

Lecture 11 (Midterm Exam Review)

Thursday, October 10, 2024 10:03

Problem 1 : An elastomer is a polymer that can stretch and contract. In a perfect elastomer, the force opposing extension is proportional to the displacement x from the resting state of the elastomer, so $|\vec{F}| = k_f x$, where k_f is a constant. But suppose that the restoring force weakens as the elastomer is stretched, and this force constant has the form

$$\underline{k_f(x) = a - b\sqrt{x}}.$$

Evaluate the work done on extending the polymer from $x=0$ to a final displacement l .

Solution : from the correct equation

sheet, we know that $dw = -|\vec{F}| dz$.

To find the total work done, we integrate both sides of the equation

$$\int dw = \int_0^l F(x) dx$$

$$w = - \int_0^l k_f(x) x dx$$

$$w = - \int_0^l (a - b\sqrt{x}) x dx$$

$$w = - \left[\frac{1}{2} ax^2 - \frac{2}{5} bx^{5/2} \right]_0^l$$

$$w = \frac{2}{5} bl^{5/2} - \frac{1}{2} al^2$$

Problem 2: Suppose that attractions are the dominant interactions between

gas molecules, and the equation of state is

$$p = \frac{nRT}{V} - \frac{an^2}{V^2}$$

Derive an expression for the work of reversible, isothermal expansion of such a gas. Compared with a perfect gas, is more or less work done on the surroundings when it expands?

Solution: the expansion work is given by

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

For a reversible expansion, $p = p_{ex}$, so

$$dw = -pdV = -\left(\frac{nRT}{V} - \frac{an^2}{V^2}\right)dV$$

Integrating both sides:

$$\begin{aligned}
 w &= - \int_{V_i}^{V_f} \left(\frac{nRT}{V} - a \frac{n^2}{V^2} \right) dV \\
 &= - \left[nRT \ln V + a \frac{n^2}{V} \right]_{V_i}^{V_f}
 \end{aligned}$$

$$w = -nRT \ln \frac{V_f}{V_i} - an^2 \left(\frac{1}{V_f} - \frac{1}{V_i} \right)$$

$$w_{\text{sur}} = \underbrace{+nRT \ln \frac{V_f}{V_i}}_{\text{perfect gas}} + \underbrace{an^2 \left(\frac{1}{V_f} - \frac{1}{V_i} \right)}_{< 0}$$

For a expansion, $V_f > V_i$, therefore $\frac{1}{V_f} < \frac{1}{V_i}$, so $an^2 \left(\frac{1}{V_f} - \frac{1}{V_i} \right) < 0$.

\therefore The work done on the surroundings is smaller than that for a

perfect gas.

Problem 3 : An average human produces about 10 MJ or 10,000,000 joules of heat each day through metabolic activity.

a) If a human body were an isolated system of mass 65 kg with the heat capacity of water, what temperature rise would the body experience?

Solution : we are working under constant pressure, so we have

$$q_p = C_p \Delta T$$

$$C_p \approx n \cdot C_{p,m}^{\ominus}(\text{H}_2\text{O}, \ell)$$

where n is the amount of "water"

in moles.

$$M = 18.0158 \text{ g} \cdot \text{mol}^{-1}$$

$$C_{p,m}^{\ominus} = 75.29 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta T = \frac{q_p}{n C_{p,m}^{\ominus}}$$

$$= \frac{10,000,000 \text{ J}}{(65,000 \text{ g}) / (18.0158 \text{ g} \cdot \text{mol}^{-1}) \cdot 75.29}$$

$$\Delta T = 37 \text{ K}$$

b) Human bodies are actually open systems, and the main mechanism of heat loss is through the evaporation of water. What mass of water should be evaporated each day to maintain a constant temperature? Nk

$$\Delta_{\text{vap}} H^{\ominus}(\text{H}_2\text{O}, \text{l} \rightarrow \text{H}_2\text{O}, \text{g}) = 44,016 \text{ J}\cdot\text{mol}^{-1}$$

Solution: now, all the heat generated needs to be consumed by the vaporization of water.

$$n = \frac{q_p}{\Delta_{\text{vap}} H^{\ominus}} = \frac{1.0 \times 10^7 \text{ J}}{44,016 \times 10^3 \text{ J}\cdot\text{mol}^{-1}}$$

