Lecture 10

Thursday, October 12, 2023 11:28

Midterm Exam Review

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

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

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

$$dw = -|\vec{F}|\, dz$$

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

$$w = \int_0^\ell k f(x)\,x\,dx$$

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

$$= \int_0^\ell ax - bx^{3/2}\,dx$$

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

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

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② Recent communication with the inhabitants of Proxima Centauri b have revealed that they have a Celsius-type temperature scale, but based on the melting point

(0 °Cb) and boiling point (100 °Cb) of their most common substance, hydrogen. Further communications have revealed that the Proxima Centaurians know about perfect gas behaviour, and they find that in the limit of zero pressure, the value of pV is 28 $\text{dm}^3\cdot\text{atm}$ at 0 °Cb and 40 $\text{dm}^3\cdot\text{atm}$ at 100 °Cb. What is the absolute zero of temperature on their temperature scale?

$$pV = nRT$$

$$pV \propto T$$ ← absolute temperature

$$T = \theta + \boxed{\theta_0}$$ ← absolute 0 on the °Cb scale

$$pV \propto (\theta + \theta_0)$$

$$\boxed{pV = a(\theta + \theta_0)}$$

$$28 = a(0 + \theta_0)$$

$$40 = a(100 + \theta_0)$$

$$28 = a\theta_0$$

$$a = \frac{28}{\theta_0}$$

$$40 = 100a + \theta_0 a$$

$$40 = 100\left(\frac{28}{\theta_0}\right) + 28$$

$$\boxed{\theta_0 = 233 \text{ K}}$$

On the °Cb scale, absolute zero is −233 °Cb.

③ From the following data, determine $\boxed{\Delta_f H^\ominus}$ for diborane, $\boxed{B_2H_6(g)}$, at 298 K.

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

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

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

$$\Delta_r H^\ominus = -2368 \text{ kJ} \cdot \text{mol}^{-1}$$

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

$$\Delta_r H^\ominus = -241.8 \text{ kJ} \cdot \text{mol}^{-1}$$

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

$$\cancel{B_2O_3(s)} + \cancel{3H_2O}(g) \rightarrow \boxed{B_2H_6(g)} + \cancel{3O_2(g)} \quad -①$$

$$\boxed{2B(s)} + \cancel{\tfrac{3}{2}O_2(g)} \rightarrow \cancel{B_2O_3(s)} \quad +②$$

$$\boxed{3H_2(g)} + \cancel{\tfrac{3}{2}O_2(g)} \rightarrow \cancel{3H_2O}(g) \quad +3③$$

$$\Delta_f H^\circ[B_2H_6(g)] = 3 \cdot \Delta_r H^\circ(\text{RXN } 3) + \Delta_r H^\circ(\text{RXN } 2) - \Delta_r H^\circ(\text{RXN } 1)$$

$$= 3 \cdot (-241.8) + (-2368) - (-1941)$$

$$\boxed{\Delta_f H^\circ[B_2H_6(g)] = -1152 \text{ kJ} \cdot \text{mol}^{-1}}$$

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④ A sample consisting of 1.00 mol of perfect gas molecules at 27°C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: a) reversibly, and b) against a constant external pressure of 1.00 atm. In each case evaluate

ΔH, q, w, ΔU, ΔS, ΔS_{sur}, and ΔS_{tot}.

$\boxed{n = 1.00\ \text{mol}}$ $T = 27 + 273.15$

$\boxed{T = 300.15\ \text{K}}$

$\boxed{p_i = 3.00\ \text{atm} \qquad p_f = 1.00\ \text{atm}}$

a) $w = -nRT \ln\left(\frac{V_f}{V_i}\right)$ $pV = nRT$

$V = \frac{nRT}{p}$

$w = -nRT \ln\left(\frac{p_i}{p_f}\right)$

$$w = -(1.00\ \cancel{\text{mol}}) \cdot (8.3145\ \text{J} \cdot \cancel{\text{K}^{-1}} \cdot \cancel{\text{mol}^{-1}}) \cdot (300.15\ \cancel{\text{K}}) \cdot \ln\left(\frac{3.00\ \text{atm}}{1.00\ \text{atm}}\right)$$

