

1(25). The temperature dependence of the molar heat capacity of gaseous ethane is given by

$$(C_{p,m}^{\circ}/R) = (0.06436) + (2.137 \times 10^{-2} \text{ K}^{-1})T - (8.263 \times 10^{-6} \text{ K}^{-2})T^2 + (1.024 \times 10^{-9} \text{ K}^{-3})T^3$$

A one-molar sample of ethane at 25 °C is isobarically heated to 1000 K by placing it in an oven at 1500 K. Calculate

a) q b) w c) ΔH d) ΔU

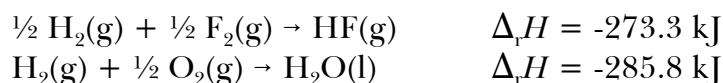
e) $\Delta S(\text{system})$ f) $\Delta S(\text{surroundings})$ g) $\Delta S(\text{universe})$

2(25). The volume of the ethane sample in the first question is isothermally and reversibly decreased from 250 L to 100 L at 1000 K. Calculate

a) q b) w c) ΔH d) ΔU

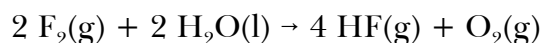
e) $\Delta S(\text{system})$ f) $\Delta S(\text{surroundings})$ g) $\Delta S(\text{universe})$

3(25). Use the thermochemical information at 298 K provided



$S/(\text{J K}^{-1} \text{ mol}^{-1}) = 130.684$ for $\text{H}_2(\text{g})$, 202.78 for $\text{F}_2(\text{g})$, 173.779 for $\text{HF}(\text{g})$, 205.138 for $\text{O}_2(\text{g})$, 69.91 for $\text{H}_2\text{O}(\text{l})$

to calculate $\Delta_r H$ and $\Delta_r S$ for



4(20). We know that for nonmetals $\Delta S = C_p/3$ from $T = 0$ to the lowest temperature at which a C_p value is given. For a metal at very low temperature, the heat capacity consists of two contributions

$$C_p = \alpha T^3 + \gamma T$$

Derive a similar expression for ΔS from $T = 0$ to the lowest temperature at which a C_p value is given.

5(15). Consider an ensemble of 1000 isolated systems (same energy E , volume V , and number of particles, N). The number of ways of having a_1 systems in state 1, a_2 systems in state 2, etc. is $W = A!/a_1!a_2!\dots$. Calculate the maximum value of W for a simple ensemble consisting of 4 states. (Hint: logarithms)

5(15). For pyradine

$T/(K)$	13.08	21.26	28.53	35.36	48.14	64.01
$C_p/(\text{cal K}^{-1} \text{mol}^{-1})$	1.063	2.888	4.610	6.049	8.060	9.739

82.91	101.39	119.37	132.32	151.57	167.60	179.44	193.02
11.093	12.156	13.175	13.940	15.161	16.265	17.150	18.276

201.61	212.16	223.74	239.70	254.41	273.75	293.93	307.16
19.081	20.183	22.545	29.213	29.765	30.575	31.521	32.159

$$S_{10} = 0.166 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\Delta_{\text{fus}}H = 1978 \text{ cal mol}^{-1} \text{ at } 231.49 \text{ K}$$

Explain in detail how to find S_{298} .