# Chemistry 431
# Exam Number 2
# Fall 2023
# 50 Minutes
# Solutions

$R$ =8.3144 J mol$^{-1}$ K$^{-1}$

$R$=.08314 L bar mol$^{-1}$ K$^{-1}$

$k$=1.381 $\times 10^{-23}$ J molecule$^{-1}$K$^{-1}$

$h$=6.626 $\times 10^{-34}$ Js

$N_A$ = 6.022 $\times$ $10^{23}$ molecules mol$^{-1}$

1 kg = 1000. g

1 L = $10^3$ cm$^3$

$10^2$ cm = 1 m

$T = t + 273.15$

0.001 m$^3$ L$^{-1}$

Name:

1. Show that for any substance

$$\left(\frac{\partial P}{\partial V}\right)_H = -\frac{1}{\kappa V} - \frac{\beta_V}{\kappa}\frac{\left(\frac{\partial H}{\partial V}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_V}$$

where $\beta_V$ is the isobaric coefficient of thermal expansion and $\kappa$ is the isothermal compressibility.
(33 Points)
**Answer**:

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$\left(\frac{\partial P}{\partial V}\right)_H = \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_H + \left(\frac{\partial P}{\partial V}\right)_T$$

$$= \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_H - \frac{1}{\kappa V}$$

where $\kappa = -V^{-1}(\partial V/\partial P)_T$ is the isobaric coefficient of thermal expansion. Now

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

or

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta_V}{\kappa}$$

where $\beta_V = V^{-1}(\partial V/\partial T)_P$ is the isobaric coefficient of thermal expansion. Then

$$\left(\frac{\partial P}{\partial V}\right)_H = -\frac{1}{\kappa V} + \frac{\beta_V}{\kappa}\left(\frac{\partial T}{\partial V}\right)_H$$

Finally,

$$\left(\frac{\partial T}{\partial V}\right)_H \left(\frac{\partial V}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_V = -1$$

and

$$\left(\frac{\partial T}{\partial V}\right)_H = -\frac{\left(\frac{\partial H}{\partial V}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_V}$$

---

Name:

so

$$\left(\frac{\partial P}{\partial V}\right)_H = -\frac{1}{\kappa V} - \frac{\beta_V}{\kappa} \frac{\left(\frac{\partial H}{\partial V}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_V}$$

2. A bomb calorimeter of fixed volume has a measured heat capacity of 2246 J $K^{-1}$. When 0.125 grams of liquid methanol ($CH_3OH$) are burned in excess oxygen in the bomb calorimeter according to the balanced reaction

$$CH_3OH_{(\ell)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$$

the temperature of the calorimeter rises from 298.15 K to 299.27 K. Given that the standard molar enthalpies of formation of carbon dioxide gas and gas-phase water at 298.15 K are respectively $\Delta_{f,m}H^{\ominus}(CO_{2(g)}) = -393.5$ kJ mol$^{-1}$ and $\Delta_{f,m}H^{\ominus}(H_2O_{(g)}) = -241.8$ kJ mol$^{-1}$, calculate the standard molar enthalpy of formation of liquid methanol at 298.15 K.
(33 Points)
**Answer**:

$$q = \Delta_r U = -C\Delta T = -(2246 \text{ J K}^{-1})(299.27K - 298.15K) = -2515 \text{ J}$$

$$n = \frac{0.125 \text{ g}}{32.0 \text{ g mol}^{-1}} = 3.91 \times 10^{-3} \text{ mol} \quad \Delta_{r,m}U = \frac{-2515 \text{ J}}{3.91 \times 10^{-3} \text{ mol}} = -643355 \text{ J mol}^{-1}$$

$$\Delta_{r,m}H^{\ominus} = \Delta_{r,m}U + RT\Delta n = -643355 \text{ J mol}^{-1} + (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298\text{ K})(1.5) = -639.63 \text{ kJ mol}^{-1}$$

$$= \Delta_{f,m}H^{\ominus}(CO_{2(g)}) + 2\Delta_{f,m}H^{\ominus}(H_2O_{(g)}) - \Delta_{f,m}H^{\ominus}(CH_3OH_{(\ell)})$$

$$= -393.5 \text{ kJ mol}^{-1} + 2(-241.8 \text{ kJ mol}^{-1}) - \Delta_{f,m}H^{\ominus}(CH_3OH_{(\ell)})$$

$$\Delta_{f,m}H^{\ominus}(CH_3OH_{(\ell)}) = -237.5 \text{ kJ mol}^{-1}$$

Name:

3. Calculate the entropy change for the system, surroundings and universe when 20.0 grams of ice at -10.0° C are placed in a freezer with the thermostat set to -40.0° and allowed to come to equilibrium at constant pressure. The constant pressure heat capacity of solid water is $C_P = 37.6$ J mol$^{-1}$K$^{-1}$ and can be assumed to be temperature independent. (34 Points)

