

# Physical chemistry I, 23421

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- 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.
- At the end of this semester you should be able to determine whether a process is possible and if possible whether it is spontaneous. You should be able to determine the equilibrium state of a thermodynamic system based on spontaneity condition.

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

- Class location: <https://vc.sharif.edu/ch/a.nassimi>

Midterm exam	17 Ordibehesht	Ch. 1–3	37.5%
	9 am		
Final exam	5 Tir 9 am	Ch. 4–6	37.5%
Quizz and Problem set			15%
TA			10%
- Raise your question and concern as it might be the question or concern of your classmates.
- Always remember that equations are the language of science but they never do suffice.

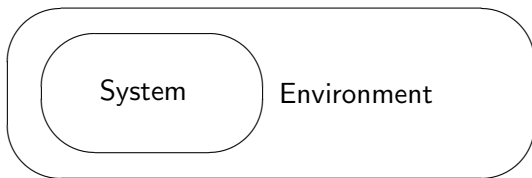
- 1st law of thermodynamics
- 2nd law of thermodynamics
- Material equilibrium and thermodynamic functions
- Chemical equilibrium in ideal gases.
- Phase equilibrium
- State function

# Thermodynamics

- Study of the underlying physical principles that govern the properties and behavior of chemical systems.
- Physical chemistry:  $\left\{ \begin{array}{l} \textit{Thermodynamics} \\ \text{Quantum Chemistry} \\ \text{Statistical mechanics} \\ \textit{Kinetics} \end{array} \right.$
- 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:  $\left\{ \begin{array}{l} \text{Equilibrium thermodynamics} \\ \text{Irreversible thermodynamics} \end{array} \right.$
- 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.
- 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.



- Mechanical equilibrium  $\rightarrow$  Pressure
- Thermal equilibrium  $\rightarrow$  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.

- 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  $M$ .
- $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$
- 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.

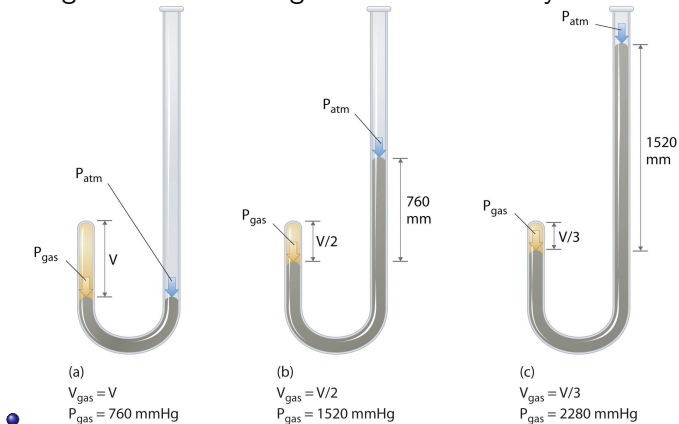
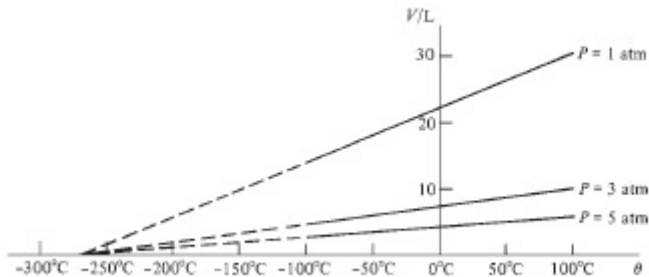


Figure: Schematic of the Boyle's experiment taken from <https://libretexts.org/>

# 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:  $\frac{V}{T} = k'(n, P)$ ).



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

- 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  $m$ ,  $V/T = V_{tr}/T_{tr} = \text{constant}$ . 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  $T = T_1$ ,  $P_1, V_1 \rightarrow P_2, V_3$  and a second at constant  $P = P_2$ ,  $V_3, T_1 \rightarrow V_2, T_2$  thus showing that  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ .
- 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.

- Avogadro's hypothesis states that at constant P and T, V is proportional to n. Thus  $\frac{PV}{T} = nR$ , where R is a 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

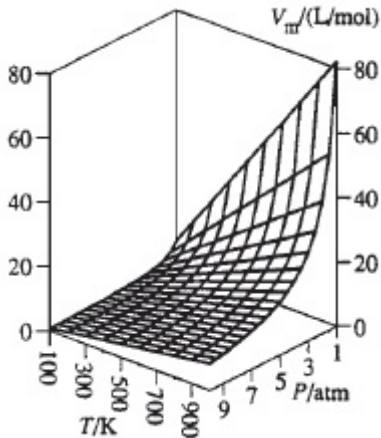
- Function is a set of ordered pairs
- Domain and range
- Limit:  $\lim_{x \rightarrow c} f(x) = L$  iff  $\forall \epsilon \exists \delta$  such that if  $|x - c| < \delta$  then  $|f(x) - L| < \epsilon$ .
- E.g.,  $\lim_{x \rightarrow 1} \frac{x^2 - 1}{x - 1} = 2$        $\lim_{x \rightarrow \infty} \frac{2x - 1}{x} = 2$ .
- Slope and Derivative
- If  $y=f(x)$ , then  $\frac{dy}{dx} = \lim_{\Delta x \rightarrow 0} \frac{\Delta y}{\Delta x} = \lim_{h \rightarrow 0} \frac{f(x+h) - f(x)}{h} = f'(x)$ .
- 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:  $(f \circ g)'(x) = f'(g(x))g'(x)$ .
- Second derivative:  $\frac{d^2y}{dx^2} \equiv \frac{d}{dx} \frac{dy}{dx}$ .



- Partial derivative of  $z=f(x,y)$ ,  $(\frac{\partial z}{\partial x})_y \equiv \lim_{\Delta x \rightarrow 0} \frac{f(x+\Delta x,y)-f(x,y)}{\Delta x}$  and  $(\frac{\partial z}{\partial y})_x \equiv \lim_{\Delta y \rightarrow 0} \frac{f(x,y+\Delta y)-f(x,y)}{\Delta y}$ .
- 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  $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$
- Volumetric equation of state:  $V = f(P, T, n_1, n_2, \dots)$

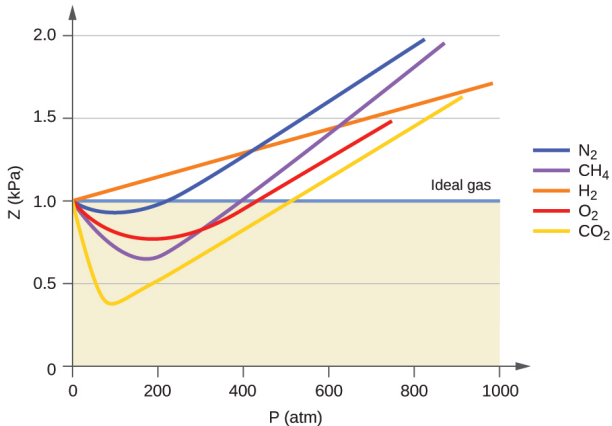
# Equation of State

- 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

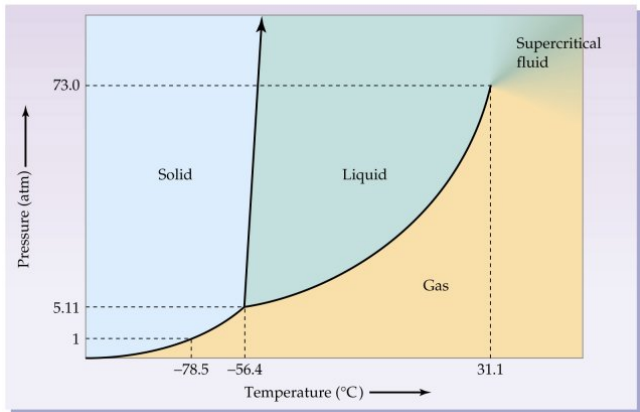
- Intermolecular forces and or molecular volume becomes important.
- Compressibility factor  $Z \equiv \frac{PV}{nRT} = \frac{PV_m}{RT}$  is used to quantify deviations of a gas from ideal behavior.



