

KMM 2621 Physical Chemistry for Engineers

Homework 3- Second Law

P1. Calculate ΔS (for the system) when the state of 2 mol diatomic perfect gas molecules, for which $C_{p,m} = 3.5 R$, is changed from 25°C and 1.5 atm to 135°C and 7 atm. How do you rationalize the sign of ΔS ?

P2. A sample consisting of 2 mol of diatomic perfect gas molecules at 250 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Given that $C_{V,m} = 27.5 \text{ J/mol K}$, calculate q , w , ΔU , ΔH , and ΔS .

P3. Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.5 bar increases from 1.2 dm³ to 4.6 dm³ in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{\text{ex}} = 0$, and (c) an adiabatic reversible expansion.

P4. Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions that bring about the Antarctic ozone hole. The thermodynamic data for the sublimation of mono-, di-, and trihydrates to nitric acid and water vapours given as below.



for $n = 1, 2$, and 3 . Given $\Delta_r G^0$ and $\Delta_r H^0$ for these reactions at 220 K, use the Gibbs–Helmholtz equation to compute $\Delta_r G^0$ at 190 K.

| n | 1 | 2 | 3 |
|---------------------------------|------|------|------|
| $\Delta_r G^0 \text{ (kJ/mol)}$ | 46.2 | 69.4 | 93.2 |
| $\Delta_r H^0 \text{ (kJ/mol)}$ | 127 | 188 | 237 |

P5. Derive Maxwell's relations.