Physical chemistry
Student Chemistry Olympiad

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Aim

- Your most valuable asset is your learning ability.
- This course is a practice in learning and specially improves your deduction skills.
- This course provides you with tools applicable in understanding many natural phenomena.
- This course teaches you the basics of thermodynamics.

References

- Physical chemistry, Sixth edition by Ira N. Levine
- Physical chemistry, 6th edition by J. Paula and P. Atkins

Topics

- 1st law of thermodynamics
- 2nd law of thermodynamics
- Material equilibrium and thermodynamic functions
- Chemical equilibrium in ideal gases.
- Phase equilibrium
- State function

Thermodynamics

- Study of the underlying physical principles that govern the properties and behavior of chemical systems.
- Physical chemistry: $\begin{cases} \textit{Thermodynamics} \\ \text{Quantum Chemistry} \\ \text{Statistical mechanics} \\ \textit{Kinetics} \end{cases}$
- Thermodynamics: Macroscopic science that studies the interrelationships of the various equilibrium properties of a system and their changes in processes.
- Quantum chemistry: Application of quantum mechanics to atomic structure, molecular bonding and spectroscopy.
- Statistical mechanics: Calculation of macroscopic thermodynamic properties from molecular properties (It also allows a microscopic interpretation of thermodynamics relations.).
- Kinetics: Study of rate processes e.g., chemical reactions, diffusion and the flow of charge.

Thermodynamics

- Study of heat, work, energy and the changes they produce in the states of systems.
- Thermodynamics: $\begin{cases}\text{Equilibrium thermodynamics}\\ \text{Irreversible thermodynamics}\end{cases}$
- System and surroundings
- Open system, closed system and an isolated system.
- Wall: Rigid, nonrigid; permeable, impermeable; adiabatic or nonadiabatic.
- Equilibrium: (a) Systems macroscopic properties remain constant with time. (b) removal of the system from surroundings causes no change in the system properties.

Thermodynamics

- Mechanical equilibrium: no unbalanced forces act on or within the system.
- Material equilibrium: no net chemical reactions occur in the system and no net flow of chemical species occur among parts of the system.
- Thermal equilibrium: no net change in the properties of a system or its surrounding when they are separated by a thermally conducting wall.
- Thermodynamic properties:
- Extensive vs. intensive
- Homogeneous system vs. inhomogeneous system.
- A homogeneous part of a system is called a phase.
- Thermodynamic state and state functions.

Thermodynamics

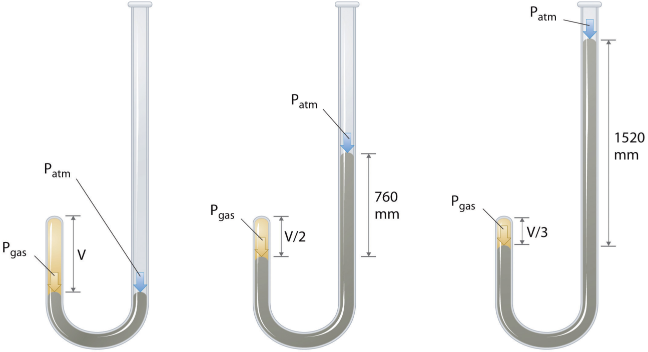
- Mechanical equilibrium →Pressure
- Thermal equilibrium→Temperature
- Zeroth law of thermodynamics: two systems that are each found to be in thermal equilibrium with a third system will be found to be in thermal equilibrium with each other.
- Thermometer: a reference system, r.
- $\theta \equiv aV_r + b = a(V_{bulb} + Al) + b = aAl + (aV_{bulb} + b) \equiv cl + d.$
- ice point and steam point for centigrade scale
- Resistance thermometer, thermistor, thermocouple, optical pyrometer.
- Temperature is an abstract property that is not measured directly.

Thermodynamics

- Atomic weight, relative atomic mass, A_r.
- Molecular weight, relative molecular mass, A_r.
- Avogadro's number
- Atomic mass or molecular mass in units of atomic mass units (amu).
- The mole, molar mass M.
- $N_A = 6.02 \times 10^{23} mol^{-1}$
- Ideal gases
- Boyle's law is an experimental gas law that describes how the pressure of a gas tends to increase as the volume of the container decreases., $PV = k(n, T)$

Ideal gas

- The absolute pressure exerted by a given mass of an ideal gas is inversely proportional to the volume it occupies if the temperature and amount of gas remain unchanged within a closed system.



(a)
$V_{gas} = V$
$P_{gas} = 760$ mmHg

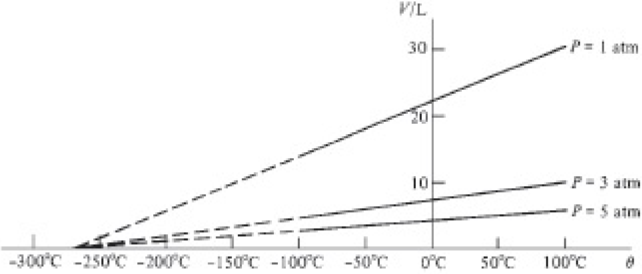
(b)
$V_{gas} = V/2$
$P_{gas} = 1520$ mmHg

(c)
$V_{gas} = V/3$
$P_{gas} = 2280$ mmHg

- Figure: Schematic of the Boyle's experiment taken from `https://libretexts.org/`

Ideal gas

- The gas becomes ideal in the zero density limit.
- Pressure and volume units.
- Charles law or law of volumes, When the pressure on a sample of a dry gas is held constant, $V = a_1 + a_2\theta$, (using the Kelvin scale, temperature and the volume will be in direct proportion: $\frac{V}{T} = k'(n, P)$).



Ideal gas

- Thermal expansion of gases and of liquid mercury are similar.
- Ideal gas thermometer (temperature scale): $T = \lim_{P\to 0} \frac{PV}{nR}$ or $T \equiv BV$.
- B is determined by assigning 273.16 K to the triple point of water.
- $T \equiv 273.16K \lim_{P\to 0} \frac{V}{V_{tr}}$
- A constant volume gas thermometer is more practical.
- Present definition of the Celsius (centigrade) scale t: $t/^{\circ}C \equiv T/K - 273.15$

Ideal gas

- Absolute ideal gas temperature is based on properties of a general class of substances, thus it has fundamental significance (determining kinetic energy and molecular energy distribution).
- At constant P and m, V/T$=V_{tr}/T_{tr}=$ constant. This is Charles' law.
- Gay-Lussac's law, $\frac{P}{T}=k''(n,V)$.
- What about a process which changes, P, V and T?
- $P_1,V_1,T_1 \rightarrow P_2,V_2,T_2$, divide this process into one at constant $T=T_1, \quad P_1,V_1 \rightarrow P_2,V_3$ and a second at constant $P=P_2, \quad V_3,T_1 \rightarrow V_2,T_2$ thus showing that $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$.
- Volume is an extensive quantity: At constant T and P, V is proportional to m. Thus $\frac{PV}{T}=cm$, where the constant c depends on the nature of gas under consideration.

Ideal gas

- Avogadro's hypothesis states that at constant P and T, V is proportional to n. Thus $\frac{PV}{T} = nR$, where R is universal constant.
- Definition: $X_i = \frac{n_i}{n_{total}}$, $P_i = X_i P_{total}$.
- Dalton's law states that the presence of other molecules has no effect on the pressure exerted by molecules of species i. I.e., $P_i = n_i \frac{RT}{V}$
- $P_{total} = \sum_i P_i = \frac{RT}{V} \sum_i n_i = \frac{RT}{V} n_{total}$
- $\frac{P_i}{P_{total}} = \frac{n_i}{n_{total}}$
- Ideal gas law can be deduced from classical mechanics

Differential calculus

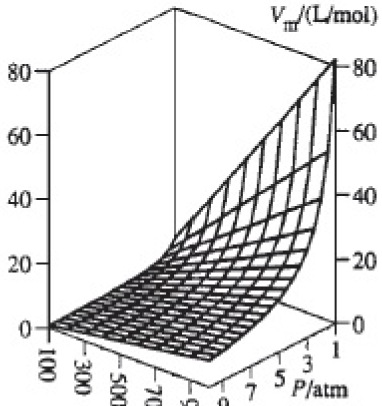
- Functions and limits
- A set of ordered pairs
- Domain and range
- Limit: $\lim_{x\to c} f(x) = L$ iff $\forall\epsilon\ \exists\delta$ such that if $|x-c| < \delta$ then $|f(x) - L| < \epsilon$.
- E.g., $\lim_{x\to 1} \frac{x^2-1}{x-1} = 2 \qquad \lim_{x\to\infty} \frac{2x-1}{x} = 2$.
- Slope
- Derivative
- If y=f(x), then $\frac{dy}{dx} = \lim_{\Delta x\to 0} \frac{\Delta y}{\Delta x} = \lim_{h\to 0} \frac{f(x+h)-f(x)}{h} = f'(x)$.
- Evaluate f'(x) for $f(x) = x^2, a, au, x^n, e^{ax}, \ln ax, \sin(ax), \cos(ax), u+v, uv, u/v$
- Chain rule: $(fog)'(x) = f'(g(x))g'(x)$.
- Second derivative: $\frac{d^2y}{dx^2} \equiv \frac{d}{dx}\frac{dy}{dx}$.

