

- please answer all 5 questions in the spaces provided
- allow about 10 minutes per question
- a calculator and the equation sheets provided may be used

- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers!

1. 3.00 moles of helium (assumed to be an ideal gas) initially at 400 K and 5.00 bar expands to a final pressure of 1.00 bar at 400 K. For this process:

a) Calculate  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ .

(ideal gas  $dU = C_v dT$   
 $dH = C_p dT$ )

use  $dS = \frac{C_v}{T} dT + \frac{nR}{V} dV$

$dS = \frac{C_p}{T} dT - \frac{nR}{P} dP$

$\Delta S = \int dS = -nR \int_{P_i}^{P_f} \frac{dP}{P}$

$= -3.00(8.314) \ln\left(\frac{1.00}{5.00}\right)$

$\Delta S = 40.1 \frac{J}{K}$

b) Can  $q$  and  $w$  be calculated? Explain.

**NO!** Path not specified.

could be reversible

$w_{rev} = nRT \ln\left(\frac{P_i}{P_f}\right)$

could be irreversible with  $P_{ext} = P_f$

$w_{irrev} = -P_f(V_f - V_i)$

could be adiabatic, etc. 1

$U, H$  depend only on  $T$   
 $T_i = T_f = 400 K$

$\Delta U = U(T_f) - U(T_i) = 0$   
 $\Delta H = H(T_f) - H(T_i) = 0$

$dG = -SdT + VdP$

$\Delta G = \int_{P_i}^{P_f} V dP$

$= \int_{P_i}^{P_f} \frac{nRT}{P} dP$

$= nRT \int_{P_i}^{P_f} \frac{dP}{P}$

$= nRT \ln\left(\frac{P_f}{P_i}\right)$

$= 3.00(8.314)400 \ln\left(\frac{1.00}{5.00}\right)$

$\Delta G = -16060 J (= -7.05)$

2 a) Analysis of the Carnot cycle for reversible heat engines provides

$$\frac{q_H}{T_H} + \frac{q_C}{T_C} = 0$$

$i \rightarrow f \rightarrow i$

How did this result lead to the discovery of the entropy?

generalized to  $\oint \frac{dq_{rev}}{T}$  for any system, any cycle

for a state function  $F$ :  $\oint dF = F_i - F_i$

suggested that  $\frac{dq_{rev}}{T}$  was the differential of a state function (call it the entropy  $S$ )

b) For a heat engine operating with  $T_H = 500$  K and  $T_C = 300$  K, calculate the minimum amount of heat that must be absorbed at  $T_H$  for the engine to do 1.00 kJ of work on the surroundings.

$$\epsilon = \frac{-W}{q_H} = 1 - \frac{T_C}{T_H}$$

$W = -1000$  J

$$\frac{-(-1000 \text{ J})}{q_H} = 1 - \frac{300 \text{ K}}{500 \text{ K}} = 0.400$$

$$q_H = \frac{1000 \text{ J}}{0.400} = \boxed{2500 \text{ J}}$$

watch the sign of  $W$ !  
 $W < 0$

check:

$$\frac{-W}{q_H} = \frac{1000}{2500} = 0.400$$

c) For a heat pump (a heat engine running in reverse) operating with  $T_H = 300$  K and  $T_C = 270$  K, calculate the minimum amount of work that must be done on the heat pump to release 1.00 kJ heat into the 300 K reservoir.

$$\epsilon = \frac{-W}{q_H} = 1 - \frac{T_C}{T_H}$$

$q_H = -1000$  J

$$\frac{-W}{-1000 \text{ J}} = 1 - \frac{270 \text{ K}}{300 \text{ K}} = 0.100$$

$$\boxed{W = 100 \text{ J}}$$

watch the sign of  $q_H$ !  
 $q_H < 0$

inefficient engine,  
but this means  
100 J work can pump  
1000 J heat!

3. a) Calorimetry is used to measure  $q$  and  $\Delta H$  for many physical and chemical processes. Another important application of calorimetry is the measurement of absolute entropies ( $S_m^\circ$ ).

Describe how absolute entropies are calculated from calorimetric data, including relevant equations. What does "absolute" mean in this context?

$$S(T, P) = S(T=0, P) + \int_{T=0}^T \frac{dq_{rev}}{T}$$

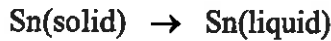
at const.  $P$   
 $dq_{rev} = C_p dT$

$$= S(T=0, P) + \int_{T=0}^T \frac{C_p dT}{T} + \sum_i \frac{\Delta H_{f,i}}{T_i}$$

perfect crystal  $\rightarrow 0$

absolute, not  $S(T, P) - S(T=0, P)$  because  $S(T=0, P)$  is zero for perfect crystals  
absolute, not  $\Delta S_f$  (entropy of formation from elements)

b) Calorimetry provides the following data for melting tin at 450 K and 1 bar



$$\Delta H^\circ_{\text{fusion,m}} = 6954 \text{ J mol}^{-1}$$

$$S_m^\circ(\text{Sn, liquid}) = 76.43 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S_m^\circ(\text{Sn, solid}) = 62.67 \text{ J K}^{-1} \text{ mol}^{-1}$$

i) Is melting tin at 450 K and 1 bar a spontaneous process? Justify your answer.