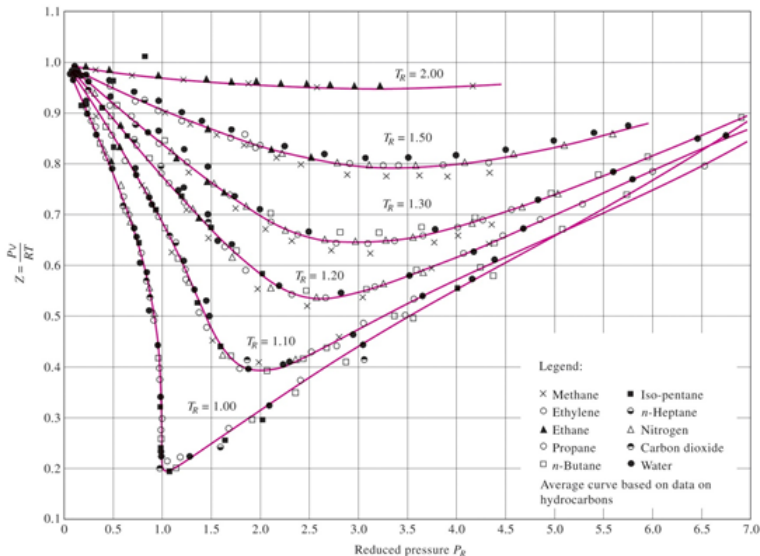


# Critical point

- 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  $T_c = 647.096 \text{ K}$  ( $373.946^\circ\text{C}$ ),  $p_c = 22.064 \text{ MPa}$  ( $217.75 \text{ atm}$ ) and  $\rho_c = 356 \text{ kg/m}^3$ .



- The law of corresponding states



# Van der Waals Equation of State

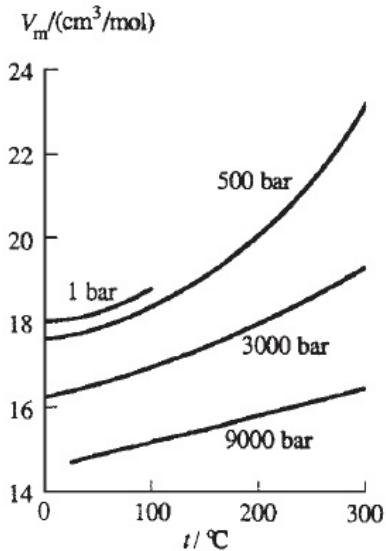
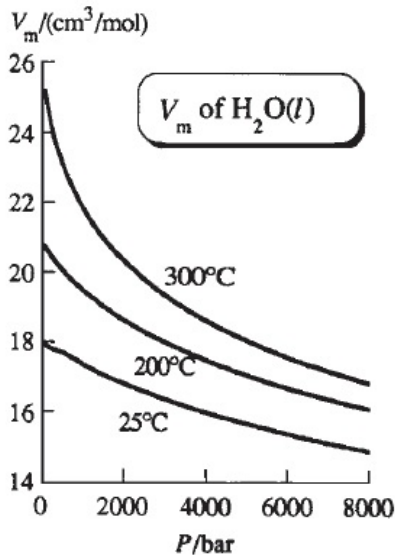
- There are many equations of state for real gases. The most conceptually appealing is the Van der Waals equation of state.
- Each molecule makes  $4/3\pi d^3$  inaccessible to other molecules. Define forbidden volume (inaccessible space) per mole  $b = N_A 4/3\pi d^3$
- Attractive forces between molecule 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 in the thermodynamic space.



# 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.
- Considering,  $P$ ,  $V$ ,  $T$  in the thermodynamic state, there are 6 first partial derivatives possible.
- Thermal expansivity,  $\alpha(T, P) \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P, n} = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_P$ .
- Isothermal compressibility,  $\kappa(T, P) \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T, n} = -\frac{1}{V_m} \left( \frac{\partial V_m}{\partial P} \right)_T$ .
- Four other partial derivatives can be computed from  $\alpha$  and  $\kappa$ .
- 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  $\kappa \approx 10^{-4} atm^{-1}$ .

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

# Integral calculus

- Definite integral:  $\int_a^b f(x)dx \equiv \lim_{n \rightarrow \infty} \sum_{i=1}^n f(x_i)\Delta x$  where  $\Delta x = \frac{b-a}{n}$ , and  $x_i = a + i\Delta x$ .
- 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

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

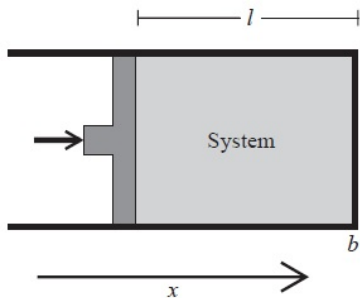
- Newton's second law of motion:  $\vec{F} = m\vec{a}$ .
- Equivalently,  $F_x = ma_x$ ,  $F_y = ma_y$ ,  $F_z = ma_z$ .
- Work  $dw \equiv \vec{F} \cdot d\vec{r}$ .
- Power:  $P \equiv dw/dt$
- The work-energy theorem: work done on a particle by the force acting on it equals the change in kinetic energy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

- For conservative forces, potential energy can be defined satisfying
$$\frac{\partial V}{\partial x} = -F_x, \quad \frac{\partial V}{\partial y} = -F_y, \quad \frac{\partial V}{\partial z} = -F_z$$
- $w = -\int_1^2 \frac{\partial V}{\partial x} dx - \int_1^2 \frac{\partial V}{\partial y} dy - \int_1^2 \frac{\partial V}{\partial z} dz = -\int_1^2 dV = V_1 - V_2$
- $w = K_2 - K_1 = V_1 - V_2$ ; 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,  $K = K_1 + K_2 + \dots + K_n = \frac{1}{2} \sum_{i=1}^n m_i v_i^2$
- $V = \sum_i \sum_{j>i} V_{ij}$
- With conservative forces  $K + V = E_{mech}$  is constant for many particle systems.



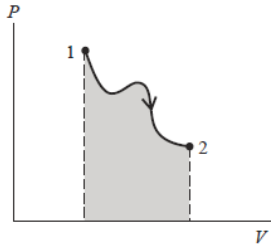
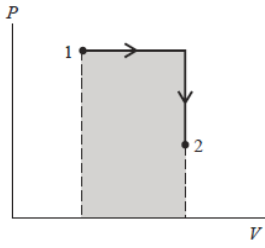
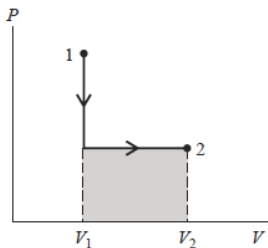
## P-V work

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



- $dw = \vec{F} \cdot d\vec{r} = PAdx$
- $dw_{rev} = -PdV$
- $w_{rev} = -\int_1^2 PdV$
- The above expression is a line integral and its value depends 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
$$m_2 c_2 (T_2 - T_f) = m_1 c_1 (T_f - T_1) \equiv q$$
- $c_{H_2O} = 1.0 \text{ cal}/(\text{g}^\circ\text{C})$  at  $15^\circ\text{C}$  and 1 atm.
- $dq_P \equiv m c_P dT$
- $q_P = m \int_{T_1}^{T_2} c_P(T) dT$
- $C_P = dq_P/dT = m c_P$
- In the absence of phase transition:
$$m_2 \int_{T_f}^{T_2} c_{P2}(T) dT = m_1 \int_{T_1}^{T_f} c_{P1}(T) dT = q_P$$
- 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,  $E \approx U$ .
- The caloric theory claim that heat consists of a self-repellent fluid called caloric that flows from hotter bodies to colder bodies.
- Caloric was also thought of as a weightless gas that could pass in and out of pores in solids and liquids.
- The "caloric theory" was superseded by the mid-19th century in favor of the mechanical theory of heat.

# The first law of thermodynamics

- 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,  $\Delta E_{syst} + \Delta E_{surr} = 0$ .
- 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.

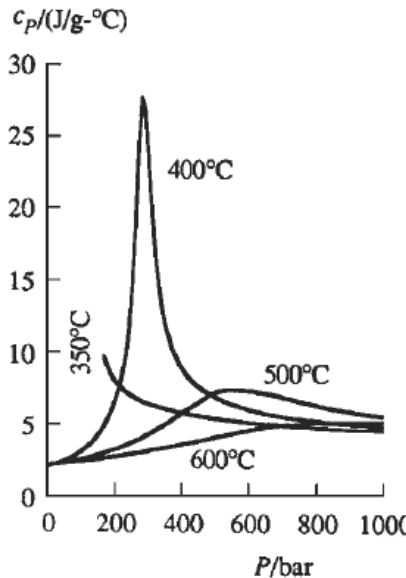
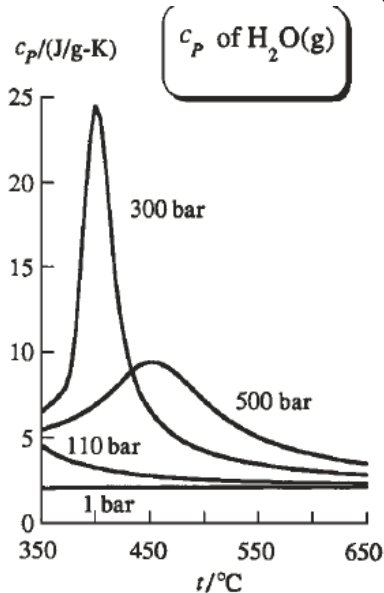
# The first law of thermodynamics

- 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:  $H \equiv U + PV$ .
- $U_2 - U_1 = q + w = q - \int_{V_1}^{V_2} P dV$ , 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,  $q_P = \Delta H$ .
- $\Delta H = \Delta U + \Delta(PV)$  but  $\Delta(PV) \neq P\Delta V + V\Delta P + \Delta(V)\Delta(P)$
- $H_m = H/n = (U + PV)/n = U_m + PV_m$
- For a constant volume process,  $\Delta U = q + w = q_V$
- When  $\Delta H \approx \Delta U$ ?

