

CY 102 Chemistry II Assignment I
Thermodynamics (First and second laws thermodynamics)

Jan 27, 2004

1. Two moles of N_2 gas at $25^{\circ}C$ and 1 atm pressure are expanded reversibly and isothermally to a pressure of 0.5 atm.
 - a) Calculate the work done (including the sign).
 - b) Calculate the heat change and the internal energy change involved in the process.
 - c) Calculate the work done in expansion against a constant external pressure of 0.5 atm (final state is 0.5 atm as in a). What is your inference of the result in comparison with the result of a) ?

Ans: a) Isothermal (reversible) expansion:

Class formula: $w = -nRT \ln V_2/V_1$.

$= -2 \text{ mol} \times 8.3145 \text{ JK}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \times 2.303 \log P_1/P_2$ as $PV = \text{Constant}$ at constant temperature.

$$= -2 \times 8.3145 \times 298.15 \times 2.303 \log 2 \text{ J}$$
$$= -3437.2 \text{ J}$$

b) Heat Change and the internal energy change.

Internal energy change is zero for an ideal gas undergoing process at constant temperature $\Delta E = 0$.

$$\therefore \text{Heat change} = - \text{work done by the gas.}$$
$$= 3437.2 \text{ J.}$$

(This much heat is absorbed by the system to do the work)

c) Work done in expansion against a constant pressure of 0.5 atm.
 $= -P\Delta V$.

To Calculate ΔV , calculate V_1 and V_2 .

$$V_1 = nRT/P_1 = 2 \text{ mol} \times 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} / 1 \text{ atm.}$$
$$= 48.09 \text{ L}$$

$$V_2 = 2V_1 \text{ as } P_2 = \frac{1}{2} P_1.$$

$$\therefore w = -P\Delta V = 0.5 \text{ atm} \times 48.90 \text{ L}$$
$$= 24.45 \text{ L atm.}$$
$$= 2479.1 \text{ J.}$$

Observation: Expansion against constant pressure is NOT a reversible process. Therefore, the work done by the gas is not the maximum possible work done, but less than the maximum. It is a path-dependent quantity.

2. An ideal gas expands reversibly and isothermally from 20 atm to 1 atm at 300 K. What are the values for
- work done by the gas per mole ?
 - heat absorbed by the gas per mole ?
 - ΔE per mole and
 - ΔH per mole ?

Ans: a) Reversible isothermal expansion from 20 atm to 1 atm at 300K.

- $w = -nRT \ln P_1/P_2$.
- $Q = -w$
- $\Delta E = 0$
- $\Delta H = q$ as the work done is reversible, under isothermal conditions.

$$\text{Ans: } w = -7473.8 \text{ j.}$$

3. The heat capacity of a gas is represented by the formula

$$C_p = \alpha + \beta T + \frac{\gamma}{T^2}$$

For O_2 , $\alpha = 29.96 \text{ J K}^{-1}$, $\beta = 0.00418 \text{ J K}^{-2}$ and $\gamma = -1.67 \times 10^{-5} \text{ J K}$.

Calculate the amount of heat required to heat the gas from 300 K to 1000K.

$$\text{Ans: } \Delta H = \int_{T_1}^{T_2} C_p(T) dT$$
$$= \int_{T_1}^{T_2} (\alpha + \beta T + \gamma/T^2) dT$$
$$= \alpha (T_2 - T_1) + \beta/2 (T_2^2 - T_1^2) - \gamma (1/T_2 - 1/T_1)$$

6. Determine whether the following are exact differentials.

a) $xy^2 dx - x^2 y dy$ b) $\frac{dx}{y} - \frac{x}{y^2} dy$

b). Verify that $dq = dE + PdV = C_V dT + RT d \ln V$ is not an exact differential but that

$$\frac{dq}{T} = C_V d \ln T + R d \ln V \text{ is an exact differential.}$$

Ans: a). Let $xy^2 dx - x^2 y dy = df$

Then $\partial^2 f / \partial x \partial y = \partial^2 f / \partial y \partial x$ must be satisfied.

It is NOT. Therefore $xy^2 dx - x^2 y dy$ is NOT an exact differential.

b) $dq = C_V dT + RT d \ln V$.

$\partial^2 q / \partial V \partial T = \partial / \partial V (C_V) = 0$ for an ideal gas.