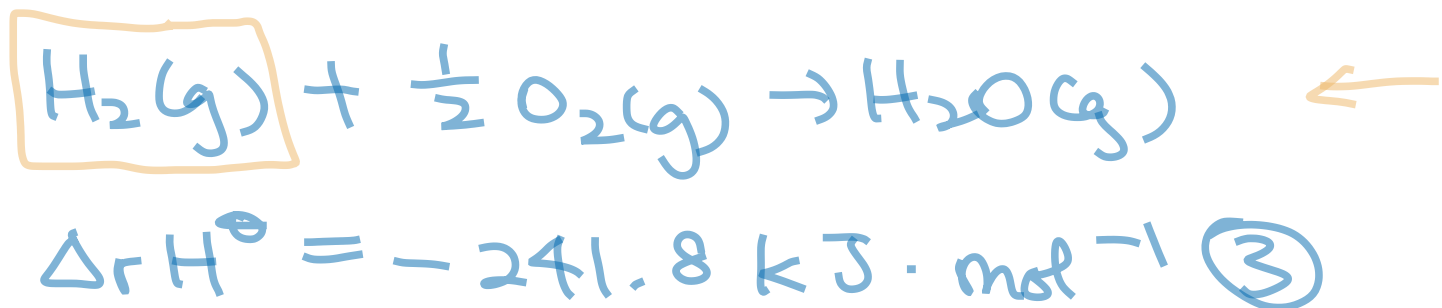
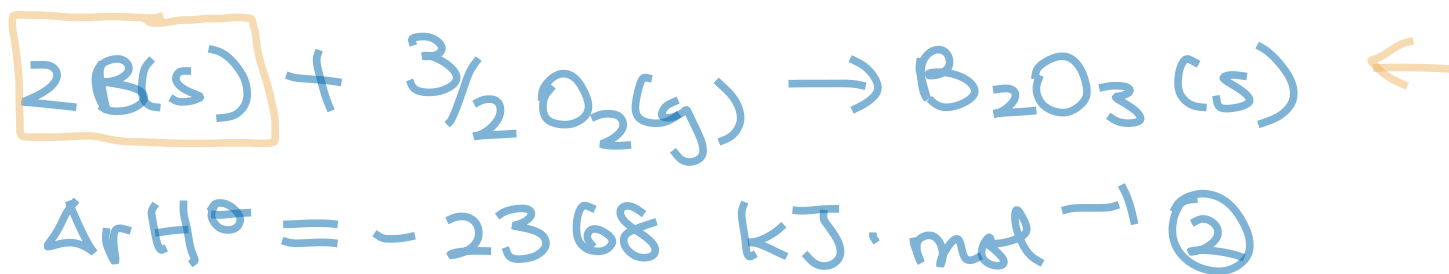
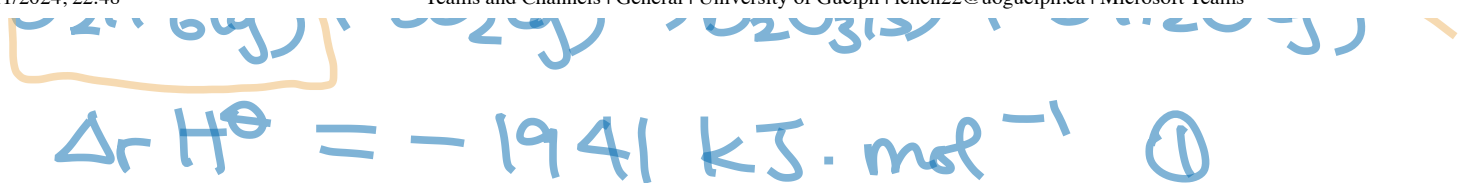
$$n = 2.27 \times 10^2 \text{ mol}$$

$$m = nM = (2.27 \times 10^2 \text{ mol})(18.0158 \text{ g}\cdot\text{mol}^{-1})$$

$$m = 4.1 \text{ kg}$$

Problem 4: From the following data determine $\Delta_f H^{\ominus}$ for diborane, B_2H_6 at 298 K:





Solution: start by writing the formation reaction for diborane.



$$\begin{aligned} \Delta_f H^\ominus &= 3 \cdot \Delta_r H^\ominus(3) + \Delta_r H^\ominus(2) - \\ &= [3 \cdot (-241.8) + (-2368)] - (-) \end{aligned}$$

$$\Delta_f H^\ominus = -1152.4 \text{ kJ} \cdot \text{mol}^{-1}$$

Problem 5 : Suppose that S is regarded as a function of p and T so that

$$dS = \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT$$

Use $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$ and an

appropriate Maxwell relation + show that

$$T dS = C_p dT - \alpha T V dp$$

where $\alpha = \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial T}\right)_p$.

Solution : we start by substituting



(20)

$\frac{C_p}{T}$ for $\left(\frac{\partial S}{\partial T}\right)_p$.

$$dS = \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT$$

$$dS = \left(\frac{\partial S}{\partial p}\right)_T dp + \frac{C_p}{T} dT$$

$$TdS = \left(\frac{\partial S}{\partial p}\right)_T T dp + C_p dT$$

Use Maxwell relation $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

$$TdS = -\underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{\alpha \cdot V} T dp + C_p dT$$

$$TdS = -\alpha TV dp + C_p dT$$

$$\therefore TdS = C_p dT - \alpha TV dp$$

