Chemistry 163B Winter 2020 , Lecture 11
Clausius Inequality and ΔS for an Ideal Gas

Lecture 11
Chemistry 163B
Winter 2020

q_{rev} , Clausius Inequality and calculating

ΔS for ideal gas P,V,T changes (HW#6)

Challenged Penmanship
Notes

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statements of the Second Law of Thermodynamics

1. Macroscopic properties of an isolated system eventually assume constant values (e.g. pressure in two bulbs of gas becomes constant; two block of metal reach same T) [*Andrews. p37]*

2. It is impossible to construct a device that operates in cycles and that converts heat into work without producing some other change in the surroundings. *Kelvin's Statement [Raff p 157]; Carnot Cycle*

3. It is impossible to have a natural process which produces no other effect than absorption of heat from a colder body and discharge of heat to a warmer body. *Clausius's Statement, refrigerator*

4. In the neighborhood of any prescribed initial state there are states which cannot be reached by any adiabatic process
~ Caratheodory's statement [Andrews p. 58]

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four steps to exactitude

I. $\varepsilon_{CARNOT[ideal\ gas]} = \frac{-w_{total}}{q_U} = 1 - \frac{T_L}{T_U} = 1 + \frac{q_L}{q_U}$

II. $\varepsilon_{ANY\ REVERSIBLE\ 'TWO\ TEMPERATURE'\ MACHINE} = \varepsilon_{CARNOT[ideal\ gas]}$
or else violation of 2nd Law

III. $\oint_{cycle} \frac{đq_{rev}}{T} = 0$ eqn 5.11 $(E \& R)_{3rd}$; ?? $(E \& R)_{4th}$ demonstrated for ideal gas Carnot;
general proof for two temperature reversible cycle;
see "a REALLY BIG RESULT" lecture 10 Slide 33
also (Dickerson p. 155; Raff p. 162-163)

IV. $\oint_{cycle} \frac{đq_{rev}}{T} = 0$ **for any reversible cyclic process**

figure 5.16 E & R_{4th} (5.4 E & R_{3rd})
(Dickerson pp.156 - 159, Raff pp.163 - 164)

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Entropy

$dS = \frac{đq_{rev}}{T}$ **is an exact differential**

S is a state function

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goals of lecture 11

1. Relate ΔS and q_{irrev}

2. Calculate ΔS for P,V, T changes of ideal gas (HW#6)
   a. using REVERSIBLE path (q_{rev}) ***[even for irreversible processes]***
   b. using partial derivatives of S with respect to P, V, T *[a look ahead]*

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entropy and heat for actual (irreversible processes): q_{irrev}

an *irreversible* (actual) ***cyclic*** engine ε_{irrev} coupled with a Carnot heat pump of ε_C **will not** violate 2nd Law if $\varepsilon_{irrev} < \varepsilon_C$ (viz section; Lect10 S30)

$\Delta U_{cyclic}=0$
$-w_{total}=q_U+q_L$
for both rev and irrev

***BUT** what about q_{irrev} with $\varepsilon_{irrev} < \varepsilon_C$??*

$$\varepsilon_{irrev} = \left(\frac{-w_{total}}{q_U}\right)_{irrev} = \left(\frac{q_U+q_L}{q_U}\right)_{irrev} = 1+\frac{(q_L)_{irrev}}{(q_U)_{irrev}} < 1-\frac{T_L}{T_U} = \varepsilon_{reversible}$$

$$\frac{(q_L)_{irrev}}{(q_U)_{irrev}} < -\frac{T_L}{T_U}$$

$$\Delta S_{\substack{cyclic\ engine \\ (reversible\ or\ irreversible)}} = \frac{(q_U)_{rev}}{T_U} + \frac{(q_L)_{rev}}{T_L} = 0$$

$$\frac{(q_L)_{irrev}}{T_L} + \frac{(q_U)_{irrev}}{T_U} < 0 = \Delta S_{cyclic\ engine\ (reversible\ or\ irreversible)}$$

$$\frac{đq_{rev}}{T} = dS \qquad \frac{đq_{irrev}}{T} < dS \qquad \frac{đq}{T} \le dS$$

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2^{nd} Law of Thermodynamics in terms of entropy

- **S is a STATE FUNCTION**
- $$\Delta S = \int_{rev} \frac{đq_{rev}}{T} > \int_{irrev} \frac{đq_{irrev}}{T}$$

