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 <u>work</u> done on extending the polymer from <u>$x=0$</u> to a final displacement <u>l</u>.

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

$$\int dw = \int_0^{\ell} F(x)\,dx$$

$$w = -\int_0^{\ell} k_f(x)\,x\,dx$$

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

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

$$\boxed{w = \frac{2}{5}b\ell^{5/2} - \frac{1}{2}a\ell^2}$$

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

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

Integrating both sides:

$$w = -\int_{V_i}^{V_f} \left(\frac{nRT}{V} - a\frac{n^2}{V^2}\right) dV$$

$$= -\left[nRT \ln V + a\frac{n^2}{V}\right]_{V_i}^{V_f}$$

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

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

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

∴ 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

$$q_p = C_p \Delta T$$

$$C_p \approx n \cdot C^{\ominus}_{p,m}(H_2O, l)$$

where n is the amount of "water"

in moles.

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

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

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

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

$$\boxed{\Delta T = 37 \; K}$$

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? No

$\Delta_{vap}H^\ominus(H_2O, l \rightarrow H_2O, g) = 44.016$ J·m

Solution: now, all the heat generat
needs to be consumed by the vapor-
ization of water.

$$n = \frac{q_p}{\Delta_{vap}H^\ominus} = \frac{1.0\times10^7\ \cancel{J}}{44.016\times10^3\ \cancel{J}\cdot mol^{-1}}$$

$$n = 2.27\times10^2\ mol$$

$$m = nM = (2.27\times10^2\ mol)(18.0158\ g\cdot mo$$

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

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

$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$ ←

$\Delta_r H^\ominus = -1941\ kJ \cdot mol^{-1}$ (1)

$2B(s) + \frac{3}{2} O_2(g) \rightarrow B_2O_3(s)$ ←

$\Delta_r H^\ominus = -2368\ kJ \cdot mol^{-1}$ (2)

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$ ←

$\Delta_r H^\ominus = -241.8\ kJ \cdot mol^{-1}$ (3)

Solution: start by writing the form
reaction for diborane.

$2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$

$\Delta_f H^\ominus = 3 \cdot \Delta_r H^\ominus(3) + \Delta_r H^\ominus(2) -$

$= [3 \cdot (-241.8) + (-2368) - (-$

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

Problem 5 : Suppose that S is regarded as a function of p and 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 t show that

$$TdS = C_p\, dT - \alpha T V dp$$

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

Solution : we start by substituting

$\boxed{\frac{c_p}{T}}$ 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 $\left(\frac{\partial S}{\partial p}\right)_T = \boxed{-\left(\frac{\partial V}{\partial T}\right)_p}$

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

$$TdS = -\alpha T V dp + c_p dT$$

$$\boxed{\therefore TdS = c_p dT - \alpha T V dp}$$