$\partial^2 q / \partial T \partial V = [\partial / \partial T (RT/V)]_V = R/V \neq \partial^2 q / \partial V \partial T$.

Hence dq is NOT an exact differential.

$dq/T = C_V/T dT + R/V dV = df$

$\partial^2 f / \partial V \partial T = (\partial / \partial T [R/V])_V = 0$.

$\partial^2 f / \partial V \partial T = (\partial / \partial V [C_V/T])_T = 0 = \partial^2 f / \partial T \partial V$.

Hence dq/T is an exact differential.

7. Derive the relation

$$C_V = - \left(\frac{\partial E}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_E$$

From the expression for the total differential of $E(T, V)$.

Ans: E, V, T follow the cyclic relation

$$(\partial E / \partial T)_V (\partial T / \partial V)_E (\partial V / \partial E)_T = -1.$$

$$\text{Or } (\partial E / \partial T)_V = -1 / (\partial T / \partial V)_E (\partial V / \partial E)_T = -(\partial V / \partial T)_E (\partial E / \partial V)_T$$

More elaborately:

$$E = E(V, T)$$

$$dE = (\partial E / \partial T)_V dT + (\partial E / \partial V)_T dV.$$

$$= C_V dT + (\partial E / \partial V)_T dV.$$

Express V as a function of E and T and substitute for dV in the above expression.

$$dV = (\partial V/\partial E)_T dE + (\partial V/\partial T)_E dT.$$

$$\Rightarrow dE = (\partial E/\partial V)_T \{(\partial V/\partial E)_T dE + (\partial V/\partial T)_E dT\} + C_V dT.$$

$$\Rightarrow 0 = \{1 - (\partial E/\partial V)_T (\partial V/\partial E)_T\} dE + \{C_V + (\partial E/\partial V)_T (\partial V/\partial T)_E\} dT$$

The equality implies the coefficients of dE and dE are zero, as two of the three variables E, v, T are independent.

$$\text{Hence: } (\partial E/\partial V)_T (\partial V/\partial E)_T = 1,$$

$$C_V = - (\partial E/\partial V)_T (\partial V/\partial T)_E.$$

8. Show that

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

Using appropriate relations between partial derivatives, show also that

$$C_p - C_v = T \frac{\left[\frac{\partial V}{\partial T} \right]_P^2}{\left[\frac{\partial V}{\partial P} \right]_T}$$

For water at 4°C , given that the density of water is maximum, what does the above result indicate. Also evaluate $(C_p - C_v)$ for an ideal gas.

$$\text{Ans: } dE = (\partial E/\partial T)_V dT + (\partial E/\partial V)_T dV = C_V dT + \pi_T dV.$$

$\pi_T \rightarrow$ internal pressure.

$$\therefore (\partial E/\partial T)_P = \pi_T (\partial V/\partial T)_P + C_V.$$

$$\Rightarrow (\partial E/\partial T)_P - C_V = \pi_T (\partial V/\partial T)_P \text{ Also, } \pi_T = T(\partial P/\partial T)_V - P$$

$$C_p - C_v = (\partial H/\partial T)_P - (\partial E/\partial T)_V; H = E + PV.$$

$$= (\partial E/\partial T)_P + P (\partial V/\partial T)_P - (\partial E/\partial T)_V.$$

$$= P(\partial V/\partial T)_P + \pi_T (\partial V/\partial T)_P.$$

$$= (\pi_T + P) (\partial V/\partial T)_P = T(\partial P/\partial T)_V (\partial V/\partial T)_P.$$

Also P, T, V

Form cyclic partial derivatives.

$$(\partial P/\partial T)_V = -1/(\partial T/\partial V)_P (\partial V/\partial P)_T = - (\partial V/\partial T)_P / (\partial V/\partial P)_T$$

$$\therefore C_p - C_v = -T(\partial V/\partial T) [(\partial V/\partial T)_P / (\partial V/\partial P)_T].$$

For an ideal gas $Pv = nRT$

$$(\partial V/\partial T)_P = nR/P.$$

$$(\partial V/\partial P)_T = -nRT/P^2$$

$$\therefore C_p - C_v = nR.$$

9. For n moles of a Van der Waals gas, whose equation of state is given by

$$\left[P + \frac{n^2 a}{V^2} \right] (V - nb) = nRT$$
 calculate the expression for the entropy change for

the system from an initial state T_1, V_1 to the final state T_2, V_2 .