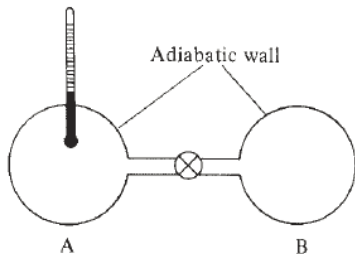
# Heat capacities

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

# Heat capacities



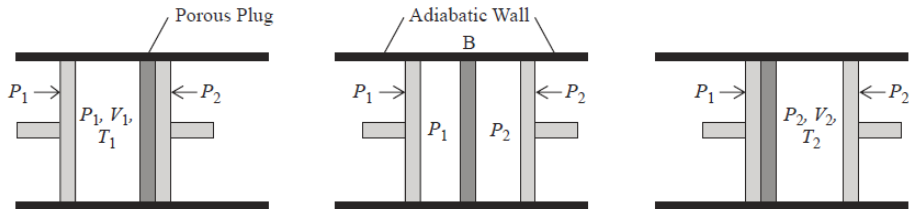
# Joule and Joule–Thompson experiments



- 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.

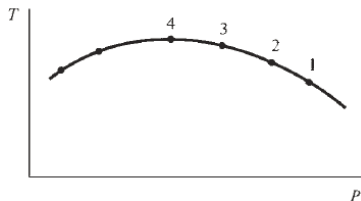


# Joule and Joule–Thompson experiments



- $w_L = P_1 V_1$ ,  $w_R = -P_2 V_2$ ,  $w = w_L + w_R = P_1 V_1 - P_2 V_2$ .
- $U_2 - U_1 = q + w = w = P_1 V_1 - P_2 V_2$ ; 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  $\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H$
- Joule–Thompson liquefaction.

# Joule and Joule–Thompson experiments

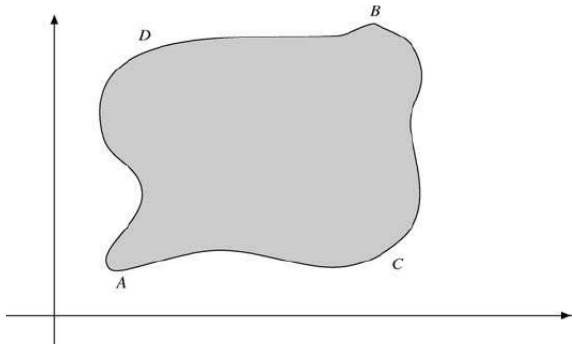


- 
- $(\frac{\partial H}{\partial P})_T = -C_P \mu_{JT}$
- Perfect gas:  $PV = nRT$  and  $(\frac{\partial U}{\partial V})_T = 0$ .
- For a perfect gas  $U = U(T)$ . Thus  $dU = C_V(T)dT$ . Also,  $H \equiv U + PV = U + nRT \rightarrow H = H(T)$ ,  $C_P = dH/dT$ ,  $C_P = C_P(T)$ .
- $C_P - C_V = P(\partial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

- For a perfect gas, PV work only,  $dU = C_V dT = dq - PdV$
- 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  $C_{V,m} dT = -(RT/V)dV$
- $\int_1^2 \frac{C_{V,m}}{T} dT = -\int_1^2 \frac{R}{V} dV = R \ln \frac{V_1}{V_2} \approx C_{V,m} \ln \frac{T_2}{T_1}$
- $\ln \frac{T_2}{T_1} = \ln \left( \frac{V_1}{V_2} \right)^{R/C_{V,m}}$
- For a reversible adiabatic process in a perfect gas,  $\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{R/C_{V,m}}$
- $P_1 V_1^{1+R/C_{V,m}} = P_2 V_2^{1+R/C_{V,m}}$
- 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 gas, adiabatic process,  $\Delta U = C_V(T_2 - T_1) = w$ .

# Potential theory, State function

- Scalar potential
- Conservative force
  - $\iff \vec{F} = -\nabla\phi \iff \nabla \times \vec{F} = 0 \iff \oint \vec{F} \cdot d\mathbf{r} = 0$
- $\nabla \times F = -\nabla \times \nabla\phi = 0$
- $\oint F \cdot d\mathbf{r} = -\oint \nabla\phi \cdot d\mathbf{r} = -\oint d\phi = 0$
- $\oint_{ACBDA} F \cdot d\mathbf{r} = 0 \iff \int_{ACB} F \cdot d\mathbf{r} = -\int_{BDA} F \cdot d\mathbf{r} = \int_{ADB} F \cdot d\mathbf{r} \iff$   
the work is path independent.

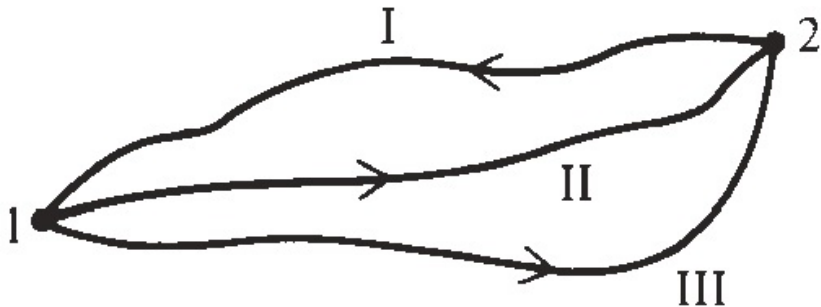


# Potential theory, State function

- $\int_A^B F \cdot dr = \phi(A) - \phi(B) \rightarrow F \cdot dr = -d\phi = -\nabla\phi \cdot dr$ . Therefore  $(F + \nabla\phi) \cdot dr = 0$
- Stokes theorem,  $\oint \vec{F} \cdot dr = \int_S \nabla \times \vec{F} \cdot d\vec{\sigma}$  by integrating over the perimeter of an arbitrary differential surface  $d\sigma$ , we see that  $\oint F \cdot dr = 0$  result in  $\nabla \times F = 0$ .
- Scalar potential for the gravitational force on a unit mass  $m_1$ ,  $F_G = -\frac{Gm_1m_2\hat{r}}{r^2} = -\frac{k\hat{r}}{r^2}$ ?
- Scalar potential for the centrifugal force and simple harmonic oscillator on a unit mass  $m_1$ ,  $\vec{F}_c = \omega^2\vec{r}$  and  $\vec{F}_{SHO} = -k\vec{r}$ .
- Exact differentials. How to know if integral of  $df = P(x, y)dx + Q(x, y)dy$  is path dependent or independent.

## State functions and line integrals:

- If  $b$  is a state function then  $\int_1^2 db = b_2 - b_1$
- 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,  $E_j = j(j+1)b$ ,  $U_{rot,m} = RT$ . 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.
- Intermolecular forces.

# Structural Interactions

- 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 is a necessary condition for molecular dipole moment.
- If a molecule is indistinguishable after rotating by  $\frac{2\pi}{n}$  radians around an axis, that symmetry axis 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  $360^\circ/n$  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.  $E_{AB}^{\text{disp}} \approx -\frac{3}{2} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{R^6}$
- $I$  represents the ionization potential while  $\alpha$  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.

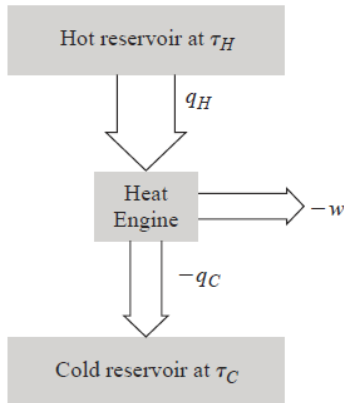
- Non-bonding intermolecular interactions are qualitatively similar to bonding interactions.
- For atoms and approximately spherical molecules LJ is a good approximation to intermolecular interaction,  
$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right].$$
- $r$  is internuclear distance while  $\sigma$  and  $\epsilon$  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- All 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

