

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. $\epsilon_{CARNOT[ideal\ gas]} = \frac{-W_{total}}{q_U} = 1 - \frac{T_L}{T_U} = 1 + \frac{q_L}{q_U}$
- II. $\epsilon_{ANY\ REVERSIBLE\ 'TWO\ TEMPERATURE'\ MACHINE} = \epsilon_{CARNOT[ideal\ gas]}$
or else violation of 2nd Law
- III. $\oint_{cycle} \frac{dq_{rev}}{T} = 0$ eqn 5.11 (E & R), and ?? (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. $\oint_{cycle} \frac{dq_{rev}}{T} = 0$ 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

$$dS = \frac{dq_{rev}}{T} \quad \text{is an exact differential}$$

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 $\epsilon_{irrev} < \epsilon_C$ (viz section, Lect10 S30)

BUT what about q_{irrev} with $\epsilon_{irrev} < \epsilon_C$??

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

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

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

$$\frac{dq_{rev}}{T} = dS \quad \frac{dq_{irrev}}{T} < dS \quad \frac{dq}{T} \leq dS$$

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2nd Law of Thermodynamics in terms of entropy

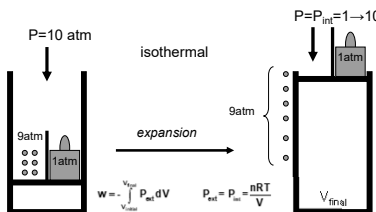
• **S is a STATE FUNCTION**

• $\Delta S = \int_{rev} \frac{dq_{rev}}{T} > \int_{irrev} \frac{dq_{irrev}}{T}$

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

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



1 mole
300K
10 atm
 V_1

$w = - \int_{V_1}^{V_2} P_{ext} dV$
 $w = - \int_{V_1}^{V_2} nRT \frac{1}{V} dV = - nRT \ln \frac{V_2}{V_1}$
 $w = - (300 \text{ K} \cdot \text{mol}) R \ln \frac{10 \text{ atm}}{1 \text{ atm}}$
 $w = -5743 \text{ J} = -5.743 \text{ kJ}$

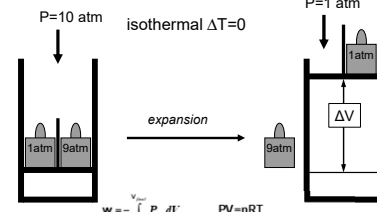
$P_{ext} = P_{int} = \frac{nRT}{V}$

1 mole
300K
1 atm
 V_2

$q_{rev} = -w = +5.743 \text{ kJ}$
(more work done ON surroundings by reversible than irreversible; $w_{irrev} = -2.244 \text{ kJ}$)

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



1 mole
300K
10 atm
 V_1

$w = - \int_{V_1}^{V_2} P_{ext} dV$
 $w = -1 \text{ atm} (V_2 - V_1)$
 $w = - (300 \text{ K} \cdot \text{mol}) R \left(\frac{1}{1 \text{ atm}} - \frac{1}{10 \text{ atm}} \right)$
 $w = -2244 \text{ J} = -2.244 \text{ kJ}$
 (- sign implies net work done ON surrounding)

1 mole
300K
1 atm
 V_2

$q_{irrev} = -w = +2.244 \text{ kJ}$

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EXAMPLE from early lectures: isothermal expansion

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

initial \rightarrow final

same initial and final $\int \frac{dq}{T} = \frac{q}{T}$ for isothermal process ΔS

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

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

$\Delta S = \int_{initial}^{final} \frac{dq_{rev}}{T} \geq \int_{initial}^{final} \frac{dq}{T}$

to calculate ΔS must use reversible path initial \Rightarrow final

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EXAMPLE from early lectures: isothermal expansion

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

initial \rightarrow final

same initial and final $\int \frac{dq}{T} = \frac{q}{T}$ for isothermal process ΔS

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

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

$\Delta S = \int_{initial}^{final} \frac{dq_{rev}}{T} \geq \int_{initial}^{final} \frac{dq}{T}$

to calculate ΔS must use reversible path initial \Rightarrow 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) \Rightarrow

- Thermal properties of entropy and entropy calculations
 - $dS = \frac{\delta q_{rev}}{T}$; $\Delta S = \int \frac{\delta q_{rev}}{T}$; $\oint \frac{\delta q_{rev}}{T} = 0$
 - $\Delta S \geq \int \frac{\delta q}{T}$; $0 \geq \oint \frac{\delta q}{T}$; (= for reversible process; > for spontaneous [real] process)
 - $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
- S is a state function, dS is an exact differential
- Dependence of S on
 - T: $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$; $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$
 - P: $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$
 - V: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
- Phase: $\Delta S = \frac{\Delta H_{fusion/vaporization}}{T}$
- Calculation of entropy changes for changes in P, V, T, phase
- Third Law and calculations using Third Law Entropies: $S^\circ(T)$
- $\Delta S^\circ_{rxn}(T) = \sum \nu_i S^\circ_i(T)$
- Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$, where $X_i = \frac{n_i}{n_{total}}$

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

also:

$S(T, V)$: coming very soon

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

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

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

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

$$\Delta S = n\bar{C}_v \ln\left(\frac{T_{final}}{T_{initial}}\right) + nR \ln\left(\frac{V_{final}}{V_{initial}}\right) \quad \text{E\&R eqn 5.14}_{th} \quad (5.18)_{id}$$

"q_{rev}/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 $\Delta S = \int_{initial}^{final} \frac{\delta q_{rev}}{T}$)

also:

$S(T, P)$: coming very soon

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

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

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

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

$$\Delta S = n\bar{C}_p \ln\left(\frac{T_{final}}{T_{initial}}\right) - nR \ln\left(\frac{P_{final}}{P_{initial}}\right) \quad \text{E\&R eqn 5.15}_{th} \quad (5.19)_{id}$$

"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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