Ans: Use: $du = Tds - PdV$ [i.e. $u \equiv u(s,v)$]

$$= C_v dT + [T(\partial P/\partial T)_V - P] dV [u \equiv u(T,V)]$$

Also, from $ds = (\partial S/\partial T)_V dT + (\partial S/\partial V)_T dV$ and the firstline,

$$(\partial S/\partial T)_V = C_v/T; (\partial S/\partial V)_T = (\partial P/\partial T)_V - P/T + P/T = (\partial P/\partial T)_V.$$

Thus the equation for entropy change you need to use is $dS = C_v dT/T + (\partial P/\partial T)_V dV$.

For a van der waals gas.

$$(P + n^2 a/V^2)(V - nb) = nRT,$$

$$P = nRT/V - nb - n^2 a/V^2$$

$$(\partial P/\partial T)_V = nR/V - nb$$

$$\therefore dS = C_v dT/T + nR/V - nb dV.$$

$$\therefore \Delta S = \int_{T_1 V_1}^{T_2 V_2} ds$$

$$= \int_{T_1}^{T_2} C_v/dT + \int_{V_1}^{V_2} nR/V - nb dV$$

$$= C_v \ln T_2/T_1 - nR \ln V_2 - nb/V_1 - nb \text{ if } C_v \text{ is independent of temperature.}$$

10. Without doing explicit calculations, predict the signs of $\Delta P, \Delta V, \Delta T, \Delta H$ and ΔS for one mole of an ideal gas taken through each of the following four steps of a Carnot cycle. Assume C_p and C_v Constants.

Step (a): Isothermal reversible expansion $P_1 V_1 T_1 \rightarrow P_2 V_2 T_1$

Step (b): Adiabatic reversible expansion $P_2 V_2 T_1 \rightarrow P_3 V_3 T_2$

Step (c): Isothermal reversible compression $P_3 V_3 T_2 \rightarrow P_4 V_4 T_2$

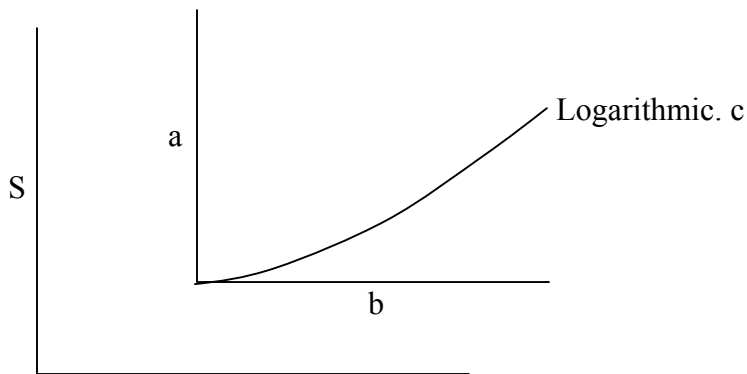
Step (d): Adiabatic reversible compression $P V T \rightarrow P_1 V_1 T_1$

Text book material.

11. On a single entropy versus temperature diagram, draw the curves for the following reversible processes for an ideal gas (the initial state is the same for all processes).

- (a) isothermal expansion,
- (b) adiabatic expansion and
- (c) isochoric process in which heat is added.

Ans:

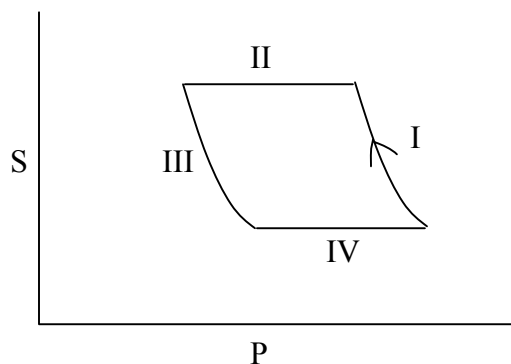


- a) Isothermal expansion. T - constant
 - b) adiabatic expansion. $q = 0$. $\Delta s = 0$
 - c) Isochoric with heat added.
- $\Delta S = C_v \ln T_2/T_1$.
- T_1 is an initial point.
- So, $S(T_2) = S_0$ (at T_1) + $C_v \ln T_2 - C_v \ln T_1$.