Differential calculus

- Partial derivative of z=f(x,y), $(\frac{\partial z}{\partial x})_y \equiv \lim_{\Delta x \to 0} \frac{f(x+\Delta x,y)-f(x,y)}{\Delta x}$ and $(\frac{\partial z}{\partial y})_x \equiv \lim_{\Delta y \to 0} \frac{f(x,y+\Delta y)-f(x,y)}{\Delta y}$.
- Total differential of z(x,y), $dz = (\frac{\partial z}{\partial x})_y dx + (\frac{\partial z}{\partial y})_x dy$.
- Total differential of z(r,s,t), $dz = (\frac{\partial z}{\partial r})_{s,t} dr + (\frac{\partial z}{\partial s})_{r,t} ds + (\frac{\partial z}{\partial t})_{r,s} dt$.
- $1 = (\frac{\partial z}{\partial x})_y \frac{dx_y}{dz_y} = (\frac{\partial z}{\partial x})_y (\frac{\partial x}{\partial z})_y$; thus $(\frac{\partial z}{\partial x})_y = \frac{1}{(\frac{\partial x}{\partial z})_y}$.
- For an infinitesimal process in which z stays constant $(\frac{\partial z}{\partial x})_y (\frac{\partial x}{\partial y})_z = -(\frac{\partial z}{\partial y})_x = -\frac{1}{(\frac{\partial y}{\partial z})_x}$
- In short $(\frac{\partial z}{\partial x})_y (\frac{\partial x}{\partial y})_z (\frac{\partial y}{\partial z})_x = -1$
- If second partial derivatives of z are continuous, then $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$

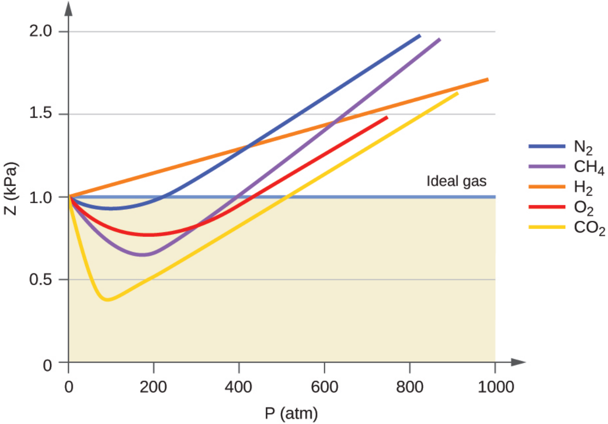
Equation of state

- Volumetric equation of state: $V = f(P, T, n_1, n_2, \cdots)$
- One phase system composed of n moles of a single pure substance, V=f(P,T,n), alternatively, P=g(V,T,n) or T=h(P,V,n).
- V=nk(T,P)
- Molar volume, $V_m = \bar{V} \equiv V/n$ and $V_m = k(T, P)$.
- A molar quantity corresponds to every extensive property.



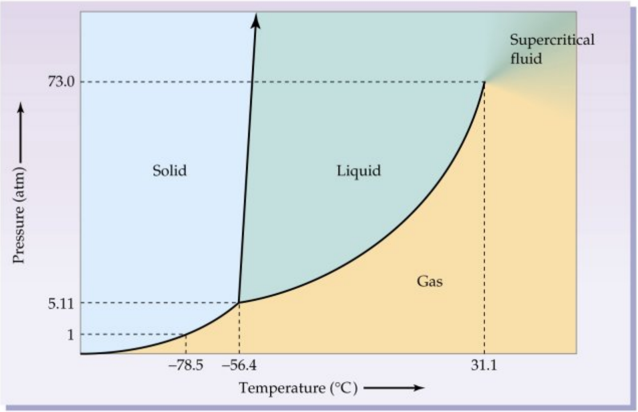
Real gases

- Intermolecular forces and or molecular volume becomes important.
- Compressibility factor $Z \equiv \frac{PV}{nRT} = \frac{PV_m}{RT}$ is used to quantify deviations of a gas from ideal behavior.



Critical point

- phase boundary between liquid and gas does not continue indefinitely. It terminates at a point on the phase diagram called the critical point.
- In water, the critical point occurs at around $T_c = 647.096$ K (373.946°C), $p_c = 22.064$ MPa (217.75 atm) and $\rho_c = 356 kg/m^3$.



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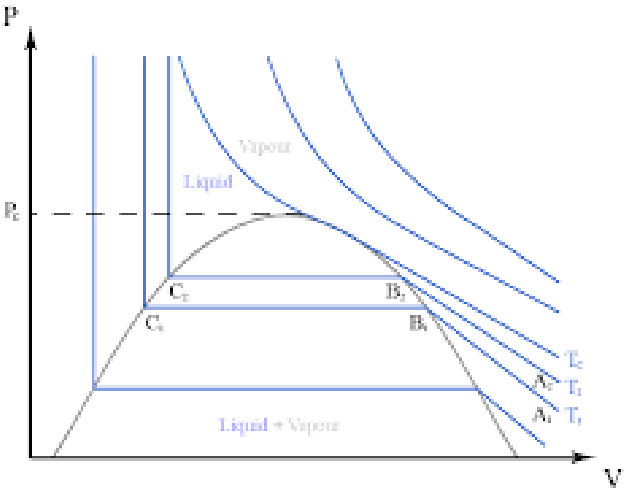
Critical point



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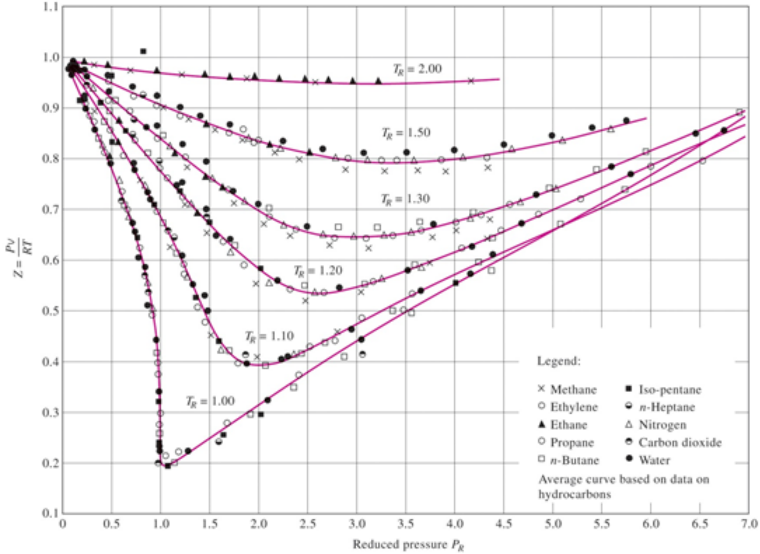
- Thermodynamic variables of a material at its critical point are denoted by T_c, P_c, V_{mc}. These are important properties of each material.

Real gases

- The law of corresponding states



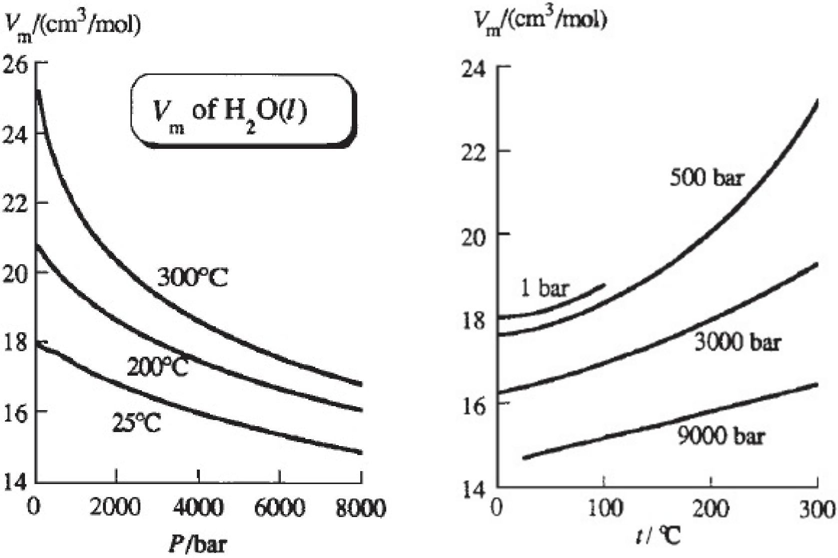
Van der Waals Equation of state

- There are many equations of state for real gases. The most conceptually appealing is the Van der Waals equation of state.
- Each molecule makes $4/3\pi d^3$ inaccessible to other molecules. Define forbidden volume (inaccessible space) per mole $b = N_A 4/3\pi d^3$
- Attractive forces between molecule A and every other molecule reduces the impact of A on the walls. Since every other molecule is affected similarly, effect of attractive forces on pressure is proportional to N^2.
- To account for the dependence of attractive forces on distance their affect on pressure is assumed to be proportional to $1/V^2$, i.e., intermolecular forces are implicitly assumed to be proportional to $1/r^6$
- Thus Start with the ideal gas equation of state and substitute V by $V - nb$. Further substitute P by $P + a\frac{n^2}{V^2}$.

Equation of state

- Van der Waals equation of state: $(P + a\frac{n^2}{V^2})(V - nb) = nRT$. Van der Waals constants a and b are treated as phenomenological constants to be determined experimentally for each material.
- $\bar{V}^3 - (b + \frac{RT}{P})\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0$
- For solids and liquids $V_m = c_1 + c_2T + c_3T^2 - c_4P - c_5PT$ is useful.
- An equation of state is the locus of all points representing a system.

Equation of state



Thermodynamic properties

- Lines of constant temperature are called isotherms, isothermal processes move the system on such lines.
- Also consider isobars and isochores.
- Thermal expansivity, $\alpha(T,P) \equiv \frac{1}{V}(\frac{\partial V}{\partial T})_{P,n} = \frac{1}{V_m}(\frac{\partial V_m}{\partial T})_P$
- Isothermal compressibility, $\kappa(T,P) \equiv -\frac{1}{V}(\frac{\partial V}{\partial P})_{T,n} = \frac{1}{V_m}(\frac{\partial V_m}{\partial P})_T$
- Four other partial derivatives can be computed from α and κ.
- For solids, $\alpha \approx 10^{-5}$ to $10^{-4} K^{-1}$ and $\kappa \approx 10^{-6}$ to $10^{-5} atm^{-1}$.
- For liquids, $\alpha \approx 10^{-3.5}$ to $10^{-3} K^{-1}$ and $\kappa \approx 10^{-4} atm^{-1}$.