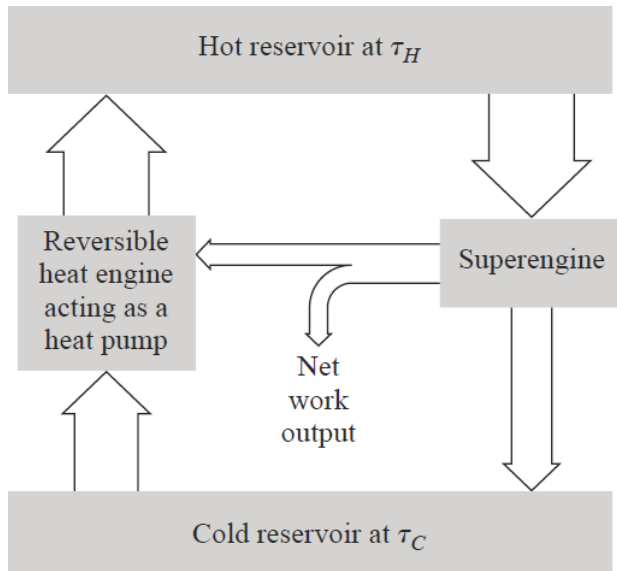
- To keep producing work a heat engine must work in cycles.
- Each cycle must contain at least three steps: 1- Absorption of the heat  $q_H$  by the system. 2- performance of the work  $-w$ , 3- Expulsion of the heat  $-q_C$  by the system.
- $e = \frac{-w}{q_H} = \frac{q_H + q_C}{q_H} = 1 + \frac{q_C}{q_H}$



# 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  $T_H$  and  $T_C$ .
- 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

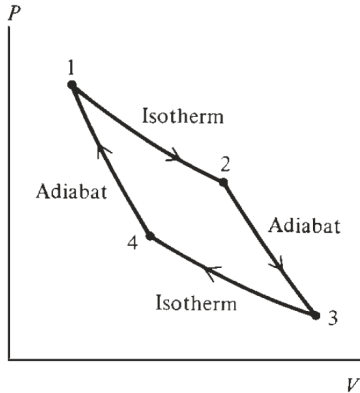
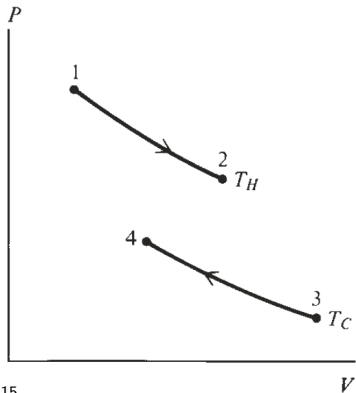


# Heat engines

- Thus  $e_{super} > e_{rev}$  is wrong. Therefore  $e \leq e_{rev}$ .
- Consider two engines A and B operating reversibly between temperatures  $\tau_H$  and  $\tau_C$ .
- 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  $\tau_H$  and  $\tau_C$  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 isotherms must be connected by two reversible adiabats.
- This is called a Carnot cycle.



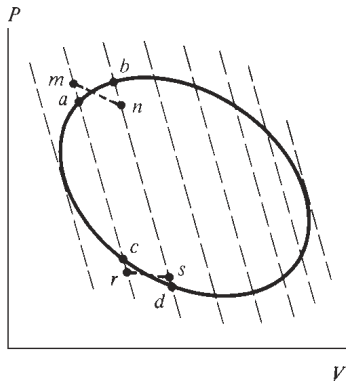


# Heat engines

- 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  
$$\frac{q_C}{q_H} = -\frac{T_C}{T_H}$$

- 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.
- Generalization to any cyclic process:

# Entropy

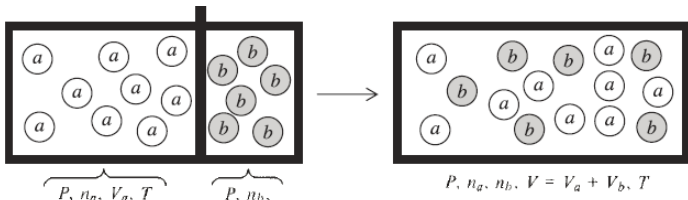


- 
- Dashed lines are reversible adiabats dividing the cycle into adjacent strips.
- Draw the reversible isotherm  $mn$  such that the area under  $amnb$  equals the area under  $ab$ . Thus  $w_{amnb} = w_{ab}$ .

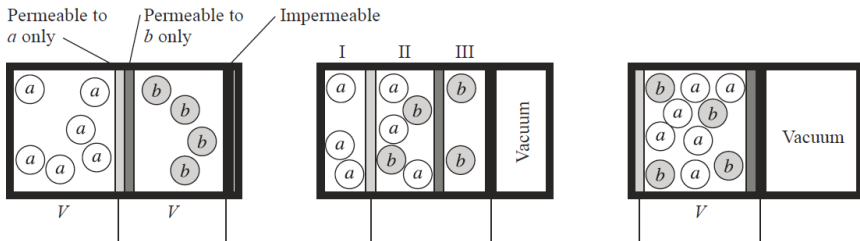
# Entropy

- $\Delta U_{amnb} = \Delta U_{ab}$ . 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  $\Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T}$ .
- If the system is composed of two subsystems,  $dS = dq/T = dq_1/T + dq_2/T = dS_1 + dS_2$ , i.e., entropy is extensive.
- Reversible change of state of a perfect gas:  
$$dq_{rev} = C_V dT + nRTdV/V \rightarrow dS = C_V dT/T + nRdV/V \rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT + nR \ln \frac{V_2}{V_1}.$$

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

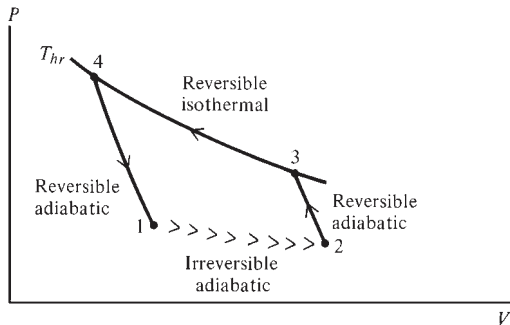


- This is an irreversible process. To calculate  $\Delta S$  we shall devise a reversible path. 1- A reversible expansion to volume  $V$ . 2- A reversible mixing of the two gases.



- $\Delta S_1 = \Delta S_a + \Delta S_b = n_a R \ln(V/V_a) + n_b R \ln(V/V_b), \quad \Delta S_2 = 0$
- $\Delta_{mix} S = -n_a R \ln x_a - n_b R \ln x_b$
- 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:  
$$dS_{univ} = dS_{syst} + dS_{surr} = \frac{dq_{rev}}{T_{syst}} + \frac{-dq_{rev}}{T_{surr}} = \frac{dq_{rev}}{T_{syst}} - \frac{dq_{rev}}{T_{syst}} = 0. \text{ Thus}$$
$$\Delta S_{univ} = 0.$$
- Adiabatic irreversible process in a closed system:

# Entropy



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

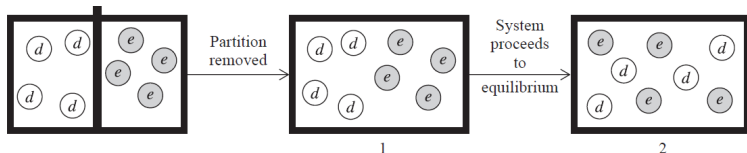
- $0 = \oint dS_{\text{sys}} = (S_2 - S_1) + 0 + q_{3 \rightarrow 4}/T_{hr} + 0 \rightarrow S_2 - S_1 = -q_{3 \rightarrow 4}/T_{hr}$
- $0 = \oint (dq + dw) = q_{3 \rightarrow 4} + w$ . Thus  $w = -q_{3 \rightarrow 4}$ .
- To avoid contradiction with the second law we must have  $S_2 - S_1 = -q_{3 \rightarrow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



- $dq_{rev}/T$  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:
  - $-q_C/q_H = 1 - f(\tau_C, \tau_H) \equiv g(\tau_C, \tau_H)$
  - Three heat reservoir at temperatures  $\tau_C, \tau_m, \tau_h$
  - Heat engine 1 acting between  $\tau_C, \tau_m$  while heat engine 2 acting between  $\tau_m, \tau_h$  such that  $q_{m1} = -q_{m2}$ .

- Consider heat engine 3 composed of heat engines 1 and 2.
- Note that  $-q_{c3}/q_{h3} = -q_{c1}/q_{h2} = -(q_{c1}/q_{m1})(q_{m2}/q_{h2}) \rightarrow g(\tau_C, \tau_h) = g(\tau_C, \tau_m)g(\tau_m, \tau_h)$
- Thus  $g(\tau_C, \tau_H) = \phi(\tau_C)/\phi(\tau_H)$
- By taking the simplest possible choice for  $\phi$  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.

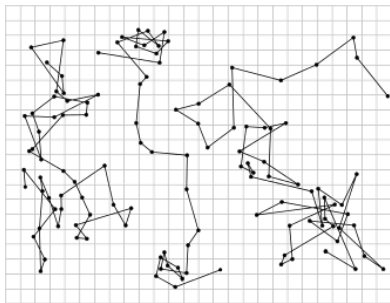
# Entropy



- 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:  
 $\Delta S = S_2 - S_1 = k \ln(p_2/p_1)$

- $p_1 = \left(\frac{1}{2}\right)^{N_d} \left(\frac{1}{2}\right)^{N_e} = \left(\frac{1}{2}\right)^{N_d+N_e}$ .
- $\Delta S = k \ln(1/p_1) = k \ln 2^{N_d+N_e} = 2N_d k \ln 2$ .
- From thermodynamics  $\Delta S = 2n_d R \ln 2$ .
- Boltzmann's constant,  $k = Rn_d/N_d = R/N_A = 1.38 \times 10^{-23} \text{ J/K}$ .
- 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.
- Equilibrium value of each property is the average of that property over all possible states.
- Thus one calculates the average value of each property and its variance.
- Fluctuations in number density are of the order of  $\sqrt{N}$ .

