











For isothermal expansion of ideal gas

$$w_{\max} = w_{\text{rev}} = -nRT \ln \frac{V_{\text{f}}}{V_{\text{i}}}$$

$$q_{\max} = -w_{\text{rev}} = nRT \ln \frac{V_{\text{f}}}{V_{\text{f}}}$$

$$V_{\rm f} > V_{\rm i} \Rightarrow q > 0$$

 \Rightarrow heat flows in







✓ Cyclic processes

 $\triangle \text{ Reversible expansion from } V_1 \Rightarrow V_2 \quad V_2 > V_1$ $q = -w = nRT\ln \frac{V_2}{V_1} \quad \text{endothermic}$ Followed by reversible compression $V_2 \Rightarrow V_1$ $q' = -w' = -nRT\ln \frac{V_2}{V_1} \quad \text{exothermic}$ $q_{\text{net}} = q + q' = 0$ $w_{\text{net}} = 0$

 \triangle One step expansion-compression (irreversible)

$$W_{\rm net} = -\frac{3}{4}P_1V_1 + 3P_1V_1 = 2.25P_1V_1$$

$$q_{\rm net} = -2.25 P_1 V$$

Positive work is done by the system and heat is released

work → heat

System returned to the original state but surroundings are changed in a permanent way

In a reversible cyclic process, both system and surroundings returned to the original conditions

In reality: all processes are irreversible The net w and q depends on path but $\Delta E = 0 \leftarrow E$ is a state function











* The quantitative definition of entropy Boltzmann defines: $S = k_{B} \ln \Omega$ $(k_{B}N_{A} = R; \Omega: \text{the number of microstates})$ $\Omega = 1 \Rightarrow S = 0$ Boltzmann constant Avogadro's number Consider one particle with volume of V_{1} $When V_{1} \rightarrow 2V_{1}$ $\Omega_{1} \rightarrow \Omega_{2} = 2\Omega_{1}$ Positions available $\Rightarrow S_{1} = k_{B} \ln \Omega_{1}$ $S_{2} = k_{B} \ln \Omega_{2}$ $\Delta S = S_{2} - S_{1} = k_{B} \ln \Omega_{2} - k_{B} \ln \Omega_{1} = k_{B} \ln (\Omega_{2}/\Omega_{1})$ $= k_{B} \ln 2$

Consider two particles with volume of
$$V_1$$

 $V_1 \rightarrow 2V_1$
 $\Omega_1 \rightarrow 2^2\Omega_1$
For n particles: $V_1 \rightarrow 2V_1$
 $\Omega_1 \rightarrow 2^n\Omega_1 = \Omega_2$
 $\Delta S = S_2 - S_1 = k_B \ln \Omega_2 - k_B \ln \Omega_1$
 $= k_B \ln 2^n \Omega_1 - k_B \ln \Omega_1 = k_B \ln(2^n)$
 $= nk_B \ln 2$
For 1 mol: $\Delta S = N_A k_B \ln 2 = R \ln 2$ (when $V \rightarrow 2V$)
For *n* mol: $\Delta S = nR \ln 2$ (when $V \rightarrow 2V$)
Expand this idea:
 $When V_1 \rightarrow V_2 \Rightarrow \frac{\Omega_2}{\Omega_1} = \frac{V_2}{V_1}$ for one particle
 $\Rightarrow \Delta S_{V_1 \rightarrow V_2} = k \ln(\frac{V_2}{V_1})$

$$\Delta S_{V_1 \to V_2} = nR \ln \frac{V_2}{V_1} \quad \text{for n moles}$$

Recall

 \square

Isothermal reversible expansion of ideal gas

$$q_{\rm rev} = nRT \ln \frac{V_2}{V_1}$$
$$= T\Delta S$$
$$\Delta S = \frac{q_{\rm rev}}{T}$$

Note: q, T, and V are measurable properties

From $T_1 \rightarrow T_2$

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$$\int_{T_1}^{T_2} \mathrm{d}S = \int_{T_1}^{T_2} nC_{\mathrm{P}} \mathrm{d}\ln T$$

$$\Rightarrow \quad (S_{T_2} - S_{T_1}) = nC_{\mathsf{P}}\ln(\frac{T_2}{T_1})$$
$$\Rightarrow \quad \Delta S_{T_1 \to T_2} = nC_{\mathsf{P}}\ln(\frac{T_2}{T_1})$$

