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

statements of the Second Law of Thermodynamics

1. Macroscopic properties of an <u>isolated system</u> 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]*

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

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

III. $\displaystyle\oint_{cycle} \dfrac{đq_{rev}}{T} = 0$ 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. $\displaystyle\oint_{cycle} \dfrac{đq_{rev}}{T} = 0$ **for any reversible cyclic process**

figure 5.16 E & R$_{4th}$ (5.4 E & R$_{3rd}$)

(Dickerson pp.156 - 159, Raff pp.163 - 164)

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

S is a state function

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]*

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* $\varepsilon_{irrev} < \varepsilon_C$ *??*

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

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

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

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

$$\frac{đq_{rev}}{T} = dS \qquad \frac{đq_{irrev}}{T} < dS \qquad \frac{đq}{T} \leq dS$$
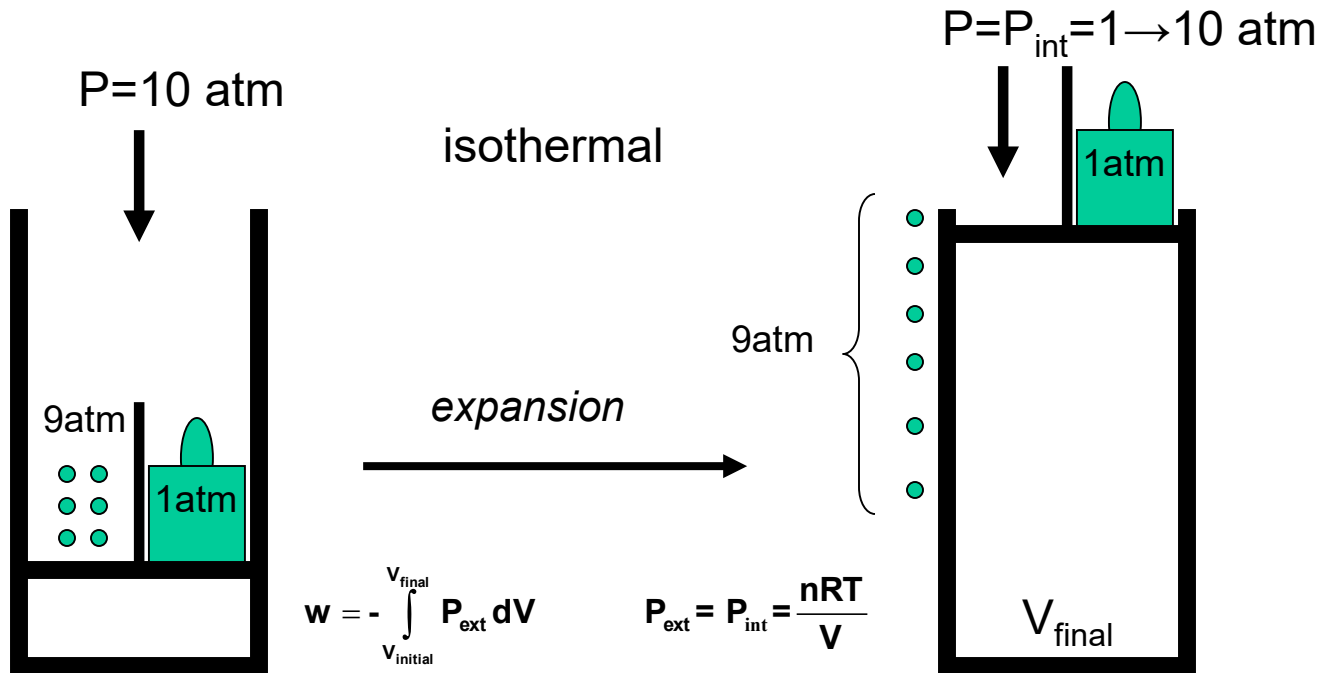
6

- S is a **STATE FUNCTION**

- $\Delta S = \displaystyle\int_{rev} \frac{đq_{rev}}{T} > \int_{irrev} \frac{đq_{irrev}}{T}$

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

$P=P_{int}=1\rightarrow10$ atm

P=10 atm

isothermal

1atm

9atm

9atm

1atm

expansion

V_{final}

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

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

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

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

w= -5743 J= -5.743 kJ

(more work done ON surroundings

by reversible than irreversible; w_{irrev} =-2.244 kJ)