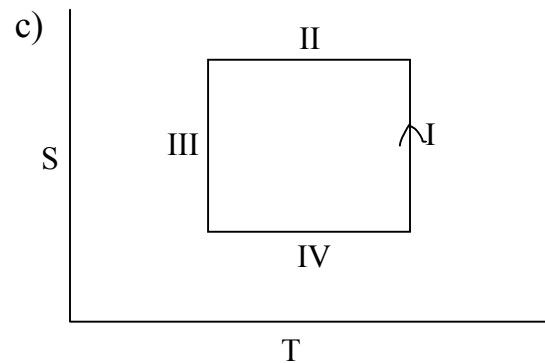
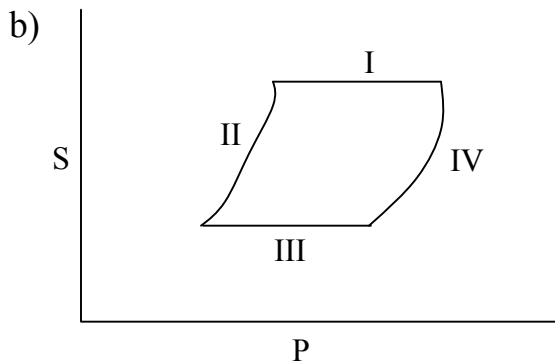
12. Sketch diagrams for the reversible Carnot cycle of an ideal gas with constant C_p and C_v ; P Vs S ; E Vs P ; T Vs P ; H Vs P ; V Vs T ; S Vs V ; V Vs E ; V Vs H ; E Vs T ; H Vs T , T Vs S , E Vs H and H Vs S .

Ans: discuss three cases. The others are similar.

- a) P . vs. S



- I → Isothermal expansion.
- II → adiabatic exp.
- III → Isothermal compression.
- IV → adiabatic compression.



Others can be constructed similarly.

13. One mole of water at 0°C is brought into contact with a large heat reservoir at 100°C . When the water reaches 100°C calculate the entropy change of water, the reservoir and the universe (which consists of water and the reservoir). If the water was brought into contact with a heat reservoir at 75°C first and then water at 75°C is brought into contact with the reservoir at 100°C so that the final state of the water is 100°C , calculate the net entropy change of water, the reservoir and the universe. Assume that the heat capacity of water to be constant at $1.0 \text{ cal g}^{-1}\text{K}^{-1}$.

Ans: For a body at temp T_1 in contact with a reservoir at T_2 with $T_1 < T_2$.

ΔS for the body

(for a suitable reversible path by which $T_1 \rightarrow T_2$) $= nC_v \ln T_2/T_1$.

ΔS for the reservoir: heat is supplied at T_2 to heat a body from T_1 to T_2 with a constant heat capacity C_v .

$$\therefore \Delta S = -nC_V (T_2 - T_1)/T_2.$$

$$\Delta S_{\text{universe}} = nC_V \ln T_2/T_1 - nC_V (T_2 - T_1)/T_2.$$

$$> 0 \quad \text{if } T_2 > T_1.$$

$$= 0 \quad \text{if } T_2 = T_1. \text{ (obvious).}$$

Apply this for each of the cases mentioned in the problem.

$$T_1 = 273 \text{ k}, T_2 = 373 \text{ k}. \quad C_V = 18.0 \text{ cal mol}^{-1} \text{ k}^{-1}$$

$$\Delta S = 18[2.303 \log 373/273 - 100/373] = 0.7938 \text{ cal.}$$

Please understand the underlying assumption. Reservoir is so huge that the process of heat transfer is assumed to be reversible! Otherwise $\Delta S \neq \text{heat}/T$.

Process 2:

$\Delta S_{\text{universe}}$ is calculated for two processes.

$$T_1 = 273 \text{ k}, T_2 = 348 \text{ k}$$

$$\text{And } T_1 = 348 \text{ k}, T_2 = 373 \text{ k}.$$

$$\Delta S = 18 [2.303 \log 348/273 - 75/348] + [2.303 \log 373/348 - 25/373]$$

$$= 0.5346 \text{ cal.}$$

What does this tell you?