- 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.
- $\left\{ \begin{array}{l} \text{Reaction equilibrium} \\ \text{Phase equilibrium} \end{array} \right.$
- Criterion for equilibrium in an isolated system is maximization of  $S$ .
- For a closed but not isolated system equilibrium criterion is maximization of  $S_{\text{syst}} + S_{\text{surr}}$ .
- For a system away from equilibrium:  $dS_{\text{univ}} = dS_{\text{syst}} + dS_{\text{surr}} > 0$  and  $dS_{\text{surr}} = dq_{\text{surr}}/T$ ; thus,  $dS_{\text{syst}} > -dS_{\text{surr}} = -dq_{\text{surr}}/T = dq_{\text{syst}}/T$ .
- For a closed system in thermal and mechanical equilibrium  $dS > dq_{\text{irrev}}/T$
- In general  $dS \geq \frac{dq}{T}$ , Clausius inequality.
- $dU \leq TdS + dw$

# Energy function interpretation

- $dU \leq TdS + SdT - SdT + dw = d(TS) - SdT + dw \rightarrow d(U - TS) \leq -SdT + dw = -SdT - PdV.$
- 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 or Gibbs free energy:  
 $G \equiv H - TS \equiv U + PV - TS$
- Equilibrium conditions  $dA = 0$  and  $dG = 0.$

# Energy function interpretation

- $\Delta S_{univ} = -\Delta H_{syst}/T + \Delta S_{syst} = -(\Delta H_{syst} - T\Delta S_{syst})/T = -\Delta G_{syst}/T$  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,  $dG \leq dw_{non,PV}$
- $\Delta G \leq w_{non,PV} \quad w_{by,non,PV} \leq -\Delta G$
- $-\Delta G$  is the maximum non-expansion work 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  
 $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$ ,       $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$ .
- The Gibbs equations:  
 $dH = TdS + VdP$ ,       $dA = -SdT - PdV$ ,       $dG = -SdT + VdP$ .
- Comparing  $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$  with the corresponding Gibbs equation,  $\left(\frac{\partial U}{\partial S}\right)_V = T$  and  $\left(\frac{\partial U}{\partial V}\right)_S = -P$ .
- Similarly,  $\left(\frac{\partial H}{\partial S}\right)_P = T$ ,    $\left(\frac{\partial H}{\partial P}\right)_S = V$ ,    $\left(\frac{\partial A}{\partial T}\right)_V = -S$ ,    $\left(\frac{\partial A}{\partial V}\right)_T = -P$ ,  
 $\left(\frac{\partial G}{\partial T}\right)_P = -S$ ,    $\left(\frac{\partial G}{\partial P}\right)_T = V$ .
- Thermodynamics, enables properties that are difficult to measure to be expressed in terms of easily measured properties like  
 $C_P(T, P)$ ,    $\alpha(T, P)$ ,    $\kappa(T, P)$ .

# Thermodynamic relations

- Euler reciprocity relation is the condition satisfied by an exact differential. When  $df = Mdx + Ndy$ ,  $f$  is an exact differential iff  $(\frac{\partial M}{\partial y})_x = (\frac{\partial N}{\partial x})_y$ . Originated from  $(\frac{\partial^2 f}{\partial x \partial y}) = (\frac{\partial^2 f}{\partial y \partial x})$ .
- The Maxwell relations:  $(\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V$ ,  $(\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P$ ,  $(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V$ ,  $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$ .
- $(\frac{\partial U}{\partial V})_T = T(\frac{\partial S}{\partial V})_T - P = T(\frac{\partial P}{\partial T})_V - P = \frac{\alpha T}{\kappa} - P$
- $(\frac{\partial H}{\partial P})_T = T(\frac{\partial S}{\partial P})_T + V = -T(\frac{\partial V}{\partial T})_P + V = -TV\alpha + V$
- $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P = -\alpha V$
- $(\frac{\partial G}{\partial T})_P = -S$ ,  $(\frac{\partial G}{\partial P})_T = V$
- (41)  $\mu_{JT} = (1/C_P)[T(\partial V/\partial T)_P - V] = (V/C_P)(\alpha T - 1)$
- (37)  $C_P - C_V = [(\partial U/\partial V)_T + P](\partial V/\partial T)_P = TV\alpha^2/\kappa$
- 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.
- (26) Estimate the internal pressure in solids and liquids.

# Thermodynamic relations

- $dS = \frac{C_P}{T} dT - \alpha V dP \rightarrow \Delta S = S_2 - S_1 = \int_1^2 \frac{C_P}{T} dT - \int_1^2 \alpha V dP$
- $\Delta H = \int_1^2 C_P dT + \int_1^2 (V - TV\alpha) dP$
- $\Delta U = \Delta H - \Delta(PV)$
- $G = G(T, P, n_1, \dots, n_k) \rightarrow dG =$   
 $(\frac{\partial G}{\partial T})_{P, n_i} dT + (\frac{\partial G}{\partial P})_{T, n_i} dP + (\frac{\partial G}{\partial n_1})_{T, P, n_{j \neq 1}} dn_1 + \dots + (\frac{\partial G}{\partial n_k})_{T, P, n_{j \neq k}} dn_k$
- Since in a reversible process on a system of constant composition  $dG = -SdT + VdP$  we have  $(\frac{\partial G}{\partial T})_{P, n_i} = -S$ ,  $(\frac{\partial G}{\partial P})_{T, n_i} = V$ .
- $dG = -SdT + VdP + \sum_{i=1}^k (\frac{\partial G}{\partial n_i})_{T, P, n_{j \neq i}} dn_i$
- $\mu_i \equiv (\frac{\partial G}{\partial n_i})_{T, P, n_{j \neq i}}$
- 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  $dG = \sum_{\alpha} dG^{\alpha}$ .
- $dG^{\alpha} = -S^{\alpha}dT + V^{\alpha}dP + \sum_{i=1}^k \mu_i^{\alpha} dn_i^{\alpha}$
- $\mu_i^{\alpha} \equiv \left(\frac{\partial G^{\alpha}}{\partial n_i^{\alpha}}\right)_{T, P, n_{j \neq i}^{\alpha}}$
- $dG = -\sum_{\alpha} S^{\alpha}dT + \sum_{\alpha} V^{\alpha}dP + \sum_{\alpha} \sum_{i=1}^k \mu_i^{\alpha} dn_i^{\alpha}$
- $dG = -SdT + VdP + \sum_{\alpha} \sum_{i=1}^k \mu_i^{\alpha} dn_i^{\alpha}$
- Condition for material equilibrium in a closed system with PV work only, at constant T and P:  $\sum_{\alpha} \sum_{i=1}^k \mu_i^{\alpha} dn_i^{\alpha} = 0$
- $\mu_i^{\alpha} = \mu_i^{\alpha}(T^{\alpha}, P^{\alpha}, x_1^{\alpha}, x_2^{\alpha}, \dots)$

# Phase equilibrium condition

- For a pure substance,  $\mu_i$  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  $\beta$  to  $\delta$ ,  
 $\mu_j^\beta dn_j^\beta + \mu_j^\delta dn_j^\delta = 0 \rightarrow \mu_j^\beta = \mu_j^\delta$ .
- Phase equilibrium condition is that  $\mu$  of a given substance is the same in every phase.
- Before equilibrium in a system with only PV work, 71,  
 $dG < -SdT + VdP$ , 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  $\mu_j$  to a phase with lower chemical potential  $\mu_j$ .
- $(\partial \mu_j^\delta / \partial x_j^\delta)_{T,P,n_{i \neq j}^\delta} > 0$
- View chemical potential as escaping tendency.