1mole
300K
10 atm
V_1

1mole
300K
1 atm
V_2

$q_{rev}=-w =+5.743$ kJ

8

P=10 atm   isothermal $\Delta T = 0$ P=1 atm

1atm 9atm

expansion

ΔV

9atm
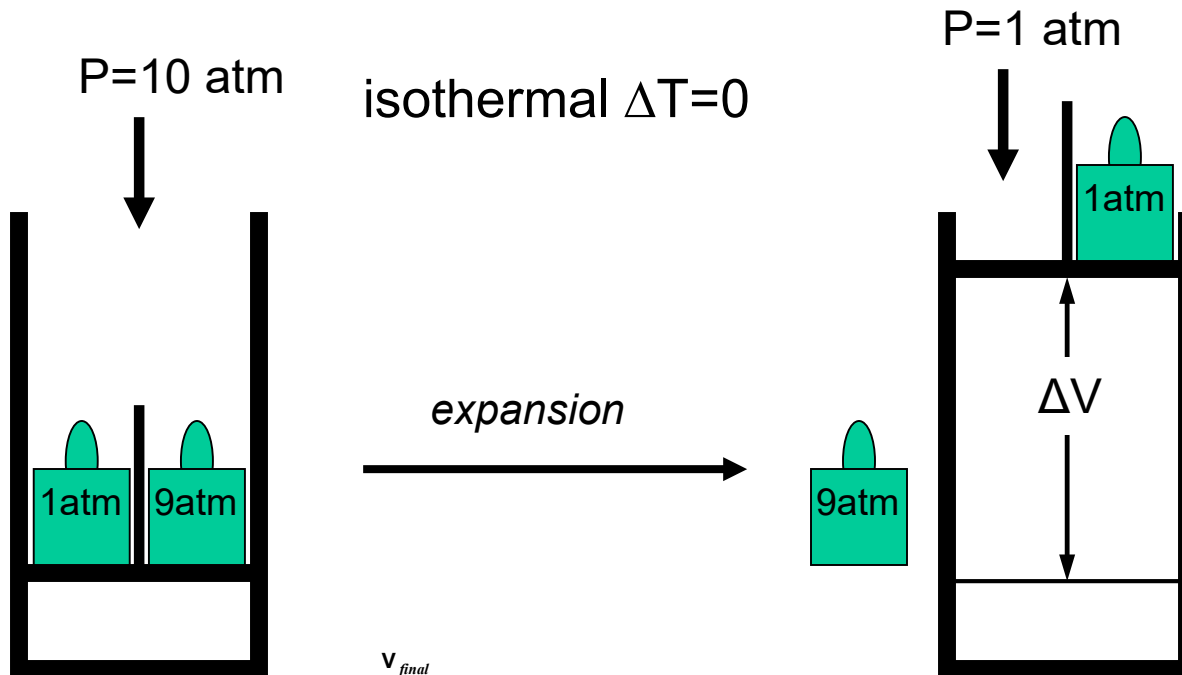
1atm

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

1mole
300K
10 atm
V_1

$w = -1\,atm\,(\textbf{V}_2 - \textbf{V}_1)$

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

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

1mole
300K
1 atm
V_2

w= -2244 J= -2.244 kJ

(- sign implies net work done ON surrounding)

q_{irrev}=-w=+2.244 kJ

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

initial $\rightarrow$ final

same initial and final

$$\int \frac{\bar{d}q}{T} = \frac{q}{T} \quad \text{for isothermal process}$$

ΔS

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

$P_{ext}= \text{const } 1 \text{ atm}; \quad q_{irrev} = 2244 \text{ J}$ $\quad \dfrac{q_{irrev}}{T} = 7.48 \text{ J K}^{-1} \begin{matrix} > \\ < \end{matrix}$ $\begin{matrix} ? \\ ? \end{matrix}$

$$\Delta S = \int_{\substack{initial \\ some\ reversible\ path}}^{final} \frac{\bar{d}q_{rev}}{T} \geq \int_{\substack{initial \\ some\ path}}^{final} \frac{\bar{d}q}{T}$$

to calculate ΔS must use reversible path initial $\Rightarrow$ final

10

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

initial $\rightarrow$ final

same initial and final

$$\int \frac{\not{d}q}{T} = \frac{q}{T} \quad \text{for isothermal process}$$

ΔS

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

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

$$\Delta S = \int_{\substack{initial \\ some\ reversible\ path}}^{final} \frac{\not{d}q_{rev}}{T} \geq \int_{\substack{initial \\ some\ path}}^{final} \frac{\not{d}q}{T}$$

to calculate ΔS must use reversible path initial $\Rightarrow$ final

11

soon :

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

disorder increases

- Thermal properties of entropy and entropy calculations

  ○ $dS = \dfrac{đq_{rev}}{T}$; $\Delta S = \int \dfrac{đq_{rev}}{T}$; $\oint \dfrac{đq_{rev}}{T} = 0$

  ○ $\Delta S \geq \int \dfrac{đq}{T}$; $0 \geq \oint \dfrac{đq}{T}$; (= *for reversible process*; > *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: $\left(\dfrac{\partial \overline{S}}{\partial T}\right)_V = \dfrac{\overline{C}_V}{T}$; $\left(\dfrac{\partial \overline{S}}{\partial T}\right)_P = \dfrac{\overline{C}_P}{T}$

  - P: $\left(\dfrac{\partial \overline{S}}{\partial P}\right)_T = -\left(\dfrac{\partial \overline{V}}{\partial T}\right)_P$

  - V: $\left(\dfrac{\partial \overline{S}}{\partial \overline{V}}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$

  - Phase: $\Delta S = \dfrac{\Delta H_{equilibrium\ phase\ change}}{T_{equilibrium\ phase\ change}}$

  ○ Calculation of entropy changes for changes in P, V, T, phase

  ○ Third Law and calculations using Third Law Entropies: $\overline{S}^o(T)$

  ○ $\Delta S^0_{reaction}(T) = \sum_i \nu_i \overline{S}^0_i(T)$

  ○ Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ where $X_i = \dfrac{n_i}{n_{total}}$

13

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

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

—— *ideal gas* ——

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

$$\Delta S = n\bar{C}_v\, ln\left(\frac{T_{final}}{T_{initial}}\right) + nR\, ln\left(\frac{V_{final}}{V_{initial}}\right) \quad \text{E\&R eqn 5.14}_{4th}\ \text{(5.18)}_{3rd}$$

"qrev/T" T vary
const V path

q_{rev}/T   V vary
const T path

14

look ahead- ΔS for changes in T,P; (always $\Delta S = \int\limits_{initial}^{final} \dfrac{\bar{d}q_{rev}}{T}$)

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

— *ideal gas* —

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

$$\Delta S = n\bar{C}_P\ ln\left(\frac{T_{final}}{T_{initial}}\right) - nR\ ln\left(\frac{P_{final}}{P_{initial}}\right) \quad \text{E\&R eqn 5.15}_{4th}\ (5.19)_{3rd}$$

"q$_{rev}$/T" vary T
const P path

q$_{rev}$/T vary P
const T path

End of Lecture 11