Integral calculus

- Properties of summation: $\sum_{i=1}^{n} ca_i = c\sum_{i=1}^{n} a_i \qquad \sum_{i=1}^{n}(a_i + b_i) = \sum_{i=1}^{n} a_i + \sum_{i=1}^{n} b_i \qquad \sum_{i=1}^{n}\sum_{j=1}^{m} a_i b_j = \sum_{i=1}^{n} a_i \sum_{j=1}^{m} b_j$.
- If dy/dx=f(x) then $y = \int f(x)dx$.
- $\int af(x)dx = a\int f(x)dx, \qquad \int[f(x)+g(x)]dx = \int f(x)dx + \int g(x)dx$
- $\int dx = x + C, \qquad \int x^n dx = \frac{x^{n+1}}{n+1} + C, \qquad \int \frac{dx}{x} = \ln x + C, \qquad \int e^{ax}dx = \frac{e^{ax}}{a} + C, \qquad \int \sin axdx = -\frac{\cos ax}{a} + C, \qquad \int \cos axdx = \frac{\sin ax}{a} + C$.

Integral calculus

- Definite integral: $\int_a^b f(x)dx \equiv \lim_{n\to\infty} \sum_{i=1}^n f(x_i)\Delta x$ where $\Delta x = \frac{b-a}{n}$.
- Fundamental theorem of calculus: if F'(x)=f(x) then $\int_a^b f(x)dx = F(b) - F(a)$.
- Summation index is a dummy index and definite integration variable is a dummy variable.
- $\int_a^b f(x)dx = -\int_b^a f(x)dx$ and $\int_a^b f(x)dx + \int_b^c f(x)dx = \int_a^c f(x)dx$.
- If $[\frac{\partial y(x,z)}{\partial x}]_z = f(x,z)$ then $\int f(x,z)dx = y(x,z)$., e.g. $f = xz^3 \Rightarrow y(x,z) = x^2z^3/2 + g(z)$
- Also, $\int_a^b f(x,z)dx = y(b,z) - y(a,z)$

Review: Integrals

- $\int x(x+a)^n dx =$
- $\int \frac{1}{a^2+x^2} dx =$
- $\int \frac{x}{a^2+x^2} dx$

- $\int \frac{x^2}{a^2+x^2} dx =$
- $\int \frac{x^3}{a^2+x^2} dx =$
- $\int \tan(ax+b) dx =$

- $\int cotan(ax+b) dx =$

Review: Integrals

- $\int x(x+a)^n dx =$
- $\int \frac{1}{a^2+x^2} dx =$
- $\int \frac{x}{a^2+x^2} dx$
- $= \frac{1}{2}\ln|a^2+x^2|$
- $\int \frac{x^2}{a^2+x^2} dx =$
- $\int \frac{x^3}{a^2+x^2} dx =$
- $\int \tan(ax+b)dx =$
- $-\frac{1}{a}\ln|\cos(ax+b)|$
- $\int cotan(ax+b)dx =$
- $\frac{1}{a}\ln|\sin(ax+b)|$

Classical mechanics

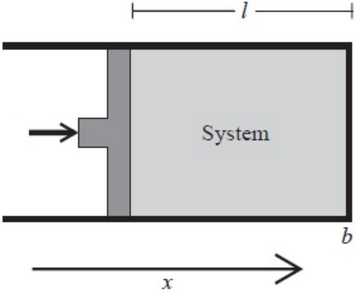
- Newton's second law of motion: $\vec{F} = m\vec{a}$.
- Equivalently, $F_x = ma_x, \qquad F_y = ma_y, \qquad F_z = ma_z.$
- Work $dw \equiv \vec{F} \cdot d\vec{r}$.
- Power: $P \equiv dw/dt$
- The work-energy theorem: work done on a particle by the force acting on it equals the change in kinetic energy of the particle.
- $F_x = m(\frac{dv_x}{dt}) = m(\frac{dv_x}{dx})v_x$
- $w = \int_1^2 mv_x dv_x + \int_1^2 mv_y dv_y + \int_1^2 mv_z dv_z =$ $\frac{m}{2}(v_{x2}^2 + v_{y2}^2 + v_{z2}^2) - \frac{m}{2}(v_{x1}^2 + v_{y1}^2 + v_{z1}^2) = K_2 - K_1 = \Delta K$
- Conservative is a force depending only on the position.

Classical mechanics

- For conservative forces, potential energy can be defined satisfying $\frac{\partial V}{\partial x} = -F_x, \qquad \frac{\partial V}{\partial y} = -F_y, \qquad \frac{\partial V}{\partial z} = -F_z$
- $w = -\int_1^2 \frac{\partial V}{\partial x} dx - \int_1^2 \frac{\partial V}{\partial y} dy - \int_1^2 \frac{\partial V}{\partial z} dz = -\int_1^2 dV = V_1 - V_2$
- $w = K_2 - K_1 = V_1 - V_2$; thus, $K_1 + V_1 = K_2 + V_2$.
- Law of conservation of mechanical energy: $E_{mech} = K + V$, when forces are conservative mechanical energy is conserved.
- E.g., potential energy and mechanical energy in the gravitational field of earth.
- For an n-particle system, $K = K_1 + K_2 + \cdots + K_n = \frac{1}{2} \sum_{i=1}^{n} m_i v_i^2$
- $V = \sum_i \sum_{j>i} V_{ij}$
- With conservative forces $K + V = E_{mech}$ is constant for many particle systems.

P-V work

- Most common type of work in thermodynamics.
- Reversible P-V work.



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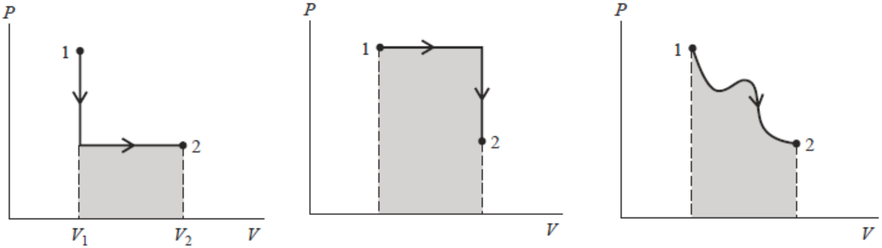
- $dw = \vec{F} \cdot \vec{dr} = PAdx$
- $dw_{rev} = -PdV$
- $w_{rev} = -\int_1^2 PdV$
- The above expression is a line integral and its value depend on the path taken by the system.
- $dw_{irrev} = -P_{ext}dV - dK_{pist}$; thus, $w_{irrev} = -\int_1^2 P_{ext}dV - \Delta K_{pist}$

Heat



- When two bodies come into thermal contact $m_2 c_2 (T_2 - T_f) = m_1 c_1 (T_f - T_1) \equiv q$
- $c_{H2O} = 1.0 cal/(g^\circ C)$ at 15 $^\circ C$ and 1 atm.
- $dq_P \equiv m c_P dT$
- $q_P = m \int_{T_1}^{T_2} c_P(T) dT$
- $C_P = dq_P/dT = m c_P$
- $m_2 \int_{T_f}^{T_2} c_{P2}(T) dT = m_1 \int_{T_1}^{T_f} c_{P1}(T) dT = q_P$
- Reversible vs. irreversible flow of heat.

The first law of thermodynamics

- Internal energy: Energy due to motions and interactions of molecules.
- E=K+V+U
- In most cases, $E \approx U$.
- Caloric theory was disproved in the 18th and 19th century.
- The law of conservation of energy.
- $U_m \equiv U/n$ is an intensive quantity.
- The first law of thermodynamics: For a closed system there exists an extensive state function E such that, $\Delta E = q + w$
- Also, $\Delta E_{syst} + E_{surr} = 0$
- For a system at rest in the absence of external fields, $\Delta U = q + w$
- $\Delta U = U_2 - U_1 = U_{final} - U_{initial}$
- Heat and work are defined only in terms of processes.
- Before and after the process of energy transfer heat and work do not exist.

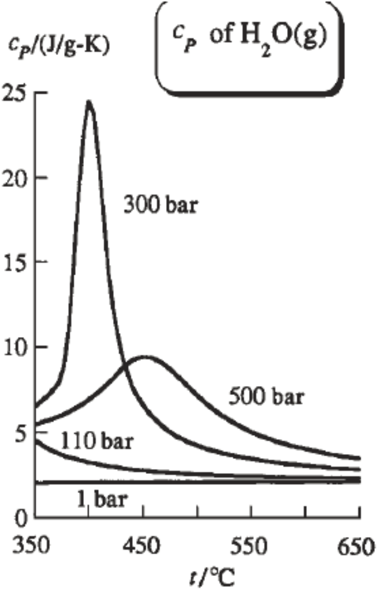
The first law of thermodynamics

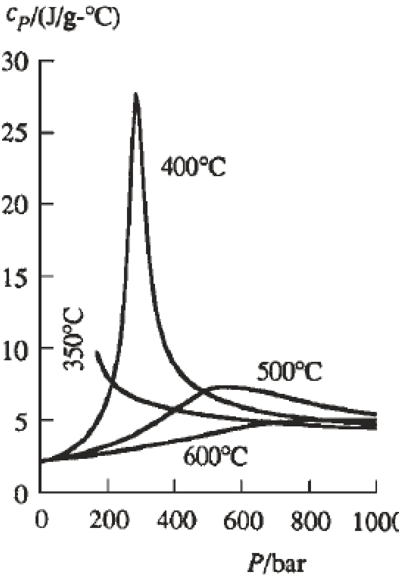
- Heat is energy transfer due to temperature difference.
- Work is energy transfer due to a macroscopic force acting through a distance.
- Heat and work are forms of energy transfer.
- Enthalpy: $H \equiv U + PV$.
- $U_2 - U_1 = q + w = q - \int_{V_1}^{V_2} PdV$, for a constant pressure process, $U_2 - U_1 = q_P - P(V_2 - V_1)$. $q_P = U_2 + PV_2 - (U_1 + PV_1) = H_2 - H_1$
- So at constant pressure, closed system and PV work only, $q_P = \Delta H$.
- $\Delta H = \Delta U + \Delta(PV)$ and $\Delta(PV) \approx P\Delta V + V\Delta P + \Delta(V)\Delta(P)$
- $H_m = H/n = (U + PV)/n = U_m + PV_m$
- For a constant volume process, $\Delta U = q + w = q_V$
- When $\Delta H \approx \Delta U$?