Assume C_P is constant over the temperature range

Similarly, at constant V

$$\Delta S_{T_1 \to T_2} = nC_v \ln(\frac{T_2}{T_1})$$

The second law: In any spontaneous process there is always an increase in the entropy of the universe

 $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$ for spontaneous process

 $\Delta S_{univ} < 0 \Rightarrow$ spontaneous for the reverse process

 $\Delta S_{univ} = 0 \Rightarrow$ at equilibrium

Ex. In a living cell, large molecules are assembled from simple ones. Against the 2nd law?

 ΔS_{svs} is negative

Need to consider ΔS_{surr} also

Ex. $Sb_2S_3(s) + 3Fe(s) \rightarrow 2Sb(s) + 3FeS(s) \Delta H = -125 \text{ kJ}$ ΔS_{surr} ? At 25 °C, 1 atm $\Delta S_{surr} = -\frac{-125 \text{ kJ}}{298 \text{ K}} = +419 \text{ J/K}$ The unit of entropy A quick analysis $\Delta S_{sys} \Delta S_{surr} \Delta S_{univ}$ + + + spontaneous + - - non-spontaneous + - ? - + ? depends on the relative size

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \quad \text{for spontaneous process}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \quad (\text{at constant P, } q_{\text{P}} = \Delta H)$$

$$T\Delta S_{\text{univ}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

Therefore S is a state function For all irreversible cycles: $\frac{q_{irr}}{T} < 0$ \checkmark The Clausius (1822 – 1888) inequality $\oint \frac{dq}{T} = \int_{1}^{2} \frac{dq_{irr}}{T} + \int_{2}^{1} \frac{dq_{rev}}{T} < 0$ For a cyclic process $\Rightarrow \int_{1}^{2} \frac{dq_{irr}}{T} + \int_{2}^{1} dS < 0$ (note: $\int_{2}^{1} dS = S_{1} - S_{2} = -\int_{1}^{2} dS$) $\Rightarrow \int_{1}^{2} \frac{dq_{irr}}{T} - \int_{1}^{2} dS < 0$ (note: $\int_{1}^{2} \frac{dq_{irr}}{T} \neq -\int_{2}^{1} \frac{dq_{irr}}{T}$) $\Rightarrow \int_{1}^{2} \frac{dq_{irr}}{T} < \int_{1}^{2} dS < 0$ (note: $\int_{1}^{2} \frac{dq_{irr}}{T} \neq -\int_{2}^{1} \frac{dq_{irr}}{T}$)

For a spontaneous process: $\Delta S > \frac{q_{irr}}{T}$ Assume constant P $\Delta S > \frac{q_p}{T} \Rightarrow \Delta S > \frac{\Delta H}{T}$ $\Rightarrow T\Delta S > \Delta H$ $\Rightarrow T\Delta S - \Delta H > 0$ (for a spontaneous process) $T\Delta S - \Delta H = T(S_f - S_i) - (H_f - H_i) = TS_f - H_f - TS_i + H_i$

| ℁ Free energy | 臺灣大學化學系 NTU Chemistry |
|---|--------------------------------|
| For a spontaneous process: $T\Delta S - \Delta H = TS_f - H_f - TS_i + H_i > 0$ | |
| Gibbs(1839 – 1903) Define: $G = H - TS$ (G: Gibb State function | os free energy) |
| $TS_{t} - H_{t} - TS_{i} + H_{i} = -G_{t} + G_{i} = -\Delta G_{t}$ | at constant T and P |
| At constant T and P $\Delta G = \Delta H - T\Delta S$ \bigstar For a spontaneous process: $-\Delta G$ or ΔG | > 0 < 0 at constant T and P |
| $\Delta G > 0 \Rightarrow$ spontaneous for the reve $\Delta G = 0 \Rightarrow$ at equilibrium | erse process |