**Answer**:

$$n = \frac{20.0 \text{ g}}{18.0 \text{ g mol}^{-1}} = 1.11 \text{ mol}$$

$$\Delta S_{system} = C_P \ln \frac{T_f}{T_i} = (1.11\text{mol})(37.6 \text{ J mol}^{-1}\text{K}^{-1}) \ln \frac{233}{263} = -5.05 \text{ kJ mol}^{-1}$$

$$q_{system} = C_P \Delta T = (1.11 \text{ mol})(37.6 \text{ J mol}^{-1}\text{K}^{-1})(-30. \text{ K}) = -1253 \text{ J}$$

$$\Delta S_{surroundings} = \frac{-q_{system}}{T_{surroundings}} = \frac{1253 \text{ J}}{233 \text{ K}} = 5.37 \text{ J K}^{-1}$$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0.32 \text{ J K}^{-1} > 0$$

---

Name:

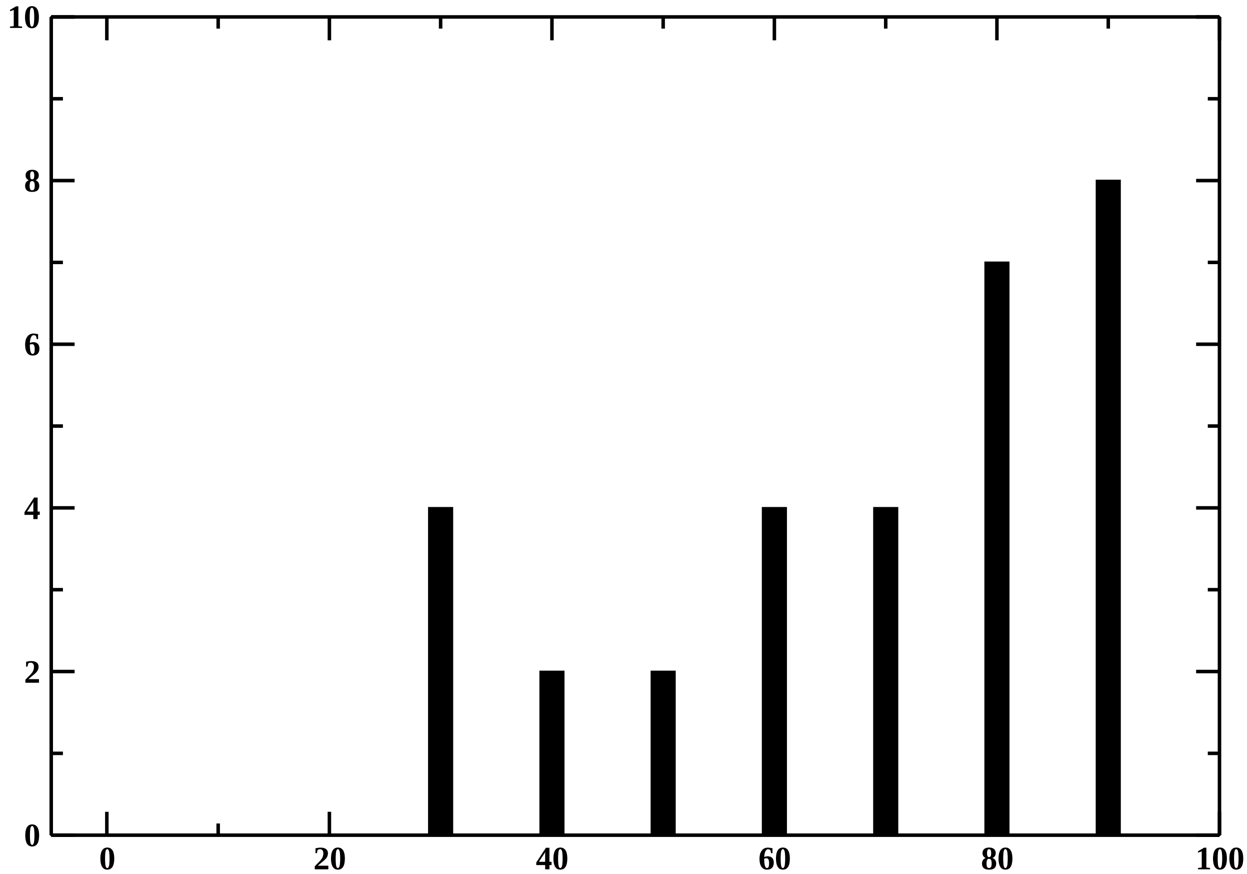


Figure 1: **High = 100, Median = 79, Mean = 73**