Heat capacities

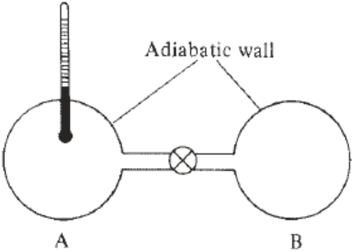
- Heat capacity of a closed system for an infinitesimal process pr, $C_{pr} \equiv dq_{pr}/dT$
- Isobaric heat capacity: $C_P \equiv \frac{dq_P}{dT} = (\frac{\partial H}{\partial T})_P$
- Isochoric heat capacity: $C_V \equiv \frac{dq_V}{dT} = (\frac{\partial U}{\partial T})_V$
- Molar heat capacities: $C_{P,m} \equiv C_P/n$ and $C_{V,m} \equiv C_V/n$.
- Specific heat capacity, $c_P \equiv C_P/m$, specific volume, $v = V/m = 1/\rho$ and specific enthalpy, $h = H/m$.
- $C_P - C_V = (\frac{\partial U}{\partial T})_P + P(\frac{\partial V}{\partial T})_P - (\frac{\partial U}{\partial T})_V$
- $dU = (\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial V})_T dV$
- $(\frac{\partial U}{\partial T})_P = (\frac{\partial U}{\partial T})_V + (\frac{\partial U}{\partial V})_T (\frac{\partial V}{\partial T})_P$
- $C_P - C_V = [(\frac{\partial U}{\partial V})_T + P](\frac{\partial V}{\partial T})_P$
- $(\frac{\partial U}{\partial V})_T$ is called the internal pressure.

Heat capacities



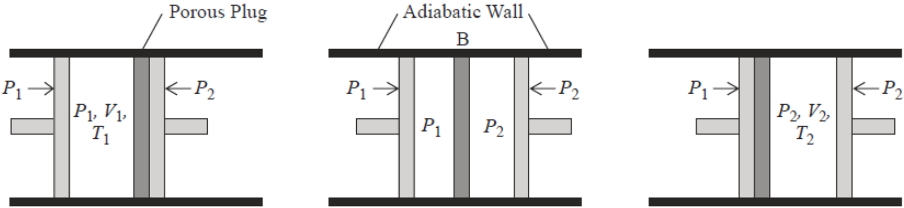


Joule and Joule-Thompson experiments

- 

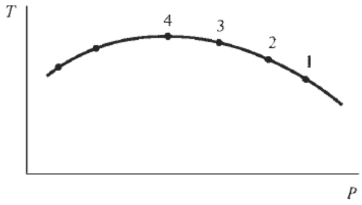
- Above apparatus is used to measure $\Delta T/\Delta V$ at constant U. From which, we derive $(\frac{\partial T}{\partial V})_U$
- Joule coefficient: $\mu_J \equiv (\frac{\partial T}{\partial V})_U$
- $(\frac{\partial U}{\partial V})_T = -(\frac{\partial U}{\partial T})_V(\frac{\partial T}{\partial V})_U = -C_V\mu_J$
- Joule-Thompson experiment involves the slow throttling of a gas through a rigid porous plug.

Joule and Joule-Thompson experiments



- $w_L = P_1 V_1, \qquad w_R = -P_2 V_2, \qquad w = w_L + w_R = P_1 V_1 - P_2 V_2.$
- $U_2 - U_1 = q + w = w = P_1 V_1 - P_2 V_2$; thus $U_2 + P_2 V_2 = U_1 + P_1 V_1$ or $\Delta H = 0$.
- Joule-Thompson experiment measures $\Delta T/\Delta P$ at constant H.
- Joule-Thompson coefficient $\mu_{JT} \equiv (\frac{\partial T}{\partial P})_H$

Joule and Joule-Thompson experiments

- 

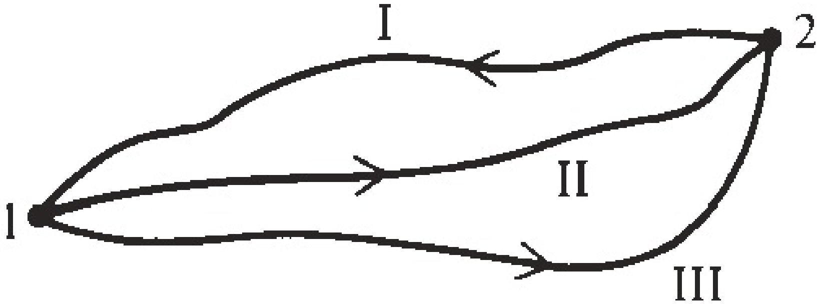
- Joule-Thompson liquefaction.
- $(\frac{\partial H}{\partial P})_T = -C_P \mu_{JT}$
- Perfect gas: $PV = nRT$ and $(\frac{\partial U}{\partial V})_T = 0$.
- For a perfect gas $U = U(T)$.Thus $dU = C_V(T)dT$. Also, $H \equiv U + PV = U + nRT \rightarrow H = H(T), \quad C_P = dH/dT, \quad C_P = C_P(T)$.
- $C_P - C_V = P(\partial V/\partial T)_P = nR$
- $(\frac{\partial U}{\partial V})_T = -C_V \mu_J$, thus $\mu_J = 0$ for a perfect gas.

Perfect gases

- $(\frac{\partial H}{\partial P})_T = -C_P \mu_{JT}$, thus $\mu_{JT} = 0$ for a perfect gas.
- $dU = C_V dT = dq - PdV$
- For a reversible isothermal process in a perfect gas: $w = -q = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1}$
- For a reversible adiabatic process in a perfect gas, $C_V dT = -PdV = -(nRT/V)dV$ or $C_{V,m} dT = -(RT/V)dV$
- $\int_1^2 \frac{C_{V,m}}{T} dT = -\int_1^2 \frac{R}{V} dV = R \ln \frac{V_1}{V_2} \approx C_{V,m} \ln \frac{T_2}{T_1}$
- $\ln \frac{T_2}{T_1} = \ln(\frac{V_1}{V_2})^{R/C_{V,m}}$
- For a reversible adiabatic process in a perfect gas, $\frac{T_2}{T_1} = (\frac{V_1}{V_2})^{R/C_{V,m}}$
- $P_1 V_1^{1+R/C_{V,m}} = P_2 V_2^{1+R/C_{V,m}}$
- For a perfect gas with constant C_V undergoing a reversible adiabatic process, $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$ where $\gamma = C_P/C_V$.

Perfect gases

- $\Delta U = C_V(T_2 - T_1) = w$
- State functions and line integrals:
- If b is a state function then ${}_L\int_1^2 db = b_2 - b_1$
- Prove that a quantity b is a state function iff $\oint db = 0$.



Molecular nature of internal energy

- Translational kinetic energy: $K_{tr,m} = 1/2mv^2$. Also average translational kinetic energy of one mole of molecules is $3/2RT$.
- For linear molecules, $E_j = j(j+1)b, \quad U_{rot,m} = RT$. For non-linear molecules $U_{rot,m} = 3/2RT$
- Molecular vibrational energy $E_n = (n + 1/2)h\nu$.
- Electronic energy: $\epsilon_{el} = \epsilon_{eq} - \epsilon_{\infty}$, changes in chemical reactions.
- Inter-molecular forces.

Intermolecular forces

- Coulomb interaction $\propto \frac{q_1 q_2}{r}$ is the strongest structural interaction.
- Van der waals interactions include Dipole-dipole interaction $\propto \frac{\mu_1 \cdot \mu_2}{r^3}$ and London interactions.
- Polar bonds as a necessary condition for molecular dipole moment.
- If a molecule is indistinguishable after rotating by $\frac{2\pi}{n}$ radians around an axes, that symmetry axes is called c_n.
- A plane of symmetry is an imaginary plane that bisects a molecule into halves that are mirror images of each other.
- An improper rotation is performed by rotating the molecule $360^\circ/\text{n}$ followed by reflection through a plane perpendicular to the rotation axis.

Intermolecular forces

- If the resulting configuration is indistinguishable from the original, we say there exists an n-fold improper rotation axis (or S_n axis) in the molecule.
- Presence of S_{2n} in a molecule results in zero dipole moment in spite of polar bonds.
- London or dispersion forces are due to spontaneous dipoles created by quantum effects. $E_{AB}^{\mathrm{disp}} \approx -\frac{3}{2}\frac{I_A I_B}{I_A + I_B}\frac{\alpha_A \alpha_B}{R^6}$
- I represents the ionization potential while α represents polarizability.
- Increasing the size and surface area of a molecule increases its polarizability which in turn increases its London forces.
- Compare the range for these three forces.

