = -802.34\ kJ$$