If you divide this further and further, (i.e. infinitely many such intermediate temperatures and attain equilibrium at each stage, what will be the value of $\Delta S_{\text{universe}}$? [zero, in the end!].

14. A mass m of liquid at temp T_1 is mixed with an equal mass of the same liquid at a temperature T_2 . If the system is isolated show that the entropy change of the universe is

$$2mC_p \ln \left[\frac{(T_1 + T_2)/2}{\sqrt{T_1 T_2}} \right]$$

Where C_p is the specific heat capacity of the liquid and is assumed to be constant over the temperature range.

Ans: Heat capacity of the liquid is mC_p .

Let $T_1 > T_2$, T be an intermediate temp. (equilibrium).

Then:

$$mC_p (T_1 - T) \quad = \quad mC_p (T - T_2).$$

Heat lost by the hot liquid. Heat gained by the hot liquid.

$T_1 - T = T - T_2$ or $T = (T_1 + T_2)/2$. It is also trivially true.

Entropy change in the liquid.

$$\Delta S_{\text{hot}} = m C_p \ln \left(\frac{T_1 + T_2}{2} / T_1 \right)$$

Entropy change in the cold liquid = $m C_p \ln \left(\frac{T_1 + T_2}{2} / T_2 \right)$.

$$\therefore \text{Total entropy change} = 2m C_p \ln \left[\frac{(T_1 + T_2)/2}{\sqrt{T_1 T_2}} \right]$$

Always positive. So long as T_1 and T_2 are different.

15. Two moles of an ideal gas are expanded isothermally at 298 K from a volume V to a final volume of $2.5 V$. Find the value of ΔS_{gas} and ΔS_{total} for the following:

- Reversible expansion
- Irreversible expansion in which the heat absorbed is 400 J mol^{-1} less than the reversible expansion and
- Free expansion.

Ans: Reversible expansion.

$$\begin{aligned} \Delta S_{\text{gas}} &= nR \ln V_2/V_1 = 2 \times 8.314 \ln 2.5 \\ &= 15.24 \text{ JK}^{-1}. \end{aligned}$$

$\Delta S_{\text{surr}} = -15.24 \text{ JK}^{-1}$ as the heat transfer takes place reversibly from surroundings at the same temperature.

$$\therefore \Delta S_{\text{tot}} = 0.$$

b) $\Delta S_{\text{gas}} = 15.24 \text{ JK}^{-1}$. Remember the initial and final states of the gas are exactly the same as in the previous case, therefore $\Delta S_{\text{gas}} = 15.24$ only still.

$$\begin{aligned} \Delta S_{\text{surr}} &= -(nRT \ln V_2/V_1 - 400)/T \\ &= -13.90 \text{ JK}^{-1}. \end{aligned}$$

$$\therefore \Delta S_{\text{tot}} = 1.34 \text{ JK}^{-1} > 0. \text{ (irreversible path).}$$

c) free expansion: system does not draw any heat from the surroundings.

$$\therefore \Delta S_{\text{surr}} = 0.$$

$$\Delta S_{\text{tot}} = 15.24 \text{ JK}^{-1}.$$

16. The molar entropy of an ideal gas at 298 K is $146 \text{ J K}^{-1} \text{ Mol}^{-1}$. Find the value of entropy of the gas at 500 K when its pressure is kept constant.

Ans: Missing statement: (C_p of the gas is a constant and is $20.97 \text{ JK}^{-1} \text{ mol}^{-1}$.) use this to calculate.

$$S_{500} = S_{298} + C_p \ln T_2/T_1$$

$$= 146 + 20.97 \times 2.303 \times \log 500/298.$$
$$= 156.85 \text{ JK}^{-1} \text{ mol}^{-1}.$$

17. How much does the entropy of an ideal gas increase when one mole is heated from 298 K to 1000 K at a constant pressure and then expanded to five times the volume at the higher temperature ?

$$C = 20.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Ans: } \Delta S = C_p \ln T_2/T_1 + R \ln V_2/V_1.$$
$$= 2.9 \times 2.303 \log 1000/298 + 8.314 \times 2.303 \times \log 5$$
$$= 25.3 + 13.4 = 38.7 \text{ JK}^{-1} \text{ mol}^{-1}.$$