

Review Topics Weeks 1-3

In reviewing material one should not memorize the entries as 'plug-in' formulas. But should understand i) how they arise from the basic laws of thermodynamics; ii) what are the limits on their generality and under what special conditions they apply; and iii) how they qualitatively reflect the 'logic' of the natural world and, in some cases, the underlying properties of molecules and matter.

- Mathematical techniques (to be employed throughout course as needed)
 - Exact and inexact differentials
 - State functions
- Equations of state
 - Thermodynamic variables (P, V, T, variables for W_{other}) and ideal gas thermometer to operationally measure T
 - $P=F/A$
 - System and surroundings
 - Ideal Gas
 - $PV=nRT$
 - $E = (3/2) nRT$ (monatomic; no "internal" structure, translational kinetic energy in 3 dimensions)
 - Approximation for real gasses
 - Van der Waals $\left(P - \frac{a}{\bar{V}^2} \right) (\bar{V} - nb) = RT$; physical meaning of a and b
 - Other approximate equations of state exist (e.g. Virial power series expansion)
- Work
 - $w = \text{force} \cdot \text{displacement}$
 - $\bar{d}w$ inexact differential, depends on path
 - $\bar{d}w = -P_{\text{ext}} dV$ (P-V work)
 - $w = \int \bar{d}w$
 - $w = -P_{\text{ext}} \Delta V$ ($P_{\text{ext}} = \text{constant}$, $W_{\text{other}} = 0$)
 - $w = -n R T \ln (V_f / V_i)$ (isothermal, reversible, ideal gas, $W_{\text{other}} = 0$)
- Heat
 - $\bar{d}q$ inexact differential depends on path
 - $\bar{d}q = C dT$
 - $q = \int C dT$
- First Law of Thermodynamics
 - U = internal energy
 - $dU = \bar{d}q + \bar{d}w$ (definition, for closed system)
 - Equivalent statements of First Law of Thermodynamics
 - U is a state function
 - dU is an exact differential
 - $\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$

- $H \equiv U + (PV)_{internal}$
- H is a state function
- $\Delta H = \Delta U + \Delta (PV) = \Delta U + P_f V_f - P_i V_i$
- Differential relationships for state functions
(n_i = number moles of substance i; $ov_1 \dots ov_M$ are "other variables" that might define the energy of the system and be involved in w_{other} . For example charge, position with respect gravitational attraction, etc)
- $$dU(T, V, n_1, \dots, n_K, ov_1, \dots, ov_M) = \left(\frac{\partial U}{\partial T}\right)_{V, n, ov} dT + \left(\frac{\partial U}{\partial V}\right)_{T, n, ov} dV + \sum_i^K \left(\frac{\partial U}{\partial n_i}\right)_{T, V, n_{j \neq i}, ov} dn_i + \sum_i^M \left(\frac{\partial U}{\partial ov_i}\right)_{T, V, n, ov_{j \neq i}} dov_i$$
- $$dH(T, P, n_1, \dots, n_K, ov_1, \dots, ov_M) = \left(\frac{\partial H}{\partial T}\right)_{P, n, ov} dT + \left(\frac{\partial H}{\partial P}\right)_{T, n, ov} dP + \sum_i^K \left(\frac{\partial H}{\partial n_i}\right)_{T, P, n_{j \neq i}, ov} dn_i + \sum_i^M \left(\frac{\partial H}{\partial ov_i}\right)_{T, P, n, ov_{j \neq i}} dov_i$$

more commonly (for closed system, $dn_i = 0$; and no work other, $\vec{d}w_{other} = 0$)