| Ex. $H_2O(s) \rightarrow H_2O(l)$ $\Delta H^0 = 6.03 \times 10^3 \text{ Jmol}^{-1}, \Delta S^0 = 22.1 \text{ JK}^{-1}\text{mol}^{-1}$ | | | | | |
|--|------------------------------|--|----------------------|--|---|
| T (°C) |) ΔH° (J/mol) | ΔS° (JK ⁻¹ mol ⁻¹) | <i>T∆S</i> ⁰ (J/mol) | $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$ | |
| -10 | $6.03 	imes 10^3$ | 22.1 | 5.81×10^3 | $+2.2 \times 10^{2}$ | ÷ |
| 0 | 6.03×10^{3} | 22.1 | 6.03×10^{3} | 0 | 与 |
| 10 | 6.03×10^{3} | 22.1 | $6.25 	imes 10^3$ | -2.2×10^{2} | → |
| (Assume ΔH^o and ΔS^o do not change at different T) | | | | | |

| Fntropy changes in chemical reactions | 零大學化學系 U Сhemistry |
|---|---------------------------------|
| $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ | volume decreases ΔS : – |
| $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ | volume increases ΔS : + |
| $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ | ∆S: + |
| $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ | volume decreases ΔS : – |
| | |
| | |

In general:

| for homogeneous | reaction |
|---------------------------|------------------------------------|
| $A + B \rightarrow C$ | ΔS: – |
| $A \rightarrow B + C$ | ∆S: + |
| $A + B \rightarrow C + D$ | ΔS : difficult to estimate |

| Ex. $AI_2O_3(s) + 3H_2(s)$ $S^{o}_{AI_2O_3(s)} = 51 JI$ $S^{o}_{AI(s)} = 28$ | g) → 2AI(s) + 3H ₂ O(g) K ⁻¹ mol ⁻¹ $S^{o}_{H_{2}(g)} = 131$ $S^{o}_{H_{2}O(g)} = 189$ | |
|---|---|--|
| Soln. $\Delta S^{\circ}_{rxn} = 2S^{\circ}_{AI} + 3S^{\circ}_{H_{2}G}$ = 2(28) + 3(189) $= 179 \text{ JK}^{-1}\text{mol}^{-1}$ | $S_0 - 3S_{H_2}^{\circ} - S_{Al_2O_3}^{\circ}$ $S_0) - 3(131) - 51$ | |
| Note: H ^{_O} _H | has more rotational and vibrational freedom than H ₂ 自由度 | |
| In general: | the more complex the molecule the higher the entropy | |
| | | |

* Free energy and chemical reactions ΔG is measured indirectly (a) Method 1 $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ Ex. $C(s) + O_{2}(g) \rightarrow CO_{2}(g)$ $\Delta H^{\circ} = -393.5 \text{ kJ}$ $\Delta S^{\circ} = 3.05 \text{ JK}^{-1}$ $\Delta G^{\circ} = -393.5 - (298)(3.05 \times 10^{-3})$ $= -394.4 \text{ kJ} (\text{per mole of } CO_{2})$

Ex. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta H_f^o(SO_2) = -297 \text{ kJ/mol} \quad S^o(SO_2) = 248 \text{ JK}^{-1}\text{mol}^{-1}$ $\Delta H_f^o(SO_3) = -396 \qquad S^o(SO_3) = 257$ $S^o(O_2) = 205$ Soln: $\Delta H^o_{rxn} = 2(-396) - 2(-297)$ = -198 kJ $\Delta S^o_{rxn} = 2(257) - 2(248) - 1(205)$ $= -187 \text{ J/K} = -187 \times 10^{-3} \text{ kJ/K}$ $\Delta G^o_{rxn} = -198 - (298)(-187 \times 10^{-3}) = -142 \text{ kJ}$ Method 2 Free energy is a state function The change is independent of the pathway

Derive from known reactions

Ex.

