Entropy and Free Energy

Problem Set 7

1) Predict the sign of $\Delta_r S$ for the following reactions:

(a) $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$

(b) $SO_2(g) + CaO(s) \rightarrow CaSO_3(s)$

(c) $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$

(d) $Ni(s) + 2\ HCl(aq) \rightarrow H_2(g) + NiCl_2(aq)$

2) Atkins 8/e, #3.36

Lysozyme transition (folded to unfolded) occurs at T = 75.5ºC with ΔH = 509 J/mole

ΔC_p = 6.28 J/K-mol, assume independent of T.

What is ΔS for unfolding at 25ºC?

3) Calculate the Third Law Entropy of Oxygen at 25ºC

Some information about oxygen on following slides....

From Wikipedia:

A total of 6 different phases of solid oxygen are known to exist: [1][5]

α-phase: *light sky-blue* — forms at 1 atm

β-phase: *pink* — forms at room temperature and high pressure

γ-phase: only stable below room temperature

δ-phase: *orange* — forms at room temperature by applying a pressure of 9 GPa [9 GPa = (9 x 10^9 Pa) x (1atm/101325 Pa) = 90,000 atm.]

ε-phase: *dark-red* — forms at room temperature at pressures greater than 10 GPa

ζ-phase: *metallic* — forms at pressures greater than 96 GPa

It has been known that oxygen is solidified into a state called the β-phase at room temperature by applying pressure, and with further increasing pressure, the β-phase undergoes phase transitions to the δ-phase at 9 GPa and the ε-phase at 10 GPa; and, due to the increase in molecular interactions, the pink color of the β-phase changes into orange (δ-phase) and red (ε-phase), and the red color of the ε-phase further changes to black with increasing pressure. It was found that a ζ-phase appears at 96 GPa when ε-phase oxygen is further compressed.[5]

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New Phase Diagram of Oxygen at High Pressures and Temperatures

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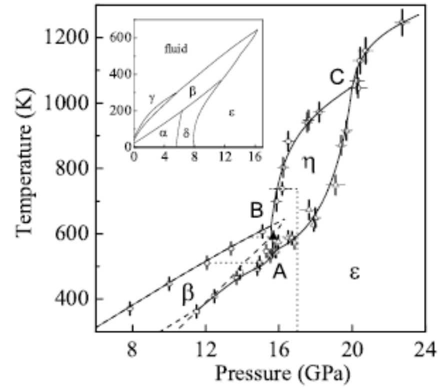


Heat capacity of Oxygen from

(1) *International Critical Tables (J/K-mol)*

(2) *1929 JACS paper by Giauque and Johnson*

O_2, Solid (6)	
O_I	
15	9.20
18	11.25
21	16.7

O_2, Solid.—(Cont'd) T, °K	C_p
O_{II}	
30	27.9
36	36.8
39	41.8
O_{III}	
46	45.2
O_2, Liquid (6)	
57 to 73	53.2
O_2, Gas (27)	
90	32.6
100	32.4
150	29.4
200	29.7
250	28.4
300	29.4

TABLE I

HEAT CAPACITY OF OXYGEN

Molecular weight, 32.000. Series I, 3.8387 moles; Series II, 3.7762 moles; Series IV, 3.9498 moles; Series V, 3.7929 moles.