E&R eqn 5.26_{4th} $(5.33)_{3rd}$ Clausius inequality

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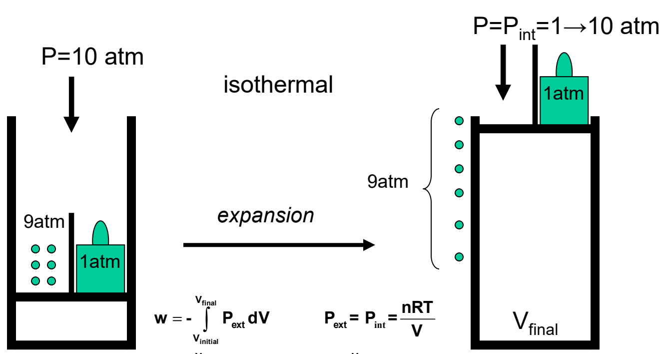
Lecture 3:
Pressure-Volume work reversible isothermal expansion; $P_{ext}=P_{int}$



1mole
300K
10 atm
V_1

$$w = -\int_{V_{initial}}^{V_{final}} P_{ext}\, dV \qquad P_{ext} = P_{int} = \frac{nRT}{V}$$

$$w = -\int_{V_{initial}}^{V_{final}} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

$$V_2 = \frac{300K\ R\ (1mol)}{1\ atm} \qquad V_1 = \frac{300K\ R\ (1mol)}{10\ atm}$$

$$w = -(300\ K\text{-}mol)\ R \ln \frac{10\ atm}{1\ atm}$$

w= -5743 J= -5.743 kJ

(more work done ON surroundings by reversible than irreversible; w_{irrev} =-2.244 kJ)

1mole
300K
1 atm
V_2

q_{rev}=-w =+5.743 kJ

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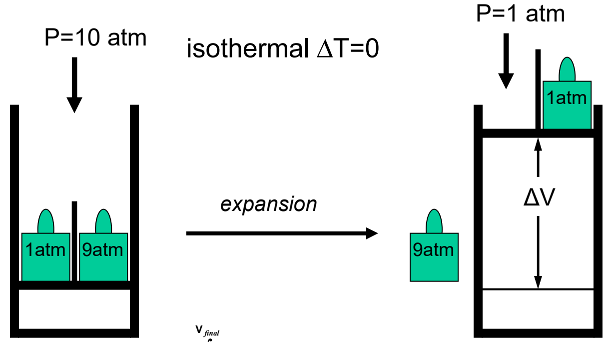
Lecture 3: Isothermal expansion: P_{ext}= const ideal gas (irreversible)



1mole
300K
10 atm
V_1

$$w = -\int_{V_{initial}}^{V_{final}} P_{ext}\, dV \qquad PV=nRT$$

$$w = -1 atm\, (V_2 - V_1)$$

$$V_2 = \frac{300K\ R\ (1 mol)}{1\ atm} \qquad V_1 = \frac{300K\ R\ (1 mol)}{10\ atm}$$

$$w = -(300\ K\text{-}mol)\ R \left(\frac{1}{1\ atm} - \frac{1}{10\ atm}\right)$$

w= -2244 J= -2.244 kJ

(- sign implies net work done ON surrounding)

1mole
300K
1 atm
V_2

q_{irrev}=-w=+2.244 kJ

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EXAMPLE from early lectures: isothermal expansion

$$(P_1=10\ atm, T_1=300K, V_1) \rightarrow (P_2=1\ atm, T_2=300K, V_2)$$

initial → final

same initial and final

$$\int \frac{đq}{T} = \frac{q}{T} \quad \text{for isothermal process} \qquad \Delta S$$

P_{ext}= P_{int}; q_{rev} = 5743 J $\quad \frac{q_{rev}}{T} = 19.14\ J\ K^{-1}$?