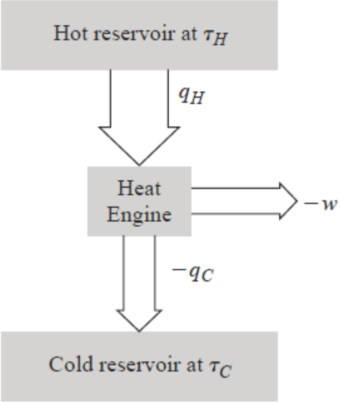
Lennard-Jones potential

- Non-bonding intermolecular interactions are qualitatively similar to bonding interactions.
- For atoms and approximately spherical molecules LJ is a good approximation to intermolecular interaction, $V_{LJ}(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}]$.
- r is internuclear distance while σ and ϵ are experimentally determined parameters. $\sigma/2$ can be ascribed to molecular (atomic) radius.
- LJ interaction can produce Van der waals molecules.

The second law of thermodynamics

- Kelvin-Planck statement: It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equivalent amount of work by the system on the surroundings.
- Second law is a generalization of experience. Its evidence include: 1- Many attempts at building a perpetual motion machine has failed. 2- Deductions from the second law of thermodynamics about chemical processes have all been confirmed. 3- This law can be deduced from statistical mechanics.
- Clausius statement: It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a cold reservoir and the flow of an equal amount of heat out of the system into a hot reservoir.

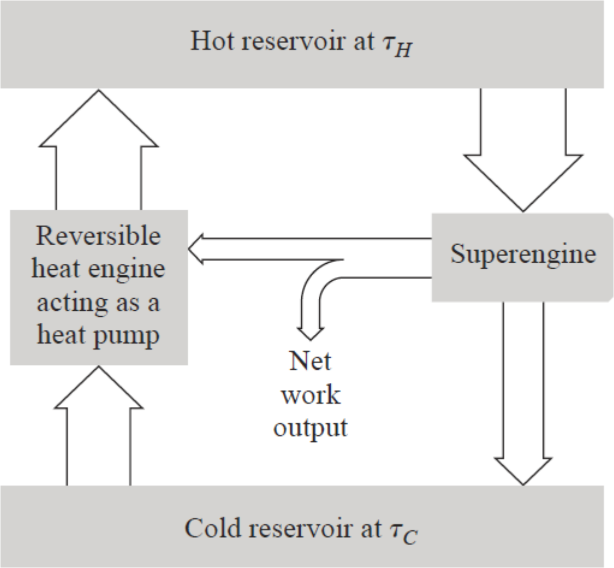
Heat engines

- To keep producing work a heat engine must work in cycles.
- Each cycle must contain at least three steps: 1- Absorption of the heat q_H by the system. 2- performance of the work -w, 3- Expulsion of the heat $-q_C$ by the system.
- $e = \frac{-w}{q_H} = \frac{q_H + q_C}{q_H} = 1 + \frac{q_C}{q_H}$
- 

Heat engines

- Carnot's principle: No heat engine can be more efficient than a reversible heat engine when both engines work between the same pair of temperatures τ_H and τ_C.
- The maximum amount of work from a given supply of heat is obtained with a reversible engine.
- Proof by contradiction:
- $e_{super} > e_{rev}$ where $e_{super} = \frac{-w_{super}}{q_{H,super}}$ and $e_{rev} = \frac{-w_{rev}}{q_{H,rev}}$.
- Run the reversible engine in reverse as a heat pump and couple it with super-engine so that the net effect of the combined system is absorbing heat from the cold reservoir and producing the same amount of work.
- This is in contradiction with the Kelvin-Planck statement of the second law.

Heat engines

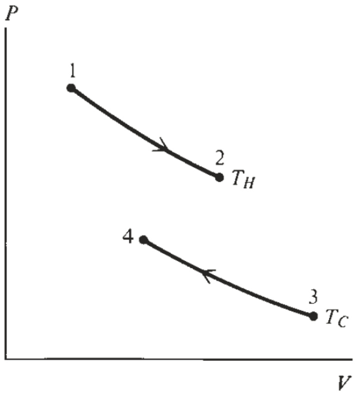
- 

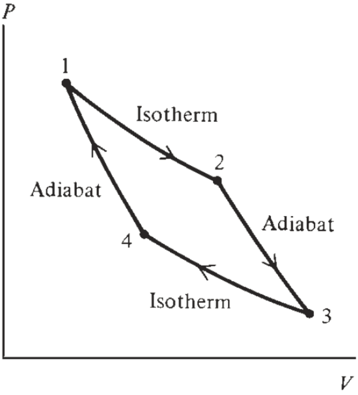
Heat engines

- Thus $e_{super} > e_{rev}$ is wrong. Therefore $e \leq e_{rev}$.
- Consider two engines A and B operating reversibly between temperatures τ_A and τ_B.
- If either $e_{A,rev} < e_{B,rev}$ or $e_{A,rev} > e_{B,rev}$ one encounter a contradiction with the second law by the same reasoning as above.
- Thus $e_{A,rev} = e_{B,rev}$.
- All reversible heat engines operating between reservoirs with temperatures τ_A and τ_B have the same efficiency e_{rev}. Which is the greatest possible efficiency for any engine operating between these two temperatures.
- $e_{irrev} \leq e_{rev}$
- $e_{rev} = f(\tau_H, \tau_C)$

Heat engines

- Without loss of generality consider ideal gas as the working substance.
- The first step (absorption of q_H) is a reversible isothermal expansion.
- The step involving expulsion of -q_C is a reversible isothermal contraction.
- Two isoterms must be connected by two reversible adiabats.
- This is called a Carnot cycle.





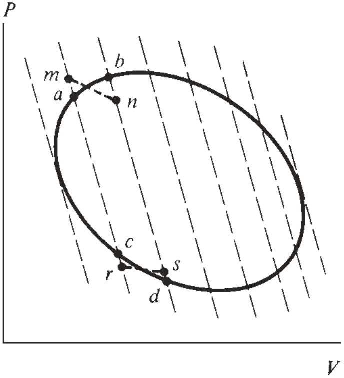
Heat engines

- For a reversible process with PV work only, $dU = dq - PdV$.
- For a perfect gas: $C_V dT = dq - nRTdV/V$.
- Dividing by T and integrating over the Carnot cycle: $\oint C_V(T)\frac{dT}{T} = \oint \frac{dq}{T} - nR\oint \frac{dV}{V}$.
- $\int C_V(T)\frac{dT}{T}$ is an ordinary integral and $C_V(T)\frac{dT}{T}$ is the differential of a state function, thus $\oint C_V(T)\frac{dT}{T} = 0$.
- Similarly, $\oint \frac{dV}{V} = \oint d\ln V = 0$
- Thus, $\oint \frac{dq}{T} = 0$. I.e. $\oint \frac{dq}{T} = \frac{q_H}{T_H} + \frac{q_C}{T_C} = 0$.
- $e_{rev} = 1 + \frac{q_C}{q_H} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H}$
- Since e_{rev} is independent of the working material, we must have $\frac{q_C}{q_H} = -\frac{T_C}{T_H}$

Entropy

- Thus for any Carnot cycle: $\oint \frac{dq}{T} = \frac{q_C}{T_C} + \frac{q_H}{T_H} = 0$.
- The lower the T_C and the higher the T_H the greater the efficiency of the thermal engine.
- We need to generalize the Carnot cycle result $\oint \frac{dq}{T} = 0$ to any cycle.
- For a perfect gas: $C_V dT = dq - nRTdV/V$.
- Dividing by T and integrating over a cycle:
  $\oint C_V(T)\frac{dT}{T} = \oint \frac{dq}{T} - nR\oint \frac{dV}{V}$.
- $\int C_V(T)\frac{dT}{T}$ is an ordinary integral and $C_V(T)\frac{dT}{T}$ is the differential of a state function, thus $\oint C_V(T)\frac{dT}{T} = 0$. Similarly, $\oint \frac{dV}{V} = \oint d\ln V = 0$
- Thus, $\oint \frac{dq}{T} = 0$, for any reversible cycle of an ideal gas, like the one depicted in the figure.

Entropy



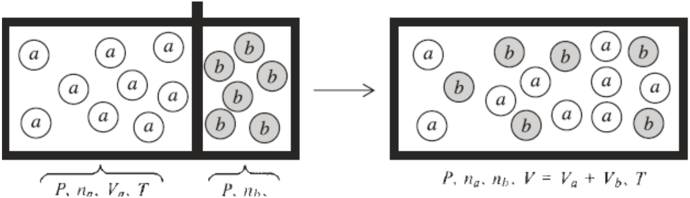
- Dashed lines are reversible adiabats dividing the cycle into adjacent strips.
- Draw the reversible isotherm mn such that the area under amnb equals the area under ab. Thus $w_{amnb} = w_{ab}$.

Entropy

- $\Delta U_{amnb} = \Delta U_{ab}$. Thus $q_{amnb} = q_{ab}$.
- Also $q_{amnb} = q_{mn}$. Hence $q_{mn} = q_{ab}$.
- Draw reversible isotherm rs such that $q_{rs} = q_{cd}$.
- The path mnsrm is a Carnot cycle. Thus $\frac{q_{mn}}{T_{mn}} + \frac{q_{sr}}{T_{sr}} = 0 = \frac{q_{ab}}{T_{mn}} + \frac{q_{dc}}{T_{sr}}$.
- In the limit of infinitesimally narrow strips between adiabats, $\frac{dq_{ab}}{T_{ab}} + \frac{dq_{dc}}{T_{dc}} = 0$.
- Taking the sum over all infinitesimal strips we have $\oint \frac{dq_{rev}}{T} = 0$
- $\frac{dq_{rev}}{T}$ is the differential of a state-function called entropy, S.
- $dS \equiv \frac{dq_{rev}}{T}$ and $\Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T}$.
- $dS = dq/T = dq_1/T + dq_2/T = dS_! + dS_2$, i.e., entropy is extensive.
- Reversible change of state of a perfect gas: $dq_{rev} = C_V dT + nRTdV/V \rightarrow dS = C_V dT/T + nRdV/V \rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT + nR \ln \frac{V_2}{V_1}$.