- $$dU(T, V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$
 - $$dH(T, P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$
- Definitions relationships (closed system)
 - $dU = \vec{d}q - P_{ext} dV + \vec{d}w_{other}$
 - $\Delta U_V = q_V + \vec{d}w_{other}$ (const V) "heat is ΔU at constant V"
 - $n\bar{C}_V \equiv \left(\frac{dq}{dT}\right)_V \Rightarrow dU_V = n\bar{C}_V dT + \vec{d}w_{other}$ (const V)
 - $dH = \vec{d}q + V dP + \vec{d}w_{other}$ ($P_{ext} = P_{internal}$; thus usually for a reversible process; but OK for any infinitesimal process)
 - $\Delta H_P = q_P + w_{other}$ (const P_{ext} ; $P_{initial} = P_{final} = P_{ext}$) "heat is ΔH at constant P"
 - $n\bar{C}_P \equiv \left(\frac{dq}{dT}\right)_P \Rightarrow dH_P = n\bar{C}_P dT + \vec{d}w_{other}$ (const P)

- Derived consequences (closed system, $\bar{d}w_{other} = 0$)

$$dU = n\bar{C}_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

- with $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{dq}{dV}\right)_T - P$

- $dU_V = n\bar{C}_V dT$ (const V, any system)

but with $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for ideal gas

- $dU = n\bar{C}_V dT$ (ideal gas, any path)

$$dH = n\bar{C}_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

- with $\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{dq}{dP}\right)_T + V$

- $dH_P = n\bar{C}_P dT$ (const P, any system)

since for ideal gas $dH = dU + d(PV) = dU + d(nRT) = dU + nR dT$
and $dU = n\bar{C}_V dT$

- $dH_P = n(\bar{C}_V + R) dT = n\bar{C}_P dT$ (ideal gas, any path)
with $\bar{C}_P = \bar{C}_V + R$ for ideal gas

- Evaluating q , w , ΔU , ΔH for various processes (closed system, no w_{other})

Constant volume

- $w = 0$
- $q_V = \Delta U_V = n\bar{C}_V \Delta T$
- $\Delta H_V = \Delta U_V + V \Delta P = \Delta U_V + V (P_f - P_i)$

Constant pressure

- $q_P = \Delta H_P = n\bar{C}_P \Delta T$
- $w = -P\Delta V$
- $\Delta U_P = q + w$

Ideal gasses

- $\bar{C}_p = \bar{C}_v + R$
- $\bar{C}_v = \frac{3}{2} R$ for monatomic ideal gas
- $\Delta U = n \bar{C}_v \Delta T$ (any path)
- $\Delta H = n \bar{C}_p \Delta T$ (any path)

Isothermal path

- $q = -w$
- $\Delta U = 0$
- $\Delta H = 0$
- $w = -n R T \ln \frac{V_f}{V_i} = \square n R T \ln \frac{P_i}{P_f}$ (reversible path, note – sign)
- $w = -P_{\text{ext}} \Delta V$ (constant P_{ext} expansion/compression)

Adiabatic path

- $q = 0$
- $\Delta U = w = n \bar{C}_v \Delta T$
- $\Delta H = \Delta U + \Delta(PV) = \Delta U + P_f V_f - P_i V_i = n \bar{C}_p \Delta T$
- $T_1^{\bar{C}_v} V_1 = T_2^{\bar{C}_v} V_2$ (adiabatic reversible path)
- $P_1 V_1^{\frac{\bar{C}_p}{\bar{C}_v}} = P_2 V_2^{\frac{\bar{C}_p}{\bar{C}_v}}$ (adiabatic reversible path, $PV^\gamma = \text{constant}$)
- $\frac{T_1^{\bar{C}_p}}{P_1} = \frac{T_2^{\bar{C}_p}}{P_2}$ (adiabatic reversible path)

• **Thermochemistry**

- $\Delta H_{\text{reaction}} = (H_{\text{products}} - H_{\text{reactants}})$ (vs ΔH for physical change)
- $\Delta H_P = q_P$
- standard states
- definition of $\bar{H}_f^\circ \equiv \Delta \bar{H}_f^\circ$
- $\Delta H_{\text{reaction}}^\circ = \sum_i \nu_i \bar{H}_f^\circ$ where ν_i are stoichiometric coefficients
- Hess's Law
- $\Delta H_{\text{reaction}} = \Delta U_{\text{reaction}} + \Delta n_{\text{gas}} RT$
- $\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$
- ΔH from bond enthalpies
- Heats of reactions in ionic solution