# Phase equilibrium condition

- When substance  $j$  is absent from phase  $\delta$ , phase equilibrium condition becomes  $\mu_j^\delta \geq \mu_j^\beta$ .
- Denote a chemical reaction by  $0 \rightarrow \nu_1 A_1 + \nu_2 A_2 + \cdots + \nu_m A_m + \nu_{m+1} A_{m+1} + \cdots$  or  $0 \rightarrow \sum_i \nu_i A_i$  where  $\nu_i$  are stoichiometric numbers or stoichiometric coefficients.
- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$      $0 \rightarrow -CH_4 - 2O_2 + CO_2 + 2H_2O$ , where  $\nu_{CH_4} = -1$ ,  $\nu_{O_2} = -2$ ,  $\nu_{CO_2} = +1$  and  $\nu_{H_2O} = +2$ .
- Extent of reaction  $\xi$ . For  $0 \rightarrow \sum_i \nu_i A_i$ ,  $\Delta n_i \equiv n_i - n_{i,0} = \nu_i \xi$ .
- 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

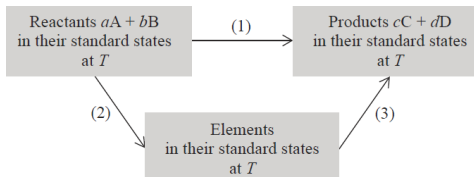
- Standard state of a pure solid or liquid is the state with pressure 1 bar and temperature T, e.g.,  $V_{m,200}^{\circ}$
- Standard state of pure gases is defined with P=1 bar and the gas behaving ideally.
- Standard enthalpy change of reaction,  $\Delta H_T^{\circ}$ : enthalpy change for the process 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 products, each in its standard state at temperature T.
- For the reaction:  $0 \rightarrow \sum_i \nu_i A_i$ ,  $\Delta H_T^{\circ} \equiv \sum_i \nu_i H_{m,T,i}^{\circ}$ .
- 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  $\Delta H^0$  for the process of forming one mole of substance in its standard state at T from the corresponding separate elements 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.
- $\text{C}(\text{graphite}, 307 \text{ K}, \text{P}^\circ) + \text{H}_2(\text{Ideal gas}, 307 \text{ K}, \text{P}^\circ) + 1/2\text{O}_2(\text{Ideal gas}, 307 \text{ K}, \text{P}^\circ) \rightarrow \text{H}_2\text{CO}(\text{Ideal gas}, 307 \text{ K}, \text{P}^\circ)$   $\Delta H = \Delta_f H_{307, \text{H}_2\text{CO}(g)}^0$
- For an element in its reference form,  $\Delta_f H_T^0$  is zero.
- The standard enthalpy change for a reaction  $\Delta H_T^0 = \sum_i \nu_i \Delta_f H_{T,i}^0$



# Standard thermodynamic functions of reaction

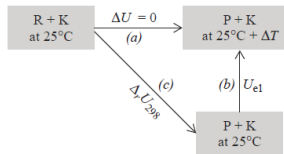
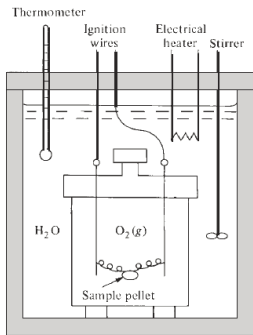


- For  $aA + bB \rightarrow cC + dD$ ,
- $\Delta H_1 = \Delta H_2 + \Delta H_3 \rightarrow \Delta H_T^0 = -a\Delta_f H_T^0(A) - b\Delta_f H_T^0(B) + c\Delta_f H_T^0(C) + d\Delta_f H_T^0(D)$
- Determination of standard enthalpies of formation:
- 1-  $\Delta H$  for hypothetical transformation of gaseous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

# Standard thermodynamic functions of reaction

- 4- Use a calorimeter to find  $\Delta H$  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  $\Delta H$  for bringing the compound from state in which it is formed to  $T$  and 1 bar.
- 6- If compound  $i$  is a gas, find  $\Delta H$  for transformation of  $i$  from a real gas to an ideal gas.
- Calorimetry  $\left\{ \begin{array}{l} \text{Constant volume calorimeter} \\ \text{Constant pressure calorimeter} \end{array} \right.$
- Standard enthalpy of combustion,  $\Delta_c H_T^0$  is measured by an adiabatic bomb calorimeter.
- For the calorimeter  $\Delta U = 0$ , after measuring  $\Delta T$  the system is cooled back to  $25^\circ\text{C}$ . Then the electrical energy to rise the temperature by  $\Delta T$  is measured.

# Standard thermodynamic functions of reaction



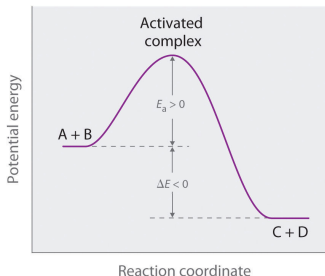
- $\Delta_r U_{298} = -U_{el} = -VIt$
- Alternatively,  $\Delta_r U_{298} = -C_{K+P}\Delta T$ . Where  $C_{K+P}$  is estimated by burning a compound with known  $\Delta_r U_{298}$  in the calorimeter.

# Standard thermodynamic functions of reaction

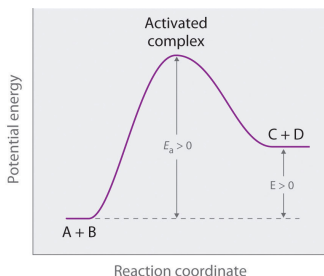
- Calorimetry measures either  $\Delta H^0$  or  $\Delta U^0$ . To relate these quantities use  $\Delta H^0 = \Delta U^0 + P^0 \Delta V^0$
- $\Delta H^0 = \sum_i \nu_i H_{m,i}^0$ ,  $\Delta V^0 = \sum_i \nu_i V_{m,i}^0$ ,  $\Delta U^0 = \sum_i \nu_i U_{m,i}^0$
- Neglect volume of solids and liquids compared with gases.  
 $\Delta V^0 = (\Delta n_g / \text{mol}) RT / P^0$ .
- Thus  $\Delta H^0 = \Delta U^0 + (\Delta n_g / \text{mol}) RT$
- 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:  
 $CH_2CHCH_3 + H_2 \rightarrow CH_3CH_2CH_3 \quad \Delta H = -124 \text{kJmol}^{-1}$   
Combustion of propane  
 $CH_3CH_2CH_3 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad \Delta H = -2220 \text{kJmol}^{-1}$   
Combustion of Hydrogen  $H_2 + 1/2O_2 \rightarrow H_2O \quad \Delta H = -286 \text{kJmol}^{-1}$

# Standard thermodynamic functions of reaction

- Calculate enthalpy of propene combustion?
- 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) graph.

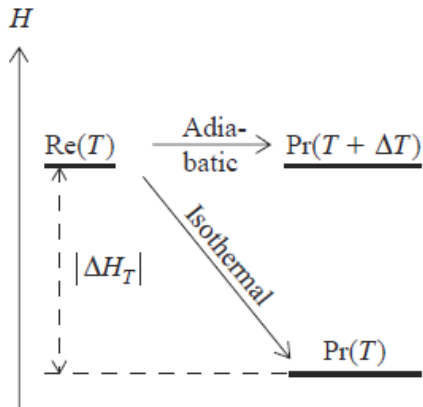


• (a)



(b)

# Thermodynamics: Thermochemistry



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

- $\Delta H = H_{id}(T, P^0) - H_{re}(T, P^0) = \Delta H_a + \Delta H_b + \Delta H_c$
- $\Delta H_a = H_{re}(T, 0 \text{ bar}) - H_{re}(T, P^0) = \int_{P^0}^0 (V - TV\alpha) dP$
- 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,  $H_{m,i}^0$ .  $\Delta H^0 = \sum_i \nu_i H_{m,i}^0$ .
- Arbitrarily, for the most stable form of each pure element,  $H_{m,298}^0 = 0$ .
- For other compounds we use experimental data like formation enthalpies to deduce values of  $H_{m,i}^0$ .

# Temperature dependence of reaction heats

- $\frac{d\Delta H^0}{dT} = \sum_i \nu_i \frac{dH_{m,i}^0}{dT} = \sum_i \nu_i C_{P,m,i}^0 \equiv \Delta C_P^0$ , standard heat capacity change in the reaction.
- $\frac{d\Delta H^0}{dT} = \frac{d(H_{pr}^0 - H_{re}^0)}{dT} = \frac{d(H_{pr}^0)}{dT} - \frac{d(H_{re}^0)}{dT} = C_{P,pr}^0 - C_{P,re}^0 = \Delta C_P^0$
- Kirshhoff's law:  $\Delta H_{T_2}^0 - \Delta H_{T_1}^0 = \int_{T_1}^{T_2} \Delta C_P^0 dT$
- $C_{P,m}^0 = a + bT + cT^2 + dT^3$ .
- $\Delta C_P^0 = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3$ .
- 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  $\Delta S$  for preparing the desired substance in its standard state from elements in their reference states.
- For a pure element in its stable condensed form
$$S_{m,0}^0 = \lim_{T \rightarrow 0} S_{m,T}^0 = 0.$$
- 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:  $\lim_{T \rightarrow 0} (\partial \Delta G / \partial T)_P = 0$
- $(\partial G / \partial T)_P = -S$ .  $(\partial \Delta G / \partial T)_P = -S_2 + S_1 = -\Delta S$ .