$T, P$  fixed, suggests using  $\Delta G$

$$\Delta S^\circ_{\text{fusion,m}} = S_m^\circ(\text{l}) - S_m^\circ(\text{s})$$

$$= (76.43 - 62.67) \text{ J K}^{-1} \text{ mol}^{-1} = 13.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_{\text{tin}} = 6954 \text{ J mol}^{-1}$$

$$\Delta S_{\text{tin}} = 13.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\circ_{\text{fusion,m}} = G^\circ_{\text{lm}} - G^\circ_{\text{sm}} = H^\circ_{\text{lm}} - TS^\circ_{\text{lm}} - (H^\circ_{\text{sm}} - TS^\circ_{\text{sm}})$$

$$= \Delta H^\circ_{\text{lm}} - \Delta H^\circ_{\text{sm}} - T(S^\circ_{\text{lm}} - S^\circ_{\text{sm}}) = \Delta H^\circ_{\text{fusion}} - T\Delta S^\circ_{\text{fusion}}$$

$$= 6954 - 450(13.76)$$

$$\Delta G^\circ_{\text{fusion,m}} = 762 \text{ J mol}^{-1} > 0$$

for melting

$$\Delta G_{T,P} > 0$$

$\therefore$  not spontaneous! Impossible!  
(freezing Sn(l) is spontaneous)

ii) The entropy of liquid tin is larger than the entropy of solid tin. Melting tin at 450 K and 1 bar is therefore spontaneous according to the Second Law because  $\Delta S > 0$ .

Is this reasoning correct? Explain.

(Tin + surroundings) isolated  
"lost" 6954 J to the tin

No! Tin not an isolated system (but tin + surroundings is isolated)

$$\Delta S_{\text{tin}} + \Delta S_{\text{sur}} = 13.76 + \frac{-6954}{450}$$

$$= 13.76 - 15.43 = -1.67 \text{ J K}^{-1} < 0$$

isolated system  
impossible

Important:  $\Delta G, \Delta H, \Delta S$  can be calculated whether or not the process is reversible, spontaneous or impossible.

4. a) Give a brief definition of a "Joule Thomson expansion".

expansion of a fluid (usually a gas) at constant enthalpy under adiabatic conditions

b) Describe a practical application of Joule-Thomson expansions.

production of liquefied gases, such as  $O_2(l)$ ,  $N_2(l)$ ,  $He(l)$ ,  $H_2(l)$

c) Starting with  $dU = TdS - pdV$ , derive the thermodynamic equation of state:

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

$$dU = TdS - pdV \quad \div dV_T$$

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

$$= T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$V, T$   
suggests  
looking at  
 $dA$

$$dA = -SdT - pdV$$

Maxwell relation:

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

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

d) Why is the equation  $(\partial U/\partial V)_T = T(\partial p/\partial T)_T - p$  both useful and convenient for studying molecular interactions?

Useful  $\rightarrow$  indicator of the strength of molecule-molecule interactions

$\rightarrow$  = zero for ideal gases

Convenient  $\rightarrow$  in terms of  $p, T$

easily  
(measurable)  
quantities

$$\rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T \frac{p}{\alpha} - p$$

5. According to the wisdom of organic chemistry, *trans*-1,2-dichloroethylene is more stable than *cis*-1,2-dichloroethylene due to reduced repulsion of the chlorine atoms in the *trans* isomer.



- a) Use the following data at 25 °C

	<i>cis</i> -HCIC=CCIH(g)	<i>trans</i> -HCIC=CCIH(g)
$\Delta H_{\text{fm}}^\circ$	-27.6 kJ mol <sup>-1</sup>	-23.14 kJ mol <sup>-1</sup>
$\Delta G_{\text{fm}}^\circ$	22.11 kJ mol <sup>-1</sup>	27.34 kJ mol <sup>-1</sup>

to show the *cis* isomer is in fact more stable at 25 °C.



$$\Delta G^\circ = \Delta G_f^\circ(\text{trans}) - \Delta G_f^\circ(\text{cis}) = (27.34 - 22.11) \text{ kJ mol}^{-1}$$

$$= 5.23 \text{ kJ mol}^{-1} > 0 \quad \text{trans isomer less stable (higher } \Delta G)$$

- b) Calculate the percentage of the *cis* isomer in a sample of 1,2-dichloroethylene gas at 25 °C.

reaction *cis* → *trans*

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{5230}{8.314(298.15)}\right)$$

$$= \exp(-2.110) = 0.1212 = \frac{P_{\text{trans}}}{P_{\text{cis}}}$$

$$\% \text{ cis} = \frac{P_{\text{cis}}}{P_{\text{cis}} + P_{\text{trans}}} \cdot 100\% = \frac{P_{\text{cis}}}{\frac{P_{\text{cis}}}{0.1212} + P_{\text{cis}}} \cdot 100\%$$

$$= \frac{1}{0.1212 + 1} \cdot 100\% = 89.2\%$$

- c) Does the *trans* isomer become more stable than the *cis* isomer if the temperature is changed? Justify your answer.

*cis* → *trans*  $\Delta H^\circ = 4.46 \text{ kJ mol}^{-1}$   
 reaction more favorable as *T* increases

$$\ln K_2 = \ln K_1 - \frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$T_1 = 298.15 \text{ K}$$

$$T_2 = \infty$$

$$\ln K_1 = -2.110$$

$$\ln K_2 = -2.110 - \frac{4460}{8.314} \left( \frac{1}{\infty} - \frac{1}{298.15} \right)$$

$$= -2.110 - 1.799 = -0.311$$

$$\max K = e^{-0.311} = 0.733$$

*cis* → *trans*  
 $K$  never  $> 1$   
*trans* never more stable than *cis*