

Homework Set #4

4.28 A quantity of 0.35 mole of an ideal gas initially at 15.6° C is expanded from 1.2 L to 7.4 L. Calculate the values of w , q , ΔU , ΔS , and ΔG if the process is carried out (a) isothermally and reversibly, and (b) isothermally and irreversibly against an external pressure of 1.0 atm.

(a) For an isothermal process of an ideal gas, $\Delta U = 0$ and $\Delta H = 0$.

$$w = -nRT \ln \frac{V_2}{V_1} = - (0.35 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (288.8 \text{ K}) \ln \frac{7.4 \text{ L}}{1.2 \text{ L}}$$

$$= -1.53 \times 10^3 \text{ J} = -1.5 \times 10^3 \text{ J}$$

$$q = \Delta U - w = 1.53 \times 10^3 \text{ J} = 1.5 \times 10^3 \text{ J}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{1.53 \times 10^3 \text{ J}}{288.8 \text{ K}} = 5.30 \text{ J K}^{-1} = 5.3 \text{ J K}^{-1}$$

$$\Delta G = \Delta H - T \Delta S = 0 - (288.8 \text{ K}) (5.30 \text{ J K}^{-1}) = -1.5 \times 10^3 \text{ J}$$

(b) Since U , S , and G are state functions, ΔU , ΔS , ΔG depend only on the initial and final states and not on the path. Therefore, they are the same as above, that is

$$\Delta U = 0 \text{ J}$$

$$\Delta S = 5.3 \text{ J K}^{-1}$$

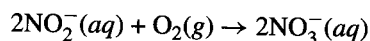
$$\Delta G = -1.5 \times 10^3 \text{ J}$$

w and q , however, are path dependent.

$$w = -P_{\text{ex}} \Delta V = - (1.0 \text{ atm}) (7.4 \text{ L} - 1.2 \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) = -6.3 \times 10^2 \text{ J}$$

$$q = \Delta U - w = 6.3 \times 10^2 \text{ J}$$

- 4.32 Certain bacteria in the soil obtain the necessary energy for growth by oxidizing nitrite to nitrate:



Given that the standard Gibbs energies of formation of NO_2^- and NO_3^- are $-34.6 \text{ kJ mol}^{-1}$ and $-110.5 \text{ kJ mol}^{-1}$, respectively, calculate the amount of Gibbs energy released when 1 mole of NO_2^- is oxidized to 1 mole of NO_3^- .

According to the chemical equation $2\text{NO}_2^-(aq) + \text{O}_2(g) \rightarrow 2\text{NO}_3^-(aq)$,

$$\begin{aligned}\Delta_r G^\circ &= 2\Delta_f G^\circ [\text{NO}_3^-(aq)] - 2\Delta_f G^\circ [\text{NO}_2^-(aq)] - \Delta_f G^\circ [\text{O}_2(g)] \\ &= 2(-110.5 \text{ kJ mol}^{-1}) - 2(-34.6 \text{ kJ mol}^{-1}) - 0 \text{ kJ mol}^{-1} \\ &= -151.8 \text{ kJ mol}^{-1}\end{aligned}$$

When 1 mole of NO_2^- is oxidized to 1 mole of NO_3^- ,

$$\Delta_r G^\circ = \frac{-151.8 \text{ kJ mol}^{-1}}{2} = -75.9 \text{ kJ mol}^{-1}$$

- 4.42 The pressure exerted on ice by a 60.0-kg skater is about 300 atm. Calculate the depression in freezing point. The molar volumes are $\bar{V}_L = 0.0180 \text{ L mol}^{-1}$ and $\bar{V}_S = 0.0196 \text{ L mol}^{-1}$.

The depression of freezing point can be obtained from the slope of the S-L curve in the phase diagram.

$$\begin{aligned}\frac{dP}{dT} &= \frac{\Delta \bar{H}}{T \Delta \bar{V}} = \frac{(6.01 \times 10^3 \text{ J mol}^{-1}) \left(\frac{1 \text{ L atm}}{101.3 \text{ J}} \right)}{(273.2 \text{ K}) (0.0180 \text{ L mol}^{-1} - 0.0196 \text{ L mol}^{-1})} \\ &= -135.7 \text{ atm K}^{-1} \\ dP &= -135.7 \text{ atm K}^{-1} dT \\ \int_{1 \text{ atm}}^{300 \text{ atm}} dP &= -135.7 \text{ atm K}^{-1} \int_{273.15 \text{ K}}^T dT \\ 299 \text{ atm} &= -135.7 \text{ atm K}^{-1} \Delta T \\ \Delta T &= \frac{299 \text{ atm}}{-135.7 \text{ atm K}^{-1}} = -2.20 \text{ K}\end{aligned}$$

Therefore, the freezing point is depressed by 2.20 K when 300 atm is applied to ice. In other words, the freezing point at this pressure is $273.15 \text{ K} - 2.20 \text{ K} = 270.95 \text{ K}$ or -2.20°C .

- 4.50 The normal boiling point of ethanol is 78.3° C, and its molar enthalpy of vaporization is 39.3 kJ mol⁻¹. What is its vapor pressure at 30° C?

$$\ln \frac{P_2}{P_1} = -\frac{\Delta_{\text{vap}}\overline{H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{P_2}{1 \text{ atm}} = -\frac{39.3 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{303.2 \text{ K}} - \frac{1}{351.5 \text{ K}} \right) = -2.142$$

$$P_2 = (1 \text{ atm}) e^{-2.142} = 0.117 \text{ atm} = 88.9 \text{ torr}$$

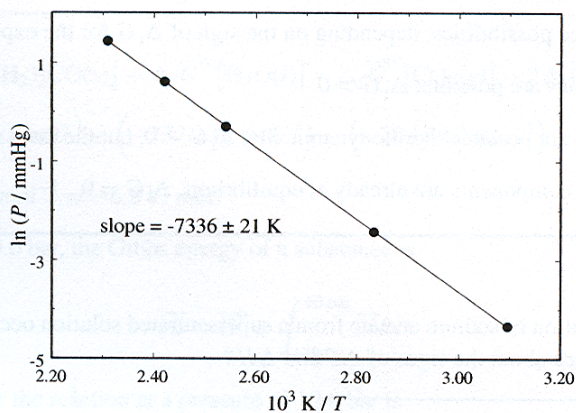
- 4.41 The vapor pressure of mercury at various temperatures has been determined as follows:

T/K	P/mmHg
323	0.0127
353	0.0888
393.5	0.7457
413	1.845
433	4.189

Calculate the value of $\Delta_{\text{vap}}\overline{H}$ for mercury.

A plot of $\ln P$ vs $1/T$ has a slope of $-\Delta_{\text{vap}}\overline{H}/R$, from which $-\Delta_{\text{vap}}\overline{H}$ is obtained.

$10^3 \text{ K}/T$	$\ln P$
3.10	-4.3362
2.83	-2.4214
2.54	-0.29343
2.42	0.61248
2.31	1.4325



The slope of the best fit straight line to the data is -7300 K, where the value has been rounded to reflect the regression estimate of uncertainty in the slope. Thus,

$$-\frac{\Delta_{\text{vap}}\overline{H}}{R} = -7300 \text{ K}$$

$$\Delta_{\text{vap}}\overline{H} = -(-7300 \text{ K}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= 6.07 \times 10^4 \text{ J mol}^{-1}$$

$$= 61 \text{ kJ mol}^{-1}$$