Entropy

- Mixing of different inert perfect gases at constant P and T:



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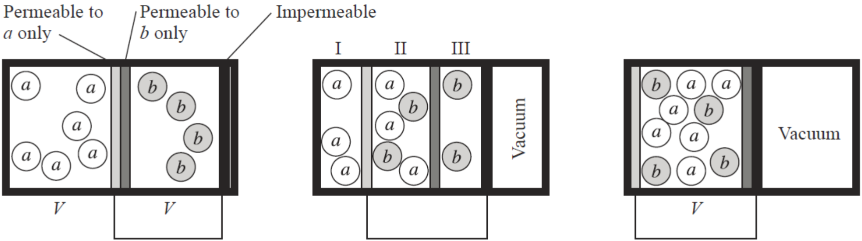
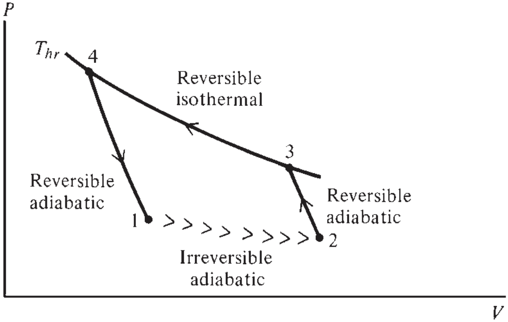
- This is an irreversible process. To calculate ΔS we shall devise a reversible path. 1- A reversible expansion to volume V. 2- A reversible mixing of the two gases.



Entropy

- $\Delta S_1 = \Delta S_a + \Delta S_b = n_a R \ln(V/V_a) + n_b R \ln(V/V_b), \quad \Delta S_2 = 0$
- $\Delta_{mix} S = -n_a R \ln x_a - n_b R \ln x_b$
- Entropy of a perfect gas mixture is equal to the sum of the entropies each pure gas would have if it alone occupied the volume of the mixture at the temperature of the mixture.
- $\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr}$
- For a reversible process: $dS_{univ} = dS_{syst} + dS_{surr} = \frac{dq_{rev}}{T_{syst}} + \frac{-dq_{rev}}{T_{surr}} = \frac{dq_{rev}}{T_{syst}} - \frac{dq_{rev}}{T_{syst}} = 0$. Thus $\Delta S_{univ} = 0$.
- Adiabatic irreversible process in a closed system:

Entropy

- 

- Bring state 2 in an adiabatic reversible process to $\mathrm{T_{hr}}$. $S_3 = S_2$.
- In a reversible isothermal process bring the system's entropy to $\mathrm{S_1}$. $S_4 = S_1$.
- $S_4 - S_3 = \int_3^4 \frac{dq_{rev}}{T} = \frac{q_{3\to 4}}{T_{hr}}$.
- Bring the system on an isentrop (reversible adiabat) to state 1.

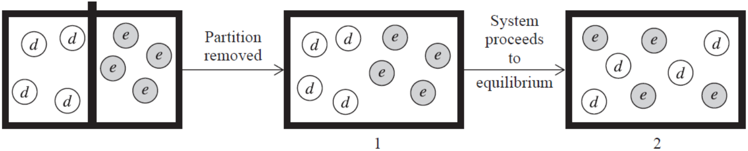
Entropy

- $0 = \oint dS_{syst} = (S_2 - S_1) + 0 + q_{3\rightarrow 4}/T_{hr} + 0 \rightarrow S_2 - S_1 = -q_{3\rightarrow 4}/T_{hr}$
- $0 = \oint (dq + dw) = q_{3\rightarrow 4} + w$. Thus $w = -q_{3\rightarrow 4}$.
- To avoid contradiction with the second law we must have $S_2 - S_1 = -q_{3\rightarrow 4}/T_{hr} \geq 0$.
- If equality occurs $q_{3\rightarrow 4} = 0$ and w=0. So after a cycle there is no change in the surroundings an nor any change in the system. But an irreversible process involve finite riving force which would result in a change in the system or the surroundings or both of them.
- For a closed system in an irreversible adiabatic process $\Delta S_{syst} > 0$.
- Since this applies to an isolated system $\Delta S_{univ} > 0$ for an irreversible process.
- In general $\Delta S_{univ} \geq 0$.

Entropy

- dq_{rev}/T is the differential of a state function S that has the property $\Delta S_{univ} \geq 0$ for every process.
- Thermodynamic equilibrium in an isolated system is reached when the system's entropy is maximized.
- Thermodynamic temperature scale:
- $-q_C/q_H = 1 - f(\tau_C, \tau_H) \equiv g(\tau_C, \tau_H) = \phi(\tau_C)/\phi(\tau_H)$
- By taking the simplest possible choice for ϕ we define the thermodynamic temperature scale: $\frac{\Theta_C}{\Theta_H} = \frac{-q_C}{q_H}$
- $\Theta_{tr} = 273.16^\circ$
- $\Theta = 273.16^\circ \frac{|q|}{|q_{tr}|}$
- Ideal gas temperature scale and the thermodynamic temperature scale are numerically equal.

Entropy

- 

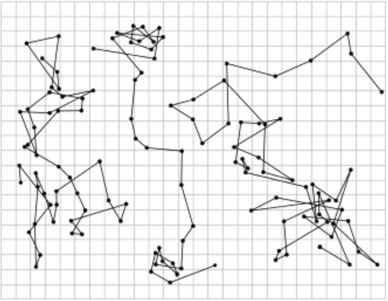
- Consider the probability for various distributions.
- equilibrium thermodynamic state of an isolated system is the most probable state.
- S=f(p)
- Entropy is extensive, for a system composed of subsystems 1 and 2, $S_{12} = S_1 + S_2 \rightarrow f(p_{12}) = f(p_1 p_2) = f(p_1) + f(p_2)$
- Thus $f(p) = k \ln p$
- Spontaneous mixing of equal volumes of different perfect gases: $\Delta S = S_2 - S_1 = k \ln(p_2/p_1)$

Entropy

- $p_1 = (\frac{1}{2})^{N_d}(\frac{1}{2})^{N_e} = (\frac{1}{2})^{N_d+N_e}$.
- $\Delta S = k\ln(1/p_1) = k\ln 2^{N_d+N_e} = 2N_d k\ln 2$.
- From thermodynamics $\Delta S = 2n_d R\ln 2$.
- Boltzmann's constant, $k = Rn_d/N_d = R/N_A = 1.38\times 10^{-23} J/K$.
- Entropy is a measure of the probability of a state.
- Probability of a thermodynamic state is proportional to the number of available energy levels of that state.
- Fluctuations in number density are of the order of $\sqrt{N}$.

Entropy

- Brownian motion is due to fluctuations in pressure.



- Fluctuations in electron densities in an electrical resistor produces noise.
- Microscopic reversibility vs. macroscopic irreversibility.

Material equilibrium

- In each phase the number of moles of each substance remains constant.
- $\begin{cases} \text{Reaction equilibrium} \\ \text{Phase equilibrium} \end{cases}$
- Criterion for equilibrium in an isolated system is maximization of S.
- For a closed but not isolated system equilibrium criterion is maximization of $S_{syst} + S_{Surr}$.
- $dS_{univ} = dS_{syst} + dS_{surr} > 0$ and $dS_{surr} = dq_{surr}/T$; thus, $dS_{syst} > -dS_{surr} = -dq_{surr}/T = dq_{syst}/T$.
- For a closed system in thermal and mechanical equilibrium $dS > dq_{irrev}/T$
- $dS \geq \frac{dq}{T}$
- $dU \leq TdS + dw$

Material equilibrium

- $dU \leq TdS + SdT - SdT + dw = d(TS) - SdT + dw \rightarrow$ $d(U - TS) \leq -SdT + dw = -SdT - PdV$
- At constant temperature and volume $d(U - TS) \leq 0$.
- Helmholtz free energy, Helmholtz energy, Helmholtz function or the work function: $A \equiv U - TS$.
- $dU \leq TdS + SdT - SdT - PdV + VdP - VdP =$ $d(TS) - SdT - d(PV) + VdP \rightarrow d(U + PV - TS) \leq -SdT + VdP$
- $d(H - TS) \leq -SdT + VdP$
- At constant T and P in a closed system in mechanical and thermal equilibrium with only PV work, $d(H - TS) \leq 0$.
- Gibbs function, Gibbs energy and Gibbs free energy: $G \equiv H - TS \equiv U + PV - TS$
- Equilibrium conditions $dA = 0$ and $dG = 0$.

Material equilibrium

- $\Delta S_{univ} = -\Delta H_{syst}/T + \Delta S_{syst} = -(\Delta H_{syst} - T\Delta S_{syst})/T = -\Delta G_{syst}/T$ for a closed system at constant T and P, PV work only.
- $dA \leq -SdT + dw$. At constant temperature, $dA \leq dw$. Thus $\Delta A \leq w$, i.e., $w_{by} \leq -\Delta A$; which is the origin of the term work function.
- Maximum work output by a closed system for an isothermal process between two given states is obtained in a reversible process and equals $-\Delta A$.
- $dG = dA + PdV + VdP$ and $dG \leq -SdT + dw + PdV + VdP$.
- In a closed system at thermal and mechanical equilibrium for a process at constant T and P, $dG \leq dw + PdV$. Thus, $dG \leq dw_{non,PV}$
- $\Delta G \leq w_{non,PV} \qquad w_{by,non,PV} \leq -\Delta G$
- $-\Delta G$ is the maximum nonexpansion done by a system in a constant T and P process.

