

Chemistry 163B

q_{rev} , Clausius Inequality and calculating
 ΔS for ideal gas P,V,T changes (HW#5)

Challenged Penmanship
Notes

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]*

four steps to exactitude

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

$$II. \quad \varepsilon_{\text{ANY REVERSIBLE 'TWO TEMPERATURE' MACHINE}} = \varepsilon_{\text{CARNOT}[ideal\ gas]}$$

or else violation of 2nd Law

$$III. \quad \oint_{\text{cycle}} \frac{dq_{rev}}{T} = 0 \quad \text{eqn 5.11 E \& R; demonstrated for ideal gas Carnot;}$$

general proof for two temperature reversible cycle;
see "a REALLY BIG RESULT" last lecture

(Dickerson p.155; Raff p.162 - 163)

$$IV. \quad \oint_{\text{cycle}} \frac{dq_{rev}}{T} = 0 \quad \text{for any reversible cyclic process}$$

figure 5.4 E & R

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

entropy

$dS = \frac{\bar{dq}_{rev}}{T}$ is an exact differential

S is a state function

goals of lecture

1. Relate ΔS and q_{irrev}

2. Calculate ΔS for P, V, T changes of ideal gas (HW#5)
 - a. using REVERSIBLE path (q_{rev}) [*even for irreversible processes*]
 - b. using partial derivatives of S with respect to P, V, T (look ahead)

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

a *irreversible* (actual) **cyclic** engine ϵ_{irrev} coupled with a Carnot refrigerator of ϵ_C **will not** violate 2nd Law if $\epsilon_{irrev} < \epsilon_C$ (viz HO#23 SL 20-26)

$$\begin{aligned} \Delta U_{cyclic} &= 0 \\ -W_{total} &= q_U + q_L \\ \text{for both rev} \\ \text{and irrev} \end{aligned}$$

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

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

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

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

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

$$\frac{\bar{d}q_{rev}}{T} = dS \quad \frac{\bar{d}q_{irrev}}{T} < dS \quad \frac{\bar{d}q}{T} \leq dS$$

2nd Law of Thermodynamics in terms of entropy

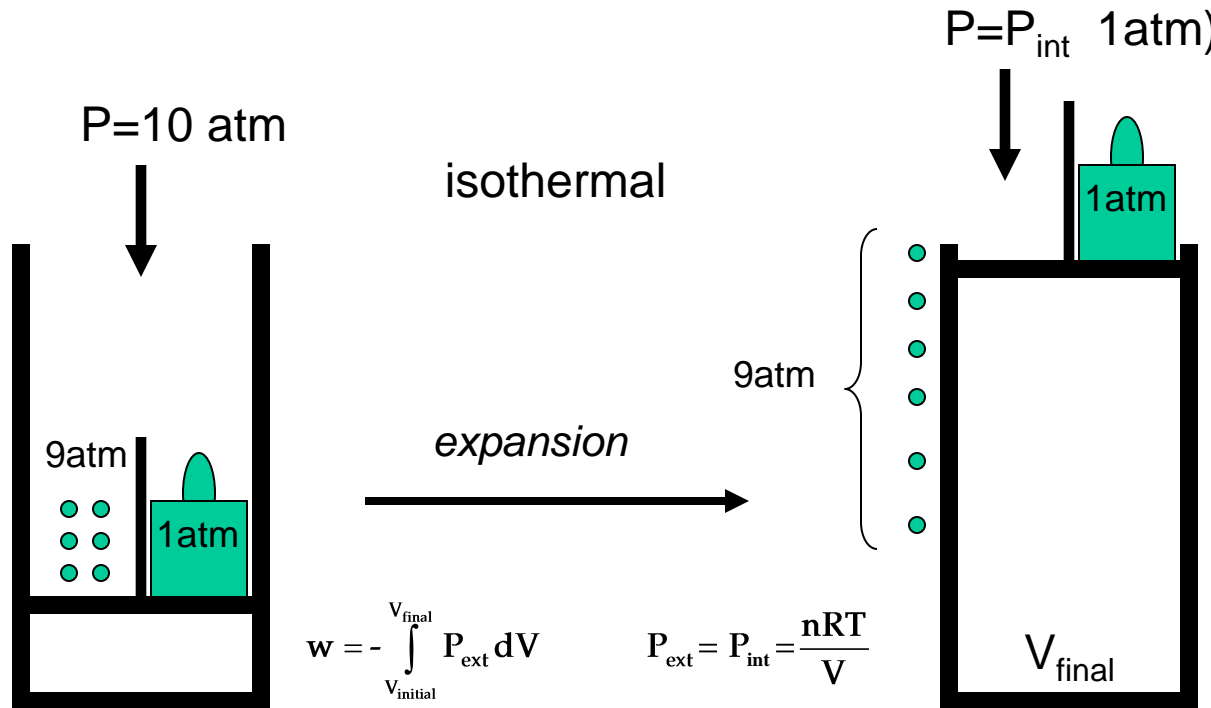
- **S is a STATE FUNCTION**

- $$\Delta S = \int_{rev} \frac{\vec{dq}_{rev}}{T} > \int_{irrev} \frac{\vec{dq}_{irrev}}{T}$$