 $\begin{array}{ll} 2\text{CO}(g) + 4\text{H}_2\text{O}(g) \xrightarrow{} 2\text{CH}_4(g) + 3\text{O}_2(g) & \Delta \text{G}^\circ = 1088 \text{ kJ} \\ 2\text{CH}_4(g) + 4\text{O}_2(g) \xrightarrow{} 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g) & \Delta \text{G}^\circ = -1602 \text{ kJ} \end{array}$

 $2CO(g) + O_2(g) \rightarrow 2CO_2(g) \Delta G^\circ = 1088 - 1602 = -514 \text{ kJ}$

Knowing Ex. $C(s)_{diamond} + O_2(g) \rightarrow CO_2(g)$ $\Delta G^{\circ} = -397 \text{ kJ}$ $C(s)_{\text{graphite}} + O_2(g) \rightarrow CO_2(g)$ $\Delta G^{\circ} = -394 \text{ kJ}$ $\Delta G^{\circ} = ?$ Q: $C(s)_{diamond} \rightarrow C(s)_{graphite}$ Soln: $C(s)_{diamond} + O_2(g) \rightarrow CO_2(g)$ $CO_2(g) \rightarrow C(s)_{\text{graphite}} + O_2(g)$ $C(s)_{diamond} \rightarrow C(s)_{graphite} \Delta G^{o} = -397 - (-394)$ = –3 kJ This process is thermally favored but kinetically very slow $C(s)_{graphite} \rightarrow C(s)_{diamond}$ In fact: Can be done at high T (> 1000 °C; increase rate) and high P (~10⁵ atm; diamond is more compact)

臺灣大學化學系 NTU Chemistry % The dependence of G on P G = H - TSFrom definition: H = E + PV \Rightarrow G = E + PV - TS dG = dE + PdV + VdP - TdS - SdTFor a reversible system with only PV work dT = 0At constant T : dE = q + w = q - PdVTdS = qTherefore dG = q - PdV + PdV + VdP - q = VdP = (nRT/P)dP⇔ $dG = RTd(\ln P)$ (1 mol and constant T)

Set a reference state with $G = G^{\circ}$ and P = 1 atm integrate from this state to any state of interest $\int_{G^{\circ}}^{G} dG = RT \int_{P=1}^{P} d(\ln P)$ $\Rightarrow G - G^{\circ} = RT \ln(P/1) = RT \ln P$ $\Rightarrow G = G^{\circ} + RT \ln P$ free energy of interestWhen P = 1 atm $\Rightarrow G = G^{\circ}$ (free energy of the gas at 1 atm) a function of T One of the principal applications of thermodynamics is to find relations between properties that might not be thought to be related

Ex.
$$N_{2}(g) + 3H_{2}(g) \rightarrow 2NH_{3}(g)$$

$$\Delta G_{rxn} = \Sigma n_{p}G_{products} - \Sigma n_{r}G_{reactants}$$

$$= 2G_{NH_{3}} - G_{N_{2}} - 3G_{H_{2}}$$
From the relationship of G and P:
$$G_{NH_{3}} = G^{\circ}_{NH_{3}} + RT\ln P_{NH_{3}}$$

$$G_{N_{2}} = G^{\circ}_{N_{2}} + RT\ln P_{N_{2}}$$

$$G_{H_{2}} = G^{\circ}_{H_{2}} + RT\ln P_{H_{2}}$$

$$\Delta G_{rxn} = 2G^{\circ}_{NH_{3}} + 2RT\ln P_{NH_{3}} - G^{\circ}_{N_{2}} - RT\ln P_{N_{2}}$$

$$= (2G^{\circ}_{NH_{3}} - G^{\circ}_{N_{2}} - 3G^{\circ}_{H_{2}}) + RT(2\ln P_{NH_{3}} - \ln P_{N_{2}} - 3\ln P_{H_{2}})$$

$$= \Delta G^{\circ}_{rxn} + RT\ln \left[\frac{P^{2}_{NH_{3}}}{P_{N_{2}}P^{3}_{H_{2}}}\right]$$
Quotient of the reaction = Q