Thermodynamic relations

- $dU = dq + dw = TdS - PdV$
- Since $dq_{rev} = TdS$ for a closed system in equilibrium we have $C_V = T(\frac{\partial S}{\partial T})_V, \qquad C_P = T(\frac{\partial S}{\partial T})_P.$
- The Gibbs equations: $dH = TdS + VdP, \qquad dA = -SdT - PdV, \qquad dG = -SdT + VdP.$
- Comparing $dU = (\frac{\partial U}{\partial S})_V dS + (\frac{\partial U}{\partial V})_S dV$ with the corresponging Gibbs equation, $(\frac{\partial U}{\partial S})_V = T$ and $(\frac{\partial U}{\partial V})_T = -P$.
- Similarly, $(\frac{\partial H}{\partial S})_P = T, \quad (\frac{\partial H}{\partial P})_S = V, \quad (\frac{\partial A}{\partial T})_V = -S, \quad (\frac{\partial A}{\partial V})_T = -P, \quad (\frac{\partial G}{\partial T})_P = -S, \quad (\frac{\partial G}{\partial P})_T = V.$
- Thermodynamics, enables properties that are difficult to measure to be expressed in terms of easily measured properties like $C_P(T,P), \quad \alpha(T,P), \quad \kappa(T,P).$
- Euler reciprocity relation

Thermodynamic relations

- The Maxwell relations: $(\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V, \quad (\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P, \quad (\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V, \quad (\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P.$
- $(\frac{\partial U}{\partial V})_T = T(\frac{\partial S}{\partial V})_T - P = T(\frac{\partial P}{\partial T})_V - P = \frac{\alpha T}{\kappa} - P$
- $(\frac{\partial H}{\partial P})_T = T(\frac{\partial S}{\partial P})_T + V = -T(\frac{\partial V}{\partial T})_P + V = -TV\alpha + V$
- $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P = -\alpha V$
- $(\frac{\partial G}{\partial T})_P = -S, \qquad (\frac{\partial G}{\partial P})_T = V$
- $\mu_{JT} = (1/C_P)[T(\partial V/\partial T)_P - V] = (V/C_P)(\alpha T - 1)$
- $C_P - C_V = [(\partial U/\partial V)_T + P](\partial V/\partial T)_P = TV\alpha^2/\kappa$
- For an ideal gas: $(\partial U/\partial V)_T = \frac{\alpha T}{\kappa} - P = P - P = 0$, thus ideal and perfect gases are the same.
- Estimate the internal pressure in solids and liquids.

Thermodynamic relations

- $dS = \frac{C_P}{T} dT - \alpha V dP \rightarrow \Delta S = S_2 - S_1 = \int_1^2 \frac{C_P}{T} dT - \int_1^2 \alpha V dP$
- $\Delta H = \int_1^2 C_P dT + \int_1^2 (V - TV\alpha) dP$
- $\Delta U = \Delta H - \Delta(PV)$
- $G = G(T, P, n_1, \cdots, n_k) \rightarrow dG = (\frac{\partial G}{\partial T})_{P,n_i} dT + (\frac{\partial G}{\partial P})_{T,n_i} dP + (\frac{\partial G}{\partial n_1})_{T,P,n_{j\neq 1}} dn_1 + \cdots + (\frac{\partial G}{\partial n_k})_{T,P,n_{j\neq k}} dn_k$
- Since in a reversible process on a system of constant composition $dG = -SdT + VdP$ we have $(\frac{\partial G}{\partial T})_{P,n_i} = -S, \quad (\frac{\partial G}{\partial P})_{T,n_i} = V$.
- $dG = -SdT + VdP + \sum_{i=1}^{k} (\frac{\partial G}{\partial n_i})_{T,P,n_{j\neq i}} dn_i$
- $\mu_i \equiv (\frac{\partial G}{\partial n_i})_{T,P,n_{j\neq i}}$
- Key equation of chemical thermodynamics: $dG = -SdT + VdP + \sum_{i=1}^{k} \mu_i dn_i$
- These are Gibbs equations: $dU = TdS - PdV + \sum_i \mu_i dn_i$
- $dH = TdS + VdP + \sum_i \mu_i dn_i$

Material equilibrium condition

- $dA = -SdT - PdV + \sum_i \mu_i dn_i$
- For a multiphase system $G = \sum_\alpha G^\alpha$ and $dG = \sum_\alpha dG^\alpha$.
- $dG^\alpha = -S^\alpha dT + V^\alpha dP + \sum_{i=1}^k \mu_i^\alpha dn_i^\alpha$
- $dG = -\sum_\alpha S^\alpha dT + \sum_\alpha V^\alpha dP + \sum_\alpha \sum_{i=1}^k \mu_i^\alpha dn_i^\alpha$
- $\mu_i^\alpha \equiv (\frac{\partial G^\alpha}{\partial n_i^\alpha})_{T,P,n_{j\neq i}^\alpha}$
- $dG = -SdT + VdP + \sum_\alpha \sum_{i=1}^k \mu_i^\alpha dn_i^\alpha$
- Condition for material equilibrium in a closed system with PV work only: $\sum_\alpha \sum_{i=1}^k \mu_i^\alpha dn_i^\alpha = 0$
- $\mu_i^\alpha = \mu_i^\alpha(T^\alpha, P^\alpha, x_1^\alpha, x_2^\alpha, \cdots)$

Phase equilibrium condition

- For a pure substance, μ_i is the molar Gibbs free energy, $\mu_i \equiv (\partial G/\partial n_i)_{T,P} = G_{m,i}$
- In a multiphase system if dn_j flows from β to δ, $\mu_j^\beta dn_j^\beta + \mu_j^\delta dn_j^\delta = 0 \rightarrow \mu_j^\beta = \mu_j^\delta$.
- Phase equilibrium condition is that μ of a given substance is the same in every phase.
- Before equilibrium, $dG < -SdT + VdP$, i.e., $-SdT + VdP + \sum_\alpha \sum_{i=1}^{k} \mu_i^\alpha dn_i^\alpha < -SdT + VdP$, i.e., $\sum_\alpha \sum_{i=1}^{k} \mu_i^\alpha dn_i^\alpha < 0$.
- Thus substance j flows spontaneously from a phase with higher chemical potential μ_j to a phase with lower chemical potential μ_j.
- $(\partial \mu_j^\delta / \partial x_j^\delta)_{T,P,n_{i \neq j}^\delta} > 0$
- View chemical potential as escaping tendency.

Phase equilibrium condition

- When j is absent from δ phase equilibrium becomes $\mu_j^\delta \geq \mu_j^\beta$.
- Denote a chemical reaction by $0 \to \nu_1 A_1 + \nu_2 A_2 + \cdots + \nu_m A_m + \nu_{m+1} A_{m+1} + \cdots$ or $0 \to \sum_i \nu_i A_i$ where ν_i are stoichiometric numbers or stoichiometric coefficients.
- $CH_4 + 2O_2 \to CO_2 + 2H_2O \qquad 0 \to -CH_4 - 2O_2 + CO_2 + 2H_2O$, where $\nu_{CH_4} = -1$, $\nu_{O_2} = -2$, $\nu_{CO_2} = +1$ and $\nu_{H_2O} = +2$.
- Extent of reaction ξ. For $0 \to \sum_i \nu_i A_i$, $\Delta n_i \equiv n_i - n_{i,0} = \nu_i \xi$.
- In material equilibrium $\sum_i \sum_\alpha \mu_i^\alpha dn_i^\alpha = \sum_i \mu_i (\sum_\alpha dn_i^\alpha) = \sum_i \mu_i dn_i = 0 = (\sum_i \mu_i \nu_i) d\xi$
- The condition for chemical reaction equilibrium is that $\sum_i \mu_i \nu_i = 0$.

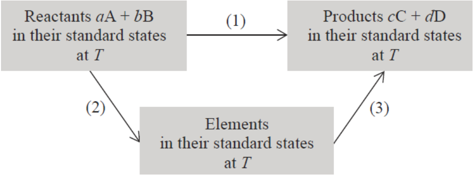
Standard thermodynamic functions of reaction

- Standard state of a pure solid or liquid is the state with pressure 1 bar and temperature T, e.g., ${V^\circ}_{m,200}$
- Standard state of pure gases is defined with P=1 bar and the gas behaving ideally.
- Standard enthalpy change of reaction, $\Delta {H_T}^\circ$: enthalpy change for the process of transforming stoichiometric numbers of moles of the pure, separated reactants, each in its standard state at temperature T, to stoichiometric numbers of moles of the pure, separated reactants, each in its standard state at temperature T.
- For the reaction: $0 \rightarrow \sum_i \nu_i A_i, \qquad \Delta {H_T}^\circ \equiv \sum_i \nu_i {H_{m,T,i}}^\circ$.
- Thermodynamics does not provide absolute values of U, H and S, but only relative values.

