**Supplement 10: Chemistry 6854**

**Physical Chemistry Alfred State College**

 **Examples of Reversible and Irreversible Adiabatic Path Calculations Using a Monatomic Ideal Gas (see also: pp 774-776 and 821-825)**

**10.1 Reversible Adiabatic Expansion**

 **(P1,V1,T1 )**

State 2 is reached from state 1 by a reversible adiabatic expansion where V1 = 1L, T1 = 300 K and V2 = 5L.

Our task is to find ΔU and ΔS for 1 mole of monatomic ideal gas using two different paths (**a** and **b**) going from state 1 to state 2 given:

 **Path a**: 1) constant volume cooling to P2 at T3

 2) constant pressure expansion at P2 to state 2

 **Path b:** 1) isothermal expansion at T1 to V2

 2) constant volume cooling to state 2

 **P**

 **b**

 **a**

P3,V2,T1

(P2,V2,T3) **(P2,V2,T2)**

 **| |**

 **1 5 V(L)**

Since this is a reversible, adiabatic process both system and surroundings are reversibly exchanging just work and only the system is changing temperature. In the reversible case:

 ΔSgas = 0

Because S and U are state functions we expect that for either path a or b, ΔS and ΔU will be the same in value. However, Q and W are not state functions and will have different values for each path.

You may be wondering why only V2 is specified here. Since this is a reversible cooling, we can easily find T2 since for reversible adiabatic processes involving an ideal gas we have already shown that for a monatomic, ideal gas (Cv =3R/2) :

 T2/T1 = (V1/V2)R/Cv =(V1/V2)2/3 .

Thus, in the current case: T2 = 300\*(1/5)2/3 =102.598 K

That T2 is less than T1 even though no heat is exchanged means that the system’s internal energy converted its internal heat to work to cause the expansion (thus resulting in the attendant lowering of the temperature.) Given now both T2 and V2 , P2 can then be extracted since P2 = RT2/V2.

In what follows, we will compute ΔU and ΔS for the reversible, adiabatic expansion using both path a and path b. To aid in numeric computations**,** recall that: **1 bar dm3 =100 J**

**Path a: step 1 (constant volume)**

Since dV = 0, W1a = 0 and dU1a =dQ1a= CvdT => we are cooling the gas to T3 at constant V

The pressure we want to reach is P2 which is computed from:

 P2 = RT2/V2 = 0.08314\*102.2598/5=1.706 bar

Thus, T3 = P2V1/R = 1.706\*1/0.08314 =20.52 K

Q1a= U1a = Cv(T3-T1) = 1.5\*8.314\*(20.52-300) = -3,485.4 J

dS1a = CvdT/T => ΔS1a = Cv ln (T3/T1) = 1.5\*8.314ln (20.52/300) =-33.452 J/K

**Path a: step 2 (constant pressure)**

dU2a = CpdT + PdV

W2a = -P2(ΔV) = -1.706\*(5-1)=-6.824 bar dm3 =-682.4 J

 Q2a = Cp(T2-T3) = 2.5\*8.314\*(102 .6-20.52) =1706.4 J

dS2a = CpdT/T => ΔS2a = Cv ln (T2/T3)= 2.5\*8.314\*ln(102.6/20.52) = +33.452 J/K

**Summing our results for path a:**

 W Q ΔU ΔS

Step 1a 0 -3485.4 -3485.4 -33.452 J/K

Step 2a -682.4 1706.4 +1024.0 +33.452

**Total -2461.6 0**

**Path b: step 1 (constant T)**

Isothermal expansion => dU1b = 0 = dW+ dQ => ΔU1b =0

dW1b = -pdV = -RT/V dV => W1b = -RT ln (V2/V1)= -8.314\*300\*ln (5/1)=-4014.2 J

Q1b = -W1b = +4014.2 J

dS1b= dQ1b/T = R/V dV => ΔS1b = R ln (V2/V1) = 8.314\*ln (5/1) =+13.381 J/K

**Path b: step 2 (constant V cooling to T2)**

dW2b = 0 so dQ2b =dU2b = CvdT => Q2b = Cv(T2-T1) = 3/2\*8.314\*(102.6-300) =-2461.7

dS2b = CvdT/T => Cv ln (T2/T1) = 3/2 \* 8.314 \* ln (102.6/300) =-13.381 J/K

**Summing our results for path b:**

 W Q ΔU ΔS

Step 1b +4014.2 -4014.2 0 +13.381 J/K

Step 2b 0 -2461.7 -2461.7 -13.381

**Total -2461.7 0**

As expected, regardless of path, the values for ΔU and ΔS are the same and in particular, ΔS=0 as predicted and natural for a reversibly performed adiabatic expansion. Note, however, that each path evolved different values of W and Q.