| At equilibrium $\Delta G = 0 = \Sigma G_{\text{products}}$ | $_{s} - \Sigma G_{re}$ | actants | |
|--|-------------------------------------|-------------------------------|-----------------------------|
| $\Rightarrow \Sigma G_{\text{products}} = \Sigma G_{\text{react}}$ If $\Sigma G_{\text{reactants}} > \Sigma G_{\text{products}}$ If $\Sigma G_{\text{reactants}} < \Sigma G_{\text{products}}$ | ants ⇔ ⇔ | $\Delta G < 0$ $\Delta G > 0$ | rxn → rxn ← |
| $\Delta G = \Delta G^{\circ} + RT \ln Q$ | | | |
| At equilibrium: $\Delta G = Q = Q$ | <mark>= 0</mark> <i>K</i> (equil | ibrium cons | tant) |
| $0 = \Delta G^{\circ} + R^{-1}$ $\Rightarrow \qquad \Delta G^{\circ} = -RT \ln q$ | Γln <i>K</i> Κ | | |
| The standard from reactants and p | ee ener roducts | gy change v at 1 atm pa | with all artial pressure |
| | | | |

 $\Delta G = \Delta G^{\circ} + RT \ln Q$ = $-RT \ln K + RT \ln Q$ = $RT \ln (Q/K)$ When Q = K, $\Delta G = RT \ln 1 = 0 \Rightarrow$ at equilibrium When Q > K, $\Delta G > 0 \Rightarrow$ backward When Q < K, $\Delta G < 0 \Rightarrow$ forward Agrees with Le Châtelier's principle!!

Ex. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ Knowing $\Delta G^\circ = -33.3$ kJ per mole N_2 at 25 °C a. $P_{NH_3} = 1.00$ atm, $P_{N_2} = 1.47$ atm, $P_{H_2} = 1.00 \times 10^{-2}$ atm $\Delta G = ?$ $\Delta G = \Delta G^\circ + RT \ln Q$ $= (-33.3) + (8.31)(298) \ln \frac{(1.00)^2}{(1.47)(1.00 \times 10^{-2})^3} = 0$ This condition is already at equilibrium b. $P_{NH_3} = 1.00$ atm, $P_{N_2} = 1.00$ atm, $P_{H_2} = 1.00$ atm $Q = 1 \Rightarrow \Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ = -33.3$ kJ A negative value Rxn \Rightarrow

Consider
$$T_1 \rightarrow T_2$$

 $\mathcal{K}_1 \rightarrow \mathcal{K}_2$
 $\ln \mathcal{K}_2 = \frac{-\Delta H^o}{RT_2} + \frac{\Delta S^o}{R} \qquad \ln \mathcal{K}_1 = \frac{-\Delta H^o}{RT_1} + \frac{\Delta S^o}{R}$
 $\ln \mathcal{K}_2 - \ln \mathcal{K}_1 = \frac{-\Delta H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
The van't Hoff equation:
 $\ln \left(\frac{\mathcal{K}_2}{\mathcal{K}_1}\right) = \frac{-\Delta H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

N₂(g) + 3H₂(g) ≒ 2NH₃(g)

$$K = 3.7 \times 10^{-6}$$
 at 900 K
 $\Delta H^{0} = -92$ kJ
 K at 550 K?

Soln.

Ex.

$$\ln \frac{K_{550}}{3.7 \times 10^{-6}} = - \frac{(-92000)}{8.31} \left[\frac{1}{550} - \frac{1}{900} \right]$$

 $ln K_{550} = -4.8$ 2.3 log $K_{550} = -4.8$ log $K_{550} = -2.1 = 0.9 - 3$

$$K_{550} = 8 \times 10^{-3}$$

| ※ Free energy and work | 臺灣大學化學系 NTU Chemistry |
|--|---|
| $\Delta G = \Delta H - T\Delta S \text{at constant T}$ $\Delta H = \Delta E + P\Delta V \text{at constant P}$ $\Delta E = q_{P} + w$ $\Rightarrow \Delta H = q_{P} + w + P\Delta V$ $\Rightarrow \Delta G = q_{P} + w + P\Delta V - T\Delta S$ | |
| Recall $\Delta S = \frac{q_{\text{rev}}}{T}$, $T\Delta S = q_{\text{rev}}$ | |
| $\Rightarrow \Delta G = q_{P} + w + P\Delta V - q_{rev}$ $\Rightarrow \Delta G = (q_{P} - q_{rev}) + w + P\Delta V$ | ESE INC |
| Recall $q_{P} \leq q_{rev}, q_{P} - q_{rev} \leq 0$ | |
| Define: $w = w_{useful} + w_{PV} \leftarrow w_{PV}$ Works other than | $= -P\Delta V$, usually useless PV work |

Ex. $CH_3OH(I) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(I)$ If define the fuel efficiency as the work output divided by the enthalpy contained in the reaction: Theoretical efficiency?