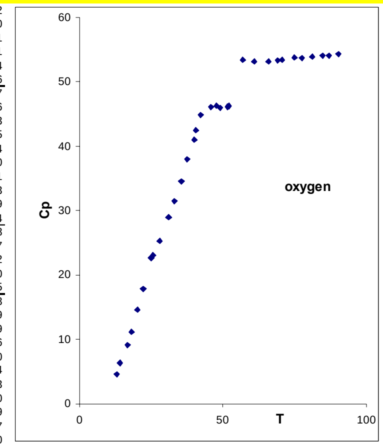
Series	T, °K.	ΔT, °K.	C_p/mole in cal./deg.	Series	T, °K.	ΔT, °K.	C_p/mole in cal./deg.
V	12.97	2.445	1.10	V	40.18	2.090	9.92
IV	14.14	1.389	1.52	II	40.67	1.474	10.16
V	15.12	1.685	1.60	V	42.21	1.903	10.73
IV	15.57	1.323	1.79		Transition at 43.76°		
II	16.65	1.324	2.33	IV	45.90	3.825	11.02
V	16.80	1.496	2.18	II	47.76	2.055	11.07
IV	16.94	1.120	2.25	V	48.11	3.723	11.01
IV	18.13	1.120	2.67	IV	48.97	2.208	10.99
II	18.32	1.604	2.71	II	50.55	3.152	11.01
V	18.45	1.676	2.79	V	51.68	3.338	11.03
IV	19.34	1.197	3.07	IV	52.12	3.979	11.06
II	20.26	1.596	3.50		Melting Point at 54.39°		
V	20.33	1.923	3.52	V	56.95	3.300	12.76
IV	20.85	1.494	3.60	II	57.95	3.056	12.72
II	21.84	1.317	4.20	V	60.97	4.596	12.71
IV	22.24	1.238	4.27	II	61.48	3.944	12.71
V	22.24	1.776	4.40	II	65.57	2.887	12.71
	Transition at 23.66°			V	65.92	4.282	12.71
IV	25.02	0.905	5.42	I	68.77	3.277	12.73
II	25.61	1.618	5.57	II	69.12	4.159	12.75
V	25.61	1.981	5.47	V	70.67	5.104	12.77
IV	26.75	2.494	5.75	I	71.38	3.245	12.78
V	28.00	2.781	6.05	II	73.31	3.848	12.81
II	28.08	2.405	6.42	I	74.95	3.767	12.85
IV	29.88	3.699	6.61	V	75.86	5.070	12.80
II	30.63	2.582	6.94	II	77.58	4.632	12.84
V	31.08	3.260	6.93	I	78.68	3.640	12.83
IV	33.05	2.580	7.52	V	81.13	5.305	12.88
II	33.33	2.787	7.73	II	82.31	4.748	12.86
V	34.41	3.244	8.08	I	82.96	4.681	12.88
IV	35.57	2.423	8.26	I	84.79	3.704	12.93
II	35.77	2.290	8.49	V	86.43	5.151	12.91
V	37.59	3.037	9.08	II	86.61	4.619	12.95
IV	37.85	2.024	9.12	II	86.97	4.526	12.92
II	38.47	2.936	9.80	I	87.32	3.924	12.91
IV	39.99	2.122	9.80	V	90.33	2.612	12.99

Oxygen at one atmosphere phase transitions **8.31451**

	T	□H/R K	□H J/K-mol
I to II	23.66	11.28	
II to III	43.75	89.4	
III to liquid	54.39	53.5	444.8
liq to gas	90.18		6820

from ICT	T (K) K	Cp J/mol-K
I	15	9.20
	18	11.25
	21	16.70
II	30	27.90
	36	36.80
	39	41.80
III	46	45.20
liquid	57	53.20
	60	53.20
	65	53.20
	70	53.20
	73	53.20
	90	32.60
gas	100	32.40
	150	29.40
	200	29.70
	250	28.40
	300	29.40

T K	Cp cal/K-mole	J/K-mol
12.97	1.10	4.602
14.14	1.52	6.360
16.80	2.18	9.121
18.13	2.67	11.171
20.26	3.50	14.644
22.24	4.27	17.866
25.02	5.42	22.677
25.61	5.52	23.096
28.00	6.05	25.313
31.08	6.93	28.995
33.05	7.52	31.464
35.57	8.26	34.560
37.59	9.08	37.991
39.99	9.80	41.003
40.67	10.16	42.509
42.21	10.73	44.894
45.90	11.02	46.108
47.76	11.07	46.317
48.97	10.99	45.982
51.68	11.03	46.150
52.12	11.06	46.275
56.95	12.76	53.388
60.97	12.71	53.179
65.92	12.71	53.179
69.12	12.75	53.346
70.67	12.77	53.430
74.95	12.85	53.764
77.58	12.84	53.723
81.13	12.88	53.890
84.79	12.93	54.099
86.97	12.92	54.057
90.33	12.99	54.350



How would you go about completing this calculation? Describe each term in the final result.

4) Measuring γ

- A classic physical chemistry experiment measures the heat capacity ratio of a gas. The gas in introduced into a large container (carboy) with pressure a bit above atmospheric pressure. The system comes to equilibrium, and the pressure (p_1) is measured.
  The stopper is released and then quickly replaced; the pressure is now equal to the pressure in the room, p_2. After the system has time to return to room temperature, the pressure is again measured (p_3).
- If the expansion is assumed to be adiabatic and reversible, show that

$$\gamma = C_p/C_v = \{\ln (p_1/p_2) / \ln (p_1/p_3)\}$$

- Some argue that the expansion is irreversible at constant $p_2 = p_{ex}$
  This gives a different equation (below), but similar numbers if $p_1 >> p_2$.)

$$\gamma = C_p/C_v = \{ p_3(p_2-p_1) / p_2(p_3-p_1)\}$$