Standard thermodynamic functions of reaction

- The standard enthalpy of formation or standard heat of formation $\Delta_f H_T^0$ of a pure substance at T is ΔH^0 for the process of forming one mole of substance in its standard state at T from the corresponding separate elemens in their reference form.
- The reference form or reference phase is taken as the form of the element most stable at T and 1 bar.
- C(graphite, 307 K, P°)+H_2(Ideal gas, 307 K, P°)+1/2O_2(Ideal gas, 307 K, P°)→H_2CO(Ideal gas, 307 K, P°) $\Delta H = \Delta_f H^0_{307,H_2CP(g)}$
- For an element in its reference form, $\Delta_f H_T^0$ is zero.
- The standard enthalpy change for a reaction $\Delta H_T^0 = \sum_i \nu_i \Delta_f H^0_{T,i}$

Standard thermodynamic functions of reaction

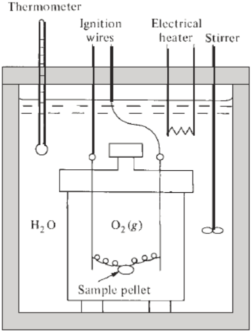


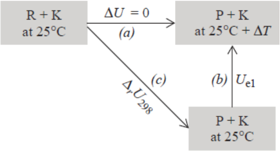
- For aA+bB→cC+dD,
- $\Delta H_1 = \Delta H_2 + \Delta H_3 \rightarrow \Delta H_T^0 = -a\Delta_f H_T^0(A) - b\Delta_f H_T^0(B) + c\Delta_f H_T^0(C) + d\Delta_f H_T^0(D)$
- Determination of standard enthalpies of formation:
- 1- ΔH for hypothetical transformation of gaseous elements from an ideal gas at T and 1 bar to a real gas at T and 1 bar.
- 2- ΔH for mixing the pure elements at T and 1 bar.
- 3- Use $\Delta H = \int_1^2 C_P dT + \int_1^2 (V - TV\alpha)dP$ to find ΔH for bringing mixture from T and 1 bar to conditions of the reaction.

Standard thermodynamic functions of reaction

- 4- Use a calorimeter to find ΔH for forming the compound from mixed elements.
- 5- Use $\Delta H = \int_1^2 C_P dT + \int_1^2 (V - TV\alpha) dP$ to find ΔH for bringing the compound from state in which it is formed to T and 1 bar.
- 6- If compound i is a gas, find ΔH for transformation of i from a real gas to an ideal gas.
- Calorimetry $\begin{cases} \text{Constant volume calorimeter} \\ \text{Constant pressure calorimeter} \end{cases}$
- Standard enthalpy of combustion, $\Delta_c H_T^0$ is measured by an adiabatic bomb calorimeter.
- For the calorimeter $\Delta U = 0$, after measuring ΔT the system is cooled back to 25°C. Then the electrical energy to rise the temperature by ΔT is measured.

Standard thermodynamic functions of reaction

- 



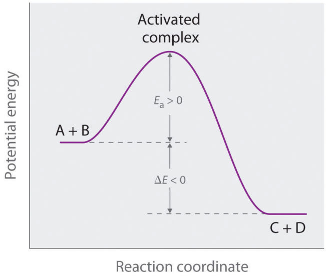
- $\Delta_r U_{298} = -U_{el} = -VIt$
- Alternatively, $\Delta_r U_{298} = -C_{K+P}\Delta T$. Where C_{K+P} is estimated by burning a compound with known $\Delta_r U_{298}$ in the calorimeter.

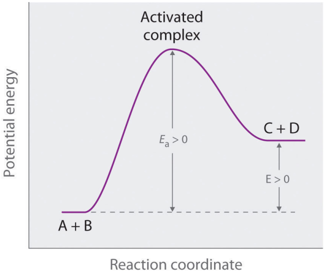
Standard thermodynamic functions of reaction

- Calorimetry measures either ΔH^0 or ΔU^0. To relate these quantities use $\Delta H^0 = \Delta U^0 + P^0 \Delta V^0$
- $\Delta H^0 = \sum_i \nu_i H^0_{m,i}, \quad \Delta V^0 = \sum_i \nu_i V^0_{m,i}, \quad \Delta U^0 = \sum_i \nu_i U^0_{m,i}$
- Neglect volume of solids and liquids compared with gases. $\Delta V^0 = (\Delta n_g/mol)RT/P^0$.
- Thus $\Delta H^0 = \Delta U^0 + (\Delta n_g/mol)RT$
- Hess's law states that enthalpy is an state function. One should combine enthalpies of reactions the same way he combines reactions themselves.
- E.g., Hydrogenation of propene:
  $CH_2CHCH_3 + H_2 \rightarrow CH_3CH_2CH_3 \quad \Delta H = -124 kJmol^{-1}$
  Combustion of propane
  $CH_3CH_2CH_3 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad \Delta H = -2220 kJmol^{-1}$
  Combustion of Hydrogen $H_2 + 1/2 O_2 \rightarrow H_2O \quad \Delta H = -286 kJmol^{-1}$

Standard thermodynamic functions of reaction

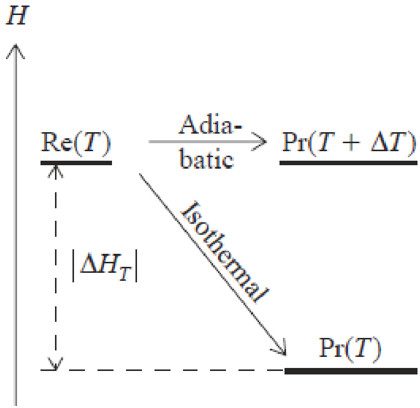
- Calculate enthalpy of propene combustion?
- While performing a formation reaction in the calorimeter may be impractical while heat of combustion can often be measured easily.
- Exothermic reaction (releasing energy, a) graph vs. Endothermic reaction (absorbing energy, b).





- (a) (b)

Thermodynamics: Thermochemistry

- 

- Calculation of $H_{id} - H_{re}$:
- Real gas at P° $\xrightarrow{(a)}$ real gas at 0 bar $\xrightarrow{(b)}$ ideal gas at 0 bar $\xrightarrow{(c)}$ ideal gas at P°

Thermodynamics: Thermochemistry

- $\Delta H = H_{id}(T, P^0) - H_{re}(T, P^0) = \Delta H_a + \Delta H_b + \Delta H_c$
- $\Delta H_a = H_{re}(T, 0 \text{ bar}) - H_{re}(T, P^0) = \int_{P^0}^{0} (V - TV\alpha) dP$
- In the zero pressure limit $U_{re} = U_{id}$ and $(PV)_{re} = (PV)_{id}$, Thus $H_{re}(T, 0 \text{ bar}) = H_{id}(T, 0 \text{ bar})$ and $\Delta H_b = 0$.
- $H_{id} = H_{id}(T)$ thus $\Delta H_c = 0$.
- $\Delta H = H_{id}(T, P^0) - H_{re}(T, P^0) = \int_{0}^{P^0} [T(\frac{\partial V}{\partial T})_P - V] dP$
- Instead of tabulating $\Delta_f H^0$, construct a table of relative (conventional) standard state enthalpies, $H^0_{m,i}$. $\Delta H^0 = \sum_i \nu_i H^0_{m,i}$.
- Arbitrarily, for the most stable form of each pure element, $H^0_{m,298} = 0$.
- For other compounds we use experimental data like formation enthalpies to deduce values of $H^0_{m,i}$.

Temperature dependence of reaction heats

- $\frac{d\Delta H^0}{dT} = \sum_i \nu_i \frac{dH^0_{m,i}}{dT} = \sum_i \nu_i C^0_{P,m,i} \equiv \Delta C^0_P$, standard heat capacity change in the reaction.
- $\frac{d\Delta H^0}{dT} = \frac{d(H^0_{pr} - H^0_{re})}{dT} = \frac{d(H^0_{pr})}{dT} - \frac{d(H^0_{re})}{dT} = C^0_{P,pr} - C^0_{P,re} = \Delta C^0_P$
- Kirshhoff's law: $\Delta H^0_{T_2} - \Delta H^0_{T_1} = \int_{T_1}^{T_2} \Delta C^0_P dT$
- $C^0_{P,m} = a + bT + cT^2 + dT^3$.
- $\Delta C^0_{P,m} = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3$.
- Use of a spreadsheet to obtain a polynomial fit.

Relative (conventional) entropies

- Assign an arbitrary entropy value to each element in a chosen reference state
- Find ΔS for preparing the desired substance in its standard state from elements in their reference states.
- For a pure element in its stable condensed form $S^0_{m,0} = \lim_{T\to 0} S^0_{m,T} = 0$.
- To find entropy at a different temperature $\Delta S = \int_{T_1}^{T_2} (C_P/T) dT$
- Reactions outside electrochemical cells are irreversible and so measuring conventional entropies for compounds is a challenge.
- Experimental observation: $\lim_{T\to 0} (\partial \Delta G/\partial T)_P = 0$
- $(\partial G/\partial T)_P = -S$. $(\partial \Delta G/\partial T)_P = -S_2 + S_1 = -\Delta S$.

Relative (conventional) entropies

- Nernst-Simon statement of the third law of thermodynamics: For any isothermal process that involves only substances in internal equilibrium, the entropy change goes to zero at T goes to zero: $\lim_{T \to 0} \Delta S = 0$.
- Consider the reaction $H_2(s) + \frac{1}{2} O_2(s) \to H_2 O(s)$, choice of elemental entropy as zero together with third law imply that $\lim_{T \to 0} S^0_m(H_2 O) = 0$
- $S^0_{m,0}(H_2 O) = 0$. By the same reasoning, for any compound $S^0_{m,0} = 0$.
- Using the third law, for any element or compound in internal equilibrium, $S^0_{m,0} = 0$. Also, $S^0_0 = 0$.
- Conventional standard state entropy at any T can be found.
- E.g., for a liquid, $S^0_{m,T_2} = \int_0^{T_{fus}} \frac{C^0_{P,m}(s)}{T} dT + \frac{\Delta_{fus} H^0_m}{T_{fus}} + \int_{T_{fus}}^{T_2} \frac{C^0_{P,m}(l)}{T} dT$.