**10.2 Ireversible Adiabatic Expansion (P1,V1,T1 )**

 **b**

Here state 2 is reached from state 1 by an **irreversible** adiabatic expansion where V1 = 1L, T1 = 300 K and V2 = 5L and V2 = 1 and T2 = 150 K from the irreversible expansion . As before, our task is to find ΔU and ΔS for 1 mole of monatomic ideal gas using two different paths (**a** and **b**) going from state 1 to state 2 given:

 **Path a**: 1) constant volume cooling to P2 at T3

 2) constant pressure expansion at P2 to state 2

 **Path b:** 1) isothermal expansion at T1 to V2

 2) constant volume cooling to state 2

 **a**

 **P2,V2, T2 = 150 K**

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The same analytical process used for the reversible case is applied here, except that there is no need to calculate T2 since it is provided from measurement assuming an irreversible expansion (which is why T2 here is different and greater that the T2(reversible) = 102.6 K)

**Path a: step 1 (constant volume)**

Since dV = 0, W1a = 0 and dU1a =dQ1a= CvdT => we are cooling the gas to T3 at constant V

The pressure we want to reach is P2 which is computed from:

 P2 = RT2/V2 = 0.08314\*150/5=2.4942 bar

Thus, T3 = P2V1/R = 2.4942\*1/0.08314 =30.0 K

Q1a= U1a = Cv(T3-T1) = 1.5\*8.314\*(30-300) = -3367.17 J

dS1a = CvdT/T => ΔS1a = Cv ln (T3/T1) = 1.5\*8.314ln (30/300) =-28.71554 J/K

**Path a: step 2 (constant pressure)**

dU2a = CpdT + PdV

W2a = -P2(ΔV) = -2.4942\*(5-1)=-9.9768 bar dm3 =-997.68 J

 Q2a = Cp(T2-T3) = 2.5\*8.314\*(150-30) =2494.2 J

dS2a = CpdT/T => ΔS2a = Cv ln (T2/T3)= 2.5\*8.314\*ln(150/30) = +33.452 J/K

**Summing our results for path a:**

 W Q ΔU ΔS

Step 1a 0 -3367.17 -3367.17 -28.716 J/K

Step 2a -997.68 2494.2 J +1496.5 **+33.452**

**Total -1870.6 + 4.736**

**Path b: step 1 (constant T)…same as reversible case done earlier**

Isothermal expansion => dU1b = 0 = dW+ dQ => ΔU1b =0

dW1b = -pdV = -RT/V dV => W1b = -RT ln (V2/V1)= -8.314\*300\*ln (5/1)=-4014.2 J

Q1b = -W1b = +4014.2 J

dS1b= dQ1b/T = R/V dV => ΔS1b = R ln (V2/V1) = 8.314\*ln (5/1) =+13.38 J/K

**Path b: step 2 (constant V cooling to T2)**

dW2b = 0 so dQ2b =dU2b = CvdT => Q2b = Cv(T2-T1) = 3/2\*8.314\*(150-300) =-1870.6

dS2b = CvdT/T => Cv ln (T2/T1) = 3/2 \* 8.314 \* ln (150/300) =-8.644 J/K

**Summing our results for path b:**

 W Q ΔU ΔS

Step 1b +4014.2 -4014.2 0 +13.381 J/K

Step 2b 0 -1870.6 -1870.6 -8.644

**Total -1870.6 4.736**

Again, by either **path a** or **b**, identical values for the state functions **ΔS** and **ΔU** are obtained.

It is notable, however, that while this is an adiabatic expansion, the fact that it was done irreversibly produces positive total **ΔS** =ΔSsystem =4.736 J/K

In contrast, since the expansion **is** adiabatic, from the perspective of the surroundings, the absence of Q exchange is still a reversible result thus, ΔSsurroundings = 0 . Thus,

**ΔStotal = ΔSsystem + ΔSsurroundings = 4.736 + 0 = 4.736 >0**

as expected from the Second Law of Thermodynamics for an irreversible process.