Soln:

In: $CH_3OH(I) CO_2(g) H_2O(I)$ $\Delta H_f^{\circ} -239 -393.5 -286 \text{ kJ/mol}$ $\Delta G_f^{\circ} -166 -394 -237$

 $\Delta H^{\circ} = -393.5 + 2(-286) - (-239) = -727 \text{ kJ}$

 $\Delta G^{\circ} = -394 + 2(-237) - (-166) = -702 \text{ kJ}$

Theoretical efficiency $=\frac{\Delta G}{\Delta H}=\frac{-702}{-727}=96.6\%$

* Driving nonspontaneous reactions

 ⊘ Free energy change is the driving force of a reaction the lower the better: ∆G more negative → stronger driving force

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Ex. $Cu_2S(s) \rightarrow 2Cu(s) + S(s)$ $\Delta G^\circ = +86.2 \text{ kJ}$ $S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta G^\circ = -300.1 \text{ kJ}$

 $Cu_2S(s) + O_2(g) \rightarrow 2Cu(s) + SO_2(g)$ $\Delta G^\circ = -213.9 \text{ kJ}$

For reversible adiabatic change from

$$V_{1} \rightarrow V_{2} \qquad T_{1} \rightarrow T_{2}$$

$$C_{V} \int_{T_{1}}^{T_{2}} \frac{dT}{T} = -R \int_{V_{1}}^{V_{2}} \frac{dV}{V}$$

$$\Rightarrow \qquad C_{V} \ln \frac{T_{2}}{T_{1}} = -R \ln \frac{V_{2}}{V_{1}} = R \ln \frac{V_{1}}{V_{2}}$$

$$\Rightarrow \qquad \left(\frac{T_{2}}{T_{1}}\right)^{C_{V}} = \left(\frac{V_{1}}{V_{2}}\right)^{R}$$
Since $C_{P} = C_{V} + R$

$$\left(\frac{T_{2}}{T_{1}}\right)^{C_{V}} = \left(\frac{V_{1}}{V_{2}}\right)^{(C_{P} - C_{V})} \Rightarrow \frac{T_{2}}{T_{1}} = \left(\frac{V_{1}}{V_{2}}\right)^{(\frac{C_{P} - 1}{C_{V}})} = \left(\frac{V_{1}}{V_{2}}\right)^{\gamma - 1} \qquad \gamma = \frac{C_{P}}{C_{V}}$$

$$\frac{T_2}{T_1} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} \qquad \Rightarrow \qquad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$
Since
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad \Rightarrow \qquad \frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

$$\Rightarrow \qquad \frac{P_2 V_2}{P_1 V_1} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} \qquad \Rightarrow \qquad \frac{P_2}{P_1} = \frac{V_1^{\gamma}}{V_2^{\gamma}}$$

$$\implies \qquad P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

Ex. 5.00 mol monoatomic ideal gas

$$25 \circ C \cdot 10.0 \text{ atm} \xrightarrow{\text{reversibly}} 1.00 \text{ atm}$$

Q: Final V, w?
 $\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$
 $P_1V_1^{\gamma} = P_2V_2^{\gamma} \Rightarrow P_1V_1^{\frac{5}{3}} = P_2V_2^{\frac{5}{3}}$
 $V_1 = \frac{nRT_1}{P_1} = \frac{(5.00 \text{ mol})(0.0826 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{10.0 \text{ atm}} = 12.2 \text{ L}$
 $(10.0 \text{ atm})(12.2 \text{ L})^{5/3} = (1.00 \text{ atm})V_2^{5/3}$