## 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 as  $T$  goes to zero:  
 $\lim_{T \rightarrow 0} \Delta S = 0$ .
- Consider the reaction  $H_2(s) + \frac{1}{2}O_2(s) \rightarrow H_2O(s)$ , choice of elemental entropy as zero together with third law imply that  
 $\lim_{T \rightarrow 0} S_m^0(H_2O) = 0$
- $S_{m,0}^0(H_2O) = 0$ . By the same reasoning, for any compound  $S_{m,0}^0 = 0$ .
- Using the third law, for any compound in internal equilibrium,  $S_{m,0}^0 = 0$ . Also,  $S_0^0 = 0$ .
- Conventional standard state entropy at any  $T$  can be found.
- E.g., for a liquid,  $S_{m,T_2}^0 = \int_0^{T_{fus}} \frac{C_{P,m}^0(s)}{T} dT + \frac{\Delta_{fus} H_m^0}{T_{fus}} + \int_{T_{fus}}^{T_2} \frac{C_{P,m}^0(l)}{T} dT$ .

# Relative (conventional) entropies

- For a gas,  $S_{m,T_2}^0 = \int_0^{T_{fus}} \frac{C_{P,m}^0(s)}{T} dT + \frac{\Delta_{fus}H_m^0}{T_{fus}} + \int_{T_{fus}}^{T_{boil}} \frac{C_{P,m}^0(l)}{T} dT + \frac{\Delta_{boil}H_m^0}{T_{boil}} + \int_{T_{boil}}^{T_2} \frac{C_{P,m}^0(g)}{T} dT$ .
- Also consider:  $S_{m,id}(T, P^\circ) - S_{m,re}(T, P^\circ) = \int_0^{P^\circ} \left[ \left( \frac{\partial V_m}{\partial T} \right)_P - \frac{R}{P} \right] dP$ .
- For non-metallic solids at very low temperatures,  $C_{P,m}^\circ \approx C_{V,m}^\circ = aT^3$ . Since  $\lim_{T \rightarrow 0} \frac{TV\alpha^2}{\kappa} = 0$
- For metals at very low  $T$ ,  $C_{P,m}^\circ \approx C_{V,m}^\circ = aT^3 + bT$
- Due to lack of data at very low  $T$ ,  
$$\int_0^{T_{fus}} \frac{C_{P,m}^\circ}{T} dT = \frac{C_{P,m}^\circ(T_{low})}{3} + \int_{T_{low}}^{T_{fus}} \frac{C_{P,m}^\circ}{T} dT$$
- Example 5.7 of the book.
- Dependence of entropy on physical state and size of molecule.
- For solids and liquids:  $H_{m,T}^\circ - H_{m,0}^\circ \approx U_{m,T}^\circ - U_{m,0}^\circ$ .
- Standard entropy of reaction:  $\Delta S_T^\circ = \sum_i \nu_i S_{m,T,i}^\circ$
- $\Delta S_{T_2}^\circ - \Delta S_{T_1}^\circ = \int_{T_1}^{T_2} \frac{\Delta C_P^\circ}{T} dT$ .
- Example 5.8 of the book.

## Relative (conventional) Gibbs energies

- Standard Gibbs energy of reaction:  $\Delta G_T^\circ = \sum_i \nu_i G_{m,T,i}^\circ$ , the change in G for converting stoichiometric numbers of moles of the separated pure reactants, each in its standard state at T, into the separated pure products in their standard states at T.
- $\Delta G_T^\circ = \sum_i \nu_i \Delta_f G_{T,i}^\circ$ .
- $\Delta_f G_{T,i}^\circ = \Delta_f H_{T,i}^\circ - T \Delta_f S_{T,i}^\circ$ .
- Instead of tabulating  $\Delta_f G_T^\circ$  it is possible to tabulate  $G_{m,T}^\circ = H_{m,T}^\circ - T S_{m,T}^\circ$
- Tabulations of thermodynamic data list:  $\Delta_f H_{298}^\circ$ ,  $S_{m,298}^\circ$ ,  $\Delta_f G_{298}^\circ$ , and  $C_{P,m,298}^\circ$ .

# Thermodynamics tables

- Change of standard from 1 atm to 1 bar. [?]
- Tabulated values depend on the reference form chosen for the elements.
- There are tables of  $\Delta_f H^\circ$ ,  $S_m^\circ$ , and  $\Delta_f G^\circ$  at various temperatures.
- Instead of tabulating  $\Delta_f H^\circ$ , and  $\Delta_f G^\circ$  vs. T, some tables list  $H_{m,T}^\circ - H_{m,298}^\circ$  (or  $H_{m,T}^\circ - H_{m,0}^\circ$ ) vs. T and  $G_{m,T}^\circ - H_{m,298}^\circ$  (or  $G_{m,T}^\circ - H_{m,0}^\circ$ ) vs. T.
- $\Delta H_T^\circ = \Delta H_{298}^\circ + \sum_i \nu_i (H_{m,T}^\circ - H_{m,298}^\circ)_i$
- $\Delta G_T^\circ = \Delta H_{298}^\circ + T \sum_i \nu_i [(G_{m,T}^\circ - H_{m,298}^\circ)/T]_i$
- Example 5.11
- $(G_{m,T}^\circ - H_{m,298}^\circ)/T = (H_{m,T}^\circ - TS_{m,T}^\circ)/T - H_{m,298}^\circ/T = (H_{m,T}^\circ - H_{m,298}^\circ)/T - S_{m,T}^\circ$

# Estimation of thermodynamic properties

- As of May 2011, about sixty million chemical compounds are known.
- Bond additivity (mostly for gases)
- E.g., bond additivity contributions to  $\Delta_f H_{298}^\circ / (kcal/mol)$  are C—C 2.73, C—H -3.83, C—O -12.0 and O—H -27.0.
- Liquid at  $P^\circ \rightarrow$  liquid at  $P_{vp} \rightarrow$  gas at  $P_{vp} \rightarrow$  gas at  $P^\circ$ .
- Using enthalpy of vaporization one can express liquid enthalpy in terms of gas phase enthalpy.
- For condensed phase:  $\Delta H_{298}^\circ \approx \Delta U_0^\circ$ .
- Gaseous reactants  $\xrightarrow{(a)}$  gaseous atoms  $\xrightarrow{(b)}$  gaseous products.
- $\Delta H_{298}^\circ = \Delta_{at} H_{298, re}^\circ - \Delta_{at} H_{298, pr}^\circ$
- Group contribution methods.
- Unattainability of absolute zero statement of the third law.

# Reaction equilibrium in ideal gas mixtures: Ideal gas chemical potential

- **Chemical potential of a pure gas**

- $dG = -SdT + VdP \rightarrow dG_m = d\mu = -S_m dT + V_m dP$

- At constant temperature for an ideal gas

$$d\mu = V_m dP = \frac{RT}{P} dP \rightarrow \mu(T, P_2) - \mu(T, P_1) = RT \ln(P_2/P_1)$$

- $\mu = \mu^\circ(T) + RT \ln(P/P^\circ)$

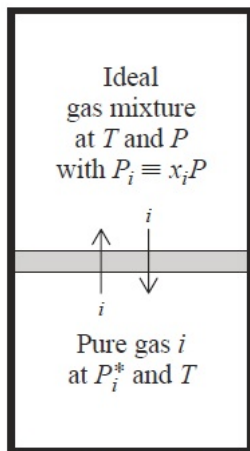
- **Chemical potential in an ideal gas mixture**

- Ideal gas mixture: (a)  $PV = n_{tot}RT$

- (b) When the gas is separated from pure component  $i$  by a thermally conducting, rigid membrane permeable to  $i$  only then at equilibrium  $P_i \equiv x_i P$  equals pressure in the pure  $i$  subsystem.

- $\mu_i(T, P, x_1, x_2, \dots) = \mu_i^*(T, x_i P) = \mu_i^*(T, P_i) = \mu_i^\circ(T) + RT \ln(P_i/P^\circ)$

## Reaction equilibrium in ideal gas mixtures



At equilibrium,  $P_i^* = P_i$ . Each of  $U$ ,  $H$ ,  $S$ ,  $G$ , and  $C_p$  for an ideal gas mixture is the sum of the corresponding thermodynamic functions for the pure gases occupying a volume equal to the mixture's volume at its partial pressure and temperature.