E&R eqn 5.33 Clausius inequality

Lecture 3:

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



1 mole
300K
10 atm
 V_1

$$w = - \int_{V_{initial}}^{V_{final}} P_{ext} dV$$

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

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

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

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

$$w = -5743 \text{ J} = -5.743 \text{ kJ}$$

(more work done ON surroundings

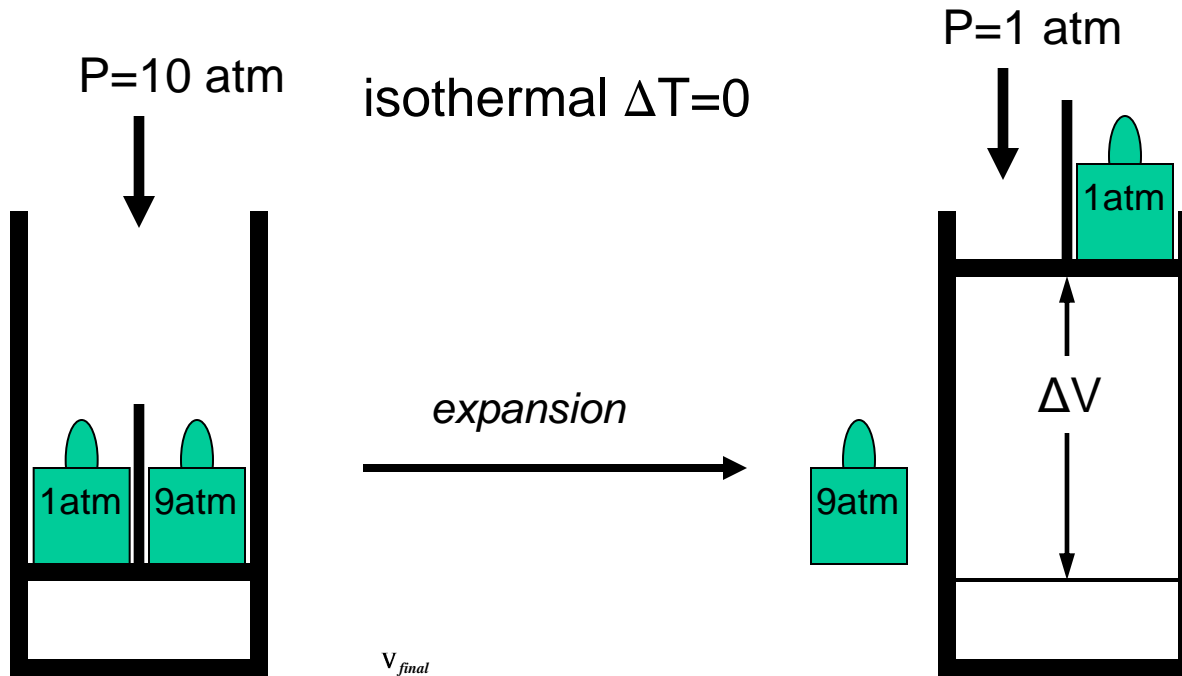
by reversible than irreversible; $w_{irrev} = -2.244 \text{ kJ}$)

V_{final}
1 mole
300K
1 atm
 V_2

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

Lecture 3:

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



1 mole
300K
10 atm
 V_1

$$w = - \int_{V_{initial}}^{V_{final}} P_{ext} dV$$

$$PV = nRT$$

$$w = -1 \text{ atm} (V_2 - V_1)$$

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

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

$$w = -2244 \text{ J} = -2.244 \text{ kJ}$$

(- sign implies net work done ON surrounding)

1 mole
300K
1 atm
 V_2

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

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 → final

same initial and final

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

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

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

$$\Delta S = \int_{\text{initial}}^{\text{final}} \frac{\bar{d}q_{\text{rev}}}{T}$$

some reversible path

to calculate ΔS must use **reversible** path initial \rightarrow final

$$\Delta S_{\text{universe}} \geq 0$$

soon :

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

disorder increases

calculating entropy (see summary on review handout)

- Thermal properties of entropy and entropy calculations

- $dS = \frac{dq_{rev}}{T}$; $\Delta S = \int \frac{dq_{rev}}{T}$; $\oint \frac{dq_{rev}}{T} = 0$

- $\Delta S \geq \int \frac{dq}{T}$; $0 \geq \oint \frac{dq}{T}$; (= 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: $\left(\frac{\partial \bar{S}}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$; $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$

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

- V: $\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_T$

- 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: $\bar{S}^o(T)$

- $\Delta S_{reaction}^o(T) = \sum_i \nu_i \bar{S}_i^o(T)$

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

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

also:

$S(T, V)$:

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

coming soon

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

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

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

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

q_{rev} T vary
const V path

q_{rev} V vary
const T path

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

also:

$S(T, P)$:

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

coming soon

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

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

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

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

q_{rev} vary T
const P path

q_{rev} vary P
const T path

End of Lecture