$$V_{2}^{5/3} = (10.0)(12.2)^{5/3}$$

$$\Rightarrow \quad \log V_{2}^{5/3} = \log[(10.0)(12.2)^{5/3}]$$

$$\Rightarrow \quad 5/_{3} \log V_{2} = \log(10.0) + 5/_{3} \log 12.2$$

$$\Rightarrow \quad V_{2} = 48.6 \text{ L}$$

$$T_{2} = \frac{P_{2}V_{2}}{nR} = \frac{(1.00)(48.6)}{(5.00)(0.08206)} = 118 \text{ K}$$

$$\Delta E = w = nC_{V}\Delta T = (5.00)(3/2)(8.3145)(118 - 298))$$

$$= -11,200 \text{ J}$$
Reversible adiabatic work

$$\begin{split} \Delta S_{\text{surr}} &= -\Delta H_{\text{sys}} / T \text{ (at 283.0 °C)} \\ \text{To find } \Delta H_{\text{fusion}} \text{ at 10.0 °C:} \\ \text{First find } q_{\text{diff}} \text{ from 25.0 } \rightarrow 10.0 °C \\ q_{\text{diff}} &= (C_{\text{p},\text{I}} - C_{\text{p},\text{s}}) (\Delta T) = (133.0 - 100.4) (10.0 - 25.0) \\ &= -489 \text{ J} = -0.489 \text{ kJ} \\ \Delta H_{\text{fusion}}(10.0) &= \Delta H_{\text{fusion}}(25.0) + q_{\text{diff}} = 10.04 - 0.489 \\ &= 9.55 \text{ kJ} \\ C_{6}H_{6}(I) \iff C_{6}H_{6}(s) \quad \Delta H = -9.55 \text{ kJ at 10.0 °C} \\ \Delta S_{\text{surr}} &= \frac{-\Delta H_{\text{sys}}}{T} = \frac{-(-9.55 \times 10^{3})}{283.0} = 33.7 \frac{\text{J}}{\text{K}} \end{split}$$

 $\Delta \text{ Decomposition of } Ag_2CO_3(s)$ $Ag_2CO_3(s) \implies Ag_2O(s) + CO_2(g) \ \Delta H^0 = 79.14 \text{ kJ/mol}$ $At equilibrium <math>P_{CO_2} = 6.23 \times 10^{-3} \text{ torr } (25 \text{ °C})$ Q: P_{CO_2} necessary to prevent the decomposition at 110. °C? Soln: To prevent decomposition: $\Delta G = \Delta G^0 + R T \ln Q_{110} > 0$ Since $\Delta G^0 = -R T \ln K_{110}$ We need a $Q_{110} > K_{110}$ Find ΔS^0 first, and then find K_{110} $K_{25} = \frac{6.23 \times 10^{-3} \text{ torr}}{760 \text{ torr}} = 8.20 \times 10^{-6}$ $-R T \ln K_{25} = -(8.315)(298) \ln(8.20 \times 10^{-6}) = 29.0 \times 10^3 \text{ J}$ $\Delta H^0 - T \Delta S^0 = -R T \ln K_{25}$ $\Rightarrow \Delta S^0 = \frac{79.14 - 29.0}{298} = 0.168 \text{ kJ/K} = 168 \text{ J/K}$

Assuming
$$\Delta H^{\circ}$$
 and ΔS° are constant over 25–125 °C
 $\Delta H^{\circ} - T\Delta S^{\circ} = -RT \ln K_{110} \quad \Rightarrow \quad \text{obtain } K_{110}$
A better way:
Assuming ΔH° is constant over 25–125 °C
 $\ln \frac{K_{110}}{K_{25}} = -\frac{\Delta H^{\circ}}{R} \left(\frac{1}{383} - \frac{1}{298}\right)$
2.303(log K_{110} - log 8.20 × 10⁻⁶) = $-\frac{79.14 \times 10^3}{8.315} \left(\frac{1}{383} - \frac{1}{298}\right)$
 $\Rightarrow \quad K_{110} = 9.86 \times 10^{-3}$
 $\Rightarrow \quad P_{CO_2} = 9.86 \times 10^{-3} \text{ atm} = 7.49 \text{ torr}$
Conclusion: P_{CO_2} has to be larger than 7.49 torr
to have $\Delta G = \Delta G^{\circ} + RT \ln Q_{110} > 0$