# Ideal gas reaction equilibrium

- $aA + bB \rightleftharpoons cC + dD$
- $c\mu_C + d\mu_D - a\mu_A - b\mu_B = 0$
- Equilibrium condition becomes  $\Delta G^\circ = -RT \ln \frac{(P_{C,eq}/P^\circ)^c (P_{D,eq}/P^\circ)^d}{(P_{A,eq}/P^\circ)^a (P_{B,eq}/P^\circ)^b}$ .
- $K_P^\circ \equiv \frac{(P_{C,eq}/P^\circ)^c (P_{D,eq}/P^\circ)^d}{(P_{A,eq}/P^\circ)^a (P_{B,eq}/P^\circ)^b} \quad P^\circ \equiv 1 \text{ bar.}$
- $\sum_i \nu_i \mu_i = \sum_i \nu_i [\mu_i^\circ + RT \ln(P_{i,eq}/P^\circ)] = 0$
- $\Delta G_T^\circ = -RT \sum_i \ln(P_{i,eq}/P^\circ)^{\nu_i}$
- Standard pressure equilibrium constant  $K_P^\circ = e^{-\Delta G^\circ/RT}$ .
- Pressure equilibrium constant  $K_P \equiv \prod_i (P_{i,eq})^{\nu_i}$ .
- **Concentration and mole fraction equilibrium constants**
- $c_i \equiv n_i/V \rightarrow P_i = c_i RT$
- For the reaction  $aA + bB \rightleftharpoons fF + dD$ ,  $K_P^\circ = \frac{(c_{F,eq}/c^\circ)^f (c_{D,eq}/c^\circ)^d}{(c_{A,eq}/c^\circ)^a (c_{B,eq}/c^\circ)^b} \left(\frac{c^\circ RT}{P^\circ}\right)^{f+d-a-b} \quad c^\circ \equiv 1 \text{ mol/L} = 1 \text{ mol/dm}^3$

# Ideal gas reaction equilibrium

- $K_c^\circ \equiv \prod_i (c_{i,eq}/c^\circ)^{\nu_i}$
- $K_p^\circ = K_c^\circ \left(\frac{c^\circ RT}{P^\circ}\right)^{\Delta n/mol}$
- Mole fraction equilibrium constant:  
 $K_x \equiv \prod_i (x_{i,eq})^{\nu_i}$ ,  $K_p^\circ = K_x (P/P^\circ)^{\Delta n/mol}$
- **Qualitative discussion of chemical equilibrium**
  - $0 < K_p^\circ < \infty$ ,  $\begin{cases} K_p^\circ \gg 1 \\ K_p^\circ \ll 1 \\ K_p^\circ \approx 1 \end{cases}$  .
  - $K_p^\circ = 1/e^{\frac{\Delta G^\circ}{RT}}$ ,  $\begin{cases} \Delta G^\circ \ll 0 \\ \Delta G^\circ \gg 0 \\ \Delta G^\circ \approx 0 \end{cases}$
- For an isothermal process:  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ .
- At low T,  $\Delta G^\circ \approx \Delta H^\circ$
- At high T,  $\Delta G^\circ \approx -T\Delta S^\circ$

# Temperature dependence of the equilibrium constant

- $\frac{d \ln K_p^\circ}{dT} = \frac{\Delta G^\circ}{RT^2} - \frac{1}{RT} \frac{d(\Delta G^\circ)}{dT} = \frac{\Delta G^\circ}{RT^2} + \frac{\Delta S^\circ}{RT} = \frac{\Delta H^\circ}{RT^2}$  :Van't Hoff equation
- Which results from the Gibbs-Helmholtz equation:  
 $(\partial(G/T)/\partial T)_P = -H/T^2$
- $d \ln K_p^\circ = \frac{\Delta H^\circ}{RT^2} dT \rightarrow \ln \frac{K_p^\circ(T_2)}{K_p^\circ(T_1)} = \int_{T_1}^{T_2} \frac{\Delta H^\circ(T)}{RT^2} dT$
- Typically:  $\Delta H_T^\circ = A + BT + CT^2 + DT^3 + ET^4$ .
- If the temperature change is small  $\ln \frac{K_p^\circ(T_2)}{K_p^\circ(T_1)} \approx \frac{\Delta H^\circ(T)}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$
- van't Hoff equation:  $\frac{d \ln K_p^\circ}{d(1/T)} = -\frac{\Delta H^\circ}{R}$
- Knowledge of  $K_p^\circ$  over a temperature range allows determination of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ .

# Temperature dependence of the equilibrium constant

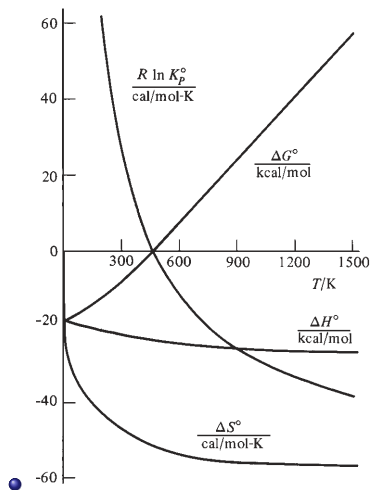


Figure: Thermodynamic quantities for  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- At high  $T$ ,  $\ln K_P^\circ \approx \frac{\Delta S^\circ}{R}$ .
- At low  $T$ ,  $\ln K_P^\circ \approx \frac{-\Delta H^\circ}{RT}$ .

# Ideal gas equilibrium calculations

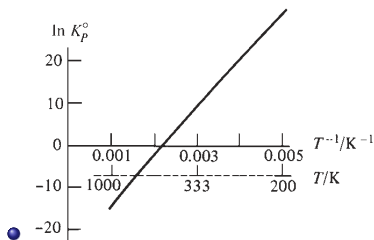


Figure: For  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- Calorimetric measurement allow calculation of  $\Delta_f G^\circ(T)$ , which enable calculation of  $\Delta G^\circ(T)$  for any reaction.
- Equilibrium composition is a function of T and P (or T and V) and initial composition.
- Equilibrium extent of reaction  $\xi_{eq}$  relate equilibrium composition to initial composition:  $\Delta n_i \equiv n_{i,eq} - n_{i,0} = \nu_i \xi_{eq}$

# Ideal gas equilibrium calculations

- Steps for finding equilibrium composition of an ideal gas reaction:
- $\Delta G^\circ(T) = \sum_i \nu_i \Delta_f G_{T,i}^\circ$
- $K_P^\circ = e^{-\Delta G^\circ(T)/RT} \left( \ln \frac{K_P^\circ(T_2)}{K_P^\circ(T_1)} \approx \frac{\Delta H^\circ(T)}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right)$ .
- At fixed T and P:  $P_{i,eq} = x_{i,eq}P = (n_{i,eq} / \sum_j n_{j,eq})P = \frac{n_{i,0} + \nu_i \xi_{eq}}{\sum_j (n_{j,0} + \nu_j \xi_{eq})} P$
- At fixed T and V:  $P_{i,eq} = \frac{n_{i,eq}RT}{V} = \frac{(n_{i,0} + \nu_i \xi_{eq})RT}{V}$
- Solve  $K_P^\circ = \prod_i (P_i/P^\circ)^{\nu_i}$  for  $\xi_{eq}$ .
- $(n_{i,0} + \nu_i \xi_{eq})$
- E.g.,  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  with  $n_{N_2,0} = 1$  mol,  $n_{H_2,0} = 2$  mol and  $n_{NH_3,0} = 0.5$  mol,  $\Delta_f G^\circ(NH_3) = -16.45$  kJ/mol, Assume  $V=10$  L, at 298 K.
- Reaction quotient  $Q_P \equiv \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$
- Find the acceptable range for extent of reaction.

# Ideal gas equilibrium calculations

- E.g.,  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$  with  $n_{N_2O_4,0} = 0.3$  mol and  $n_{NO_2,0} = 0.5$  mol at  $25^\circ\text{C}$  and 2 atm.
- $\Delta_f G^\circ = -26.81$  kJ/mol for  $O(g)$  at 4200 K. Find equilibrium composition of 1 mol  $O_2$  at 4200 K and 3.00 bar.
- $K_p^\circ(800\text{K}) = 6.51$  for  $2A + B \rightleftharpoons C + D$ . If 3.000 mol A, 1.000 mol B and 4.000 mol C are placed in an 8 L vessel at 800 K.
- Use solver in excel.
- $K_p^\circ(400\text{K}) = 3.33$  for ideal gas reaction  $2R + 2S \rightleftharpoons V + W$ ,  $n_{R,0} = 0.400$  mol and  $n_{S,0} = 0.400$  mol in a 5.00 l vessel at 400 K.
- Isomerization:  $A \rightleftharpoons B$ ,  $A \rightleftharpoons C$  and  $B \rightleftharpoons C$ . Express mole fractions in terms of equilibrium constants.
- If at 300 K,  $n_A = 0.16$ ,  $n_B = 0.24$  and  $n_C = 0.72$ , find  $K_{B/A}$  and  $K_{C/A}$ .
- Fluctuations

# Simultaneous equilibrium

- Propagation of error in evaluating  $K_P^\circ$ .
- (1)  $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$   
(2)  $\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4\text{H}_2$
- $n_{0,\text{CH}_4} = 1 \text{ mol}$ ,  $n_{0,\text{H}_2\text{O}} = 1 \text{ mol}$ ,  $n_{0,\text{CO}_2} = 1 \text{ mol}$ ,  $n_{0,\text{H}_2} = 1 \text{ mol}$ ,  
 $n_{0,\text{CO}} = 2 \text{ mol}$ ,
- $P_i/P^\circ = x_i P/P^\circ = n_i P/n_{\text{tot}}/P^\circ$ ,  $K_{P,1}^\circ