$$\boxed{w = -2.74\ \text{kJ}}$$

$\Delta U = C_V \Delta T$ $\Delta H = C_p \Delta T$

$\boxed{\Delta U = 0}$ $\boxed{\Delta H = 0}$

$\Delta U = q + w$

$0 = q + (-2.74\ \text{kJ})$

$$\boxed{q = +2.74\ \text{kJ}}$$

$$\Delta S = \frac{q_{rev}}{T}$$

$$\Delta S = \frac{+2.74 \times 10^{3}\ \text{J}}{300.15\ \text{K}}$$

$$\boxed{\Delta S = +9.13\ \text{J}\cdot\text{K}^{-1}}$$

$$\boxed{\Delta S_{tot} = 0}$$ reversible process

$$\Delta S_{tot} = \Delta S + \Delta S_{sur}$$

$$0 = +9.13\ \text{J}\cdot\text{K}^{-1} + \Delta S_{sur}$$

$$\boxed{\Delta S_{sur} = -9.13\ \text{J}\cdot\text{K}^{-1}}$$

b) $w = -p_{ex}(V_f - V_i)$

$$= -p_{ex}\left(\frac{nRT}{p_f} - \frac{nRT}{p_i}\right)$$

$$= -nRT\left(\frac{p_{ex}}{p_f} - \frac{p_{ex}}{p_i}\right)$$

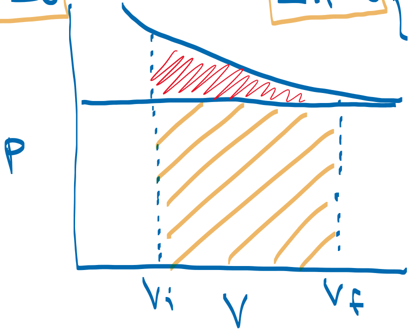
$$= -(1.00\ \text{mol})\cdot(8.3145\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$$

$$\cdot(300.15\ \text{K})\cdot\left[\frac{1.00\ \text{atm}}{1.00\ \text{atm}} - \frac{1.00\ \text{atm}}{3.00\ \text{atm}}\right]$$

$$\boxed{w = -1.66\ \text{kJ}}$$

$$\Delta U = C_v\Delta T \qquad \Delta H = C_p\Delta T$$

$$\boxed{\Delta U = 0} \qquad \boxed{\Delta H = 0} \qquad |w_{rev}| > |w|$$



$$\Delta U = q + w$$

$$0 = q + (-1.66\ \text{kJ})$$

$$\boxed{q = +1.66\ \text{kJ}}$$

S is a state function.

$$\boxed{\Delta S = +9.13 \text{ J} \cdot \text{K}^{-1}}$$

$$\Delta S_{sur} = \frac{q_{sur}}{T}$$

$$= -\frac{q}{T}$$

$$= \frac{-1.66 \times 10^{3} \text{ J}}{300.15 \text{ K}}$$

$$\boxed{\Delta S_{sur} = -5.54 \text{ J} \cdot \text{K}^{-1}}$$

$$\Delta S_{tot} = \Delta S + \Delta S_{sur}$$

$$= +9.13 \text{ J} \cdot \text{K}^{-1} + (-5.54 \text{ J} \cdot \text{K}^{-1})$$

$$\boxed{\Delta S_{tot} = +3.59 \text{ J} \cdot \text{K}^{-1}}$$

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⑤ Start with

$$H = U + pV$$

from the exact differential

$$dH = dU + pdV + Vdp$$

then substitute

$$\boxed{dU = TdS - pdV}$$

Find the resulting Maxwell relation.

$$H = U + pV$$

$U(S, V)$

$H(S, p)$

$$dH = dU + d(pV)$$

$$dH = \boxed{dU} + pdV + Vdp$$

$$dH = TdS - \cancel{pdV} + \cancel{pdV} + Vdp$$

$$\boxed{dH = TdS + Vdp}$$

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

$$dH = TdS + V\,dp$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_s dp$$

$$T = \left(\frac{\partial H}{\partial S}\right)_p \qquad V = \left(\frac{\partial H}{\partial p}\right)_s$$

$$\boxed{\left(\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right)_s = \left(\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_s\right)_p}$$