

PHYSICAL CHEMISTRY 5200

MIDTERM EXAM

October 7, 2021

Please write neatly and clearly, and show all working. Allocate time to each question in proportion to the available credit. Keep any explanations brief and clear.

NAME

SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

$$N_A \text{ or } L = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$k \text{ or } k_B = R/N_A$$

$$dU = dq + dw$$

$$dw = -p_{\text{ex}} dV$$

$$\text{Perfect gas: } pV = nRT \quad \text{and}$$

$$\text{van der Waals gas: } p = nRT/(V-b) - a(n/V)^2$$

$$\text{Adiabat: } pV^\gamma \text{ is constant}$$

$$H = U + pV$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$dS = dq_{\text{rev}}/T$$

$$\gamma = C_p/C_v$$

$$C_p - C_v = nR$$

$$\text{Heat engine } \varepsilon = (T_h - T_c)/T_h$$

1) 40 points

(a) 1 mol of CO_2 (g), the system, initially at $p = 7 \times 10^5$ Pa and $V = 3 \times 10^{-3} \text{ m}^3$, is expanded reversibly and isothermally until $p = 1 \times 10^5$ Pa. C_p is 37 J K^{-1} . Calculate q , w , ΔU , ΔH and ΔS for the system.

(b) Suppose instead, from the same initial conditions, 1 mol of CO_2 (g) expands until $p = 1 \times 10^5$ Pa reversibly and adiabatically. Now what are q , w , ΔU , ΔH and ΔS for the system?

a) At const. T , $\Delta U = \Delta H = 0$ so $q = -w$,
 Reversible so $dw = -pdV = -\frac{RT}{V}dV \therefore w = \int_{V_1}^{V_2} -\frac{RT}{V}dV = -RT \ln\left(\frac{V_2}{V_1}\right)$,
 $\frac{V_2}{V_1} = p_1/p_2 = 7$ so $w = -RT \ln 7 \approx -4090 \text{ J}$. $q = +4090 \text{ J}$,
 $\Delta S = q_{\text{rev}}/T = 16.2 \text{ J K}^{-1}$.

b) $q = 0$ and $\Delta S = 0$, $\Delta U = C_V \cdot \Delta T$. $\gamma = \frac{C_p}{C_V} = \frac{C_p}{C_p - R} = \frac{37}{37 - 8.314} = 1.29$
 $\frac{p_1}{p_2} = \left(\frac{V_2}{V_1}\right)^\gamma = 7 \therefore \ln 7 = \gamma \ln\left(\frac{V_2}{V_1}\right) \therefore \ln\left(\frac{V_2}{V_1}\right) = \frac{\ln 7}{\gamma} = 1.51 \therefore \frac{V_2}{V_1} = 4.52$
 $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \therefore T_2 = \frac{p_2 V_2}{p_1 V_1} \cdot T_1 = \frac{1}{7} \times 4.52 \times T_1 = 0.646 T_1$
 $T_1 = \frac{p_1 V_1}{nR} = \frac{7 \times 10^5 \text{ Pa} \times 3 \times 10^{-3} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 1 \text{ mol}} = 253 \text{ K} \therefore T_2 = 163 \text{ K}$
 $\therefore \Delta T = -90 \text{ K}$,
 $C_V = C_p - R = 28.7 \text{ J K}^{-1} \therefore \Delta U = C_V \Delta T = -2580 \text{ J} = w$,
 $\Delta H = C_p \cdot \Delta T = -3330 \text{ J}$.

2) 20 points

ΔC_p for a chemical reaction is given by $a + b/T^2$. By how much does the reaction enthalpy ΔH alter when the temperature changes from T_1 to T_2 ? How much does the entropy change ΔS alter by going from T_1 to T_2 ?

$$\begin{aligned} \text{Change in } \Delta H &= \int_{T_1}^{T_2} \Delta C_p \cdot dT = \int_{T_1}^{T_2} (a + bT^{-2}) dT \\ &= \left[aT - bT^{-1} \right]_{T_1}^{T_2} = a(T_2 - T_1) - b \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \end{aligned}$$

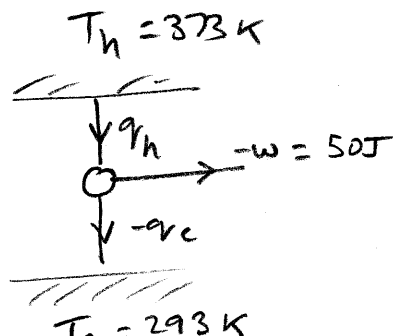
$$\begin{aligned} \text{Change in } \Delta S &= \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT = \int_{T_1}^{T_2} (aT^{-1} + bT^{-3}) dT \\ &= \left[a \ln T - \frac{1}{2} b T^{-2} \right]_{T_1}^{T_2} = a \ln \left(\frac{T_2}{T_1} \right) - \frac{1}{2} b \left(\frac{1}{T_2^2} - \frac{1}{T_1^2} \right) \end{aligned}$$

3) 20 points

(a) Imagine an ideal Carnot heat engine operates between $100\text{ }^\circ\text{C}$ and $20\text{ }^\circ\text{C}$. How much heat will be rejected at $20\text{ }^\circ\text{C}$ when the engine performs work $-w = 50\text{ J}$?

(b) An ideal Carnot heat engine operates in reverse to move heat from cold ($5\text{ }^\circ\text{C}$) to hot ($25\text{ }^\circ\text{C}$). How much work must be provided to move heat $q_c = 1000\text{ J}$ from the low temperature region?

a)



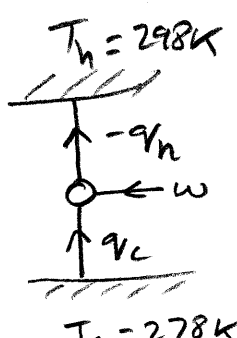
efficiency is $\frac{-w}{q_h} = \frac{T_h - T_c}{T_h} = \frac{373 - 293}{373} = 0.214$

$q_h = \frac{-w}{0.214} = 233\text{ J}$

$$q_h = -w - q_c \quad \therefore \quad q_c = -w - q_h = 50\text{ J} - 233\text{ J} = \underline{\underline{-183\text{ J}}}$$

183 J rejected at 293 K.

b)



$\frac{w}{-q_h} = \frac{298 - 278}{298} = 0.0671$

$q_c + w = -q_h = \frac{w}{0.0671}$

$$\therefore q_c = w \left(\frac{1}{0.0671} - 1 \right) = 13.9 w$$

$$\therefore w = \frac{q_c}{13.9} = \underline{\underline{72\text{ J}}}$$

4) 20 points

(a) A system changes in a way that its entropy decreases by 36 J K^{-1} . During this change 15 kJ mol^{-1} left the system and entered the surroundings at 298 K . Deduce whether this change is spontaneous (irreversible) or not?

(b) For N_2 gas at 298 K and $1 \times 10^5 \text{ Pa}$, attractive forces between the molecules dominate over repulsions. Explain if you expect the gas to heat up, cool down or stay the same temperature if it undergoes a Joule-Thompson expansion.

a)

$$\Delta S_{\text{sys}} = -36 \text{ J K}^{-1}$$
$$\Delta S_{\text{surr}} = \frac{15 \text{ kJ mol}^{-1}}{298 \text{ K}} = 50.3 \text{ J K}^{-1}$$
$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \approx 14 \text{ J K}^{-1} > 0$$

\therefore spontaneous.

b) As p goes down, the molecules are separated against the intermolecular attraction. The energy comes from the kinetic energy of the molecules, so the average goes down, i.e., the temperature drops.