P_{ext}= const 1 atm; q_{irrev} = 2244 J $\quad \frac{q_{irrev}}{T} = 7.48\ J\ K^{-1}$ $\overset{?}{>}$ $<$?

$$\Delta S = \int_{\substack{initial \\ some\ reversible\ path}}^{final} \frac{đq_{rev}}{T} \geq \int_{\substack{initial \\ some\ path}}^{final} \frac{đq}{T}$$

to calculate ΔS must use reversible path initial⇒ final

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EXAMPLE from early lectures: isothermal expansion

$(P_1=10\text{ atm}, T_1=300K, V_1) \rightarrow (P_2=1\text{ atm}, T_2=300K, V_2)$

initial → final

same initial and final

$\int \frac{đq}{T} = \frac{q}{T}$ for isothermal process — ΔS

$P_{ext}= P_{int}$; q_{rev} = 5743 J $\frac{q_{rev}}{T} = 19.14\text{ J K}^{-1}$ — 19.14 J K^{-1}

P_{ext}= const 1 atm; q_{irrev} = 2244 J $\frac{q_{irrev}}{T} = 7.48\text{ J K}^{-1}$ < 19.14 J K^{-1}

$$\Delta S = \underset{\text{some reversible path}}{\int_{initial}^{final}} \frac{đq_{rev}}{T} \geq \underset{\text{some path}}{\int_{initial}^{final}} \frac{đq}{T}$$

to calculate ΔS must use reversible path initial ⇒ final

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$\Delta S_{universe} \geq 0$

soon :

$$\Delta S_{system} + \Delta S_{surroundings} = \Delta S_{universe} \geq 0$$

disorder increases

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calculating entropy (see summary on review handout)

- Thermal properties of entropy and entropy calculations
  - $dS = \frac{đq_{rev}}{T}$; $\Delta S = \int \frac{đq_{rev}}{T}$; $\oint \frac{đq_{rev}}{T} = 0$
  - $\Delta S \geq \int \frac{đq}{T}$; $0 \geq \oint \frac{đq}{T}$; $(= \text{for reversible process}; > \text{for spontaneous ['real'] process})$
  - $\Delta S_{total \equiv universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
  - S is a state function; dS is an exact differential
  - Dependence of S on
    - T: $\left(\frac{\partial \bar{S}}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$; $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
    - P: $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
    - V: $\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\bar{V}}$
    - Phase: $\Delta S = \frac{\Delta H_{equilibrium\ phase\ change}}{T_{equilibrium\ phase\ change}}$
  - Calculation of entropy changes for changes in P, V, T, phase
  - Third Law and calculations using Third Law Entropies: $\bar{S}^o(T)$
  - $\Delta S^0_{reaction}(T) = \sum_i \nu_i \bar{S}_i^0(T)$
  - Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i \quad where\ X_i = \frac{n_i}{n_{total}}$

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look ahead - ΔS for changes in T,V; (always $\Delta S = \int_{initial}^{final} \frac{đq_{rev}}{T}$)

also:

$S(T,V)$:

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

coming very soon

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{n\bar{C}_v}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

so: $dS = \frac{n\bar{C}_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$ *always (no w_{other}, closed system)*

ideal gas

$$dS = \frac{n\bar{C}_V}{T} dT + \frac{nR}{V} dV \qquad \Delta S = \int_{rev\ const\ V\ path} \frac{n\bar{C}_V}{T} dT + \int_{rev\ const\ T\ path} \frac{nR}{V} dV$$

$$\Delta S = n\bar{C}_v \ln\left(\frac{T_{final}}{T_{initial}}\right) + nR \ln\left(\frac{V_{final}}{V_{initial}}\right)$$

E&R eqn 5.14 $_{4th}$ (5.18) $_{3rd}$

"qrev/T" T vary const V path

q_{rev}/T V vary const T path

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look ahead- ΔS for changes in T,P; (always $\Delta S = \int_{initial}^{final} \frac{đq_{rev}}{T}$ *)*

also:

$S(T,P)$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

coming very soon

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{n\bar{C}_P}{T} \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

so: $dS = \frac{n\bar{C}_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$ *always (no w_{other}, closed system)*

ideal gas

$$dS = \frac{n\bar{C}_P}{T} dT - \frac{nR}{P} dP \qquad \Delta S = \int_{rev\ const\ P\ path} \frac{n\bar{C}_P}{T} dT - \int_{rev\ const\ T\ path} \frac{nR}{P} dP$$

$$\Delta S = n\bar{C}_P \ln\left(\frac{T_{final}}{T_{initial}}\right) - nR \ln\left(\frac{P_{final}}{P_{initial}}\right)$$

E&R eqn 5.15_{4th} $(5.19)_{3rd}$

"q_{rev}/T" vary T const P path

q_{rev}/T vary P const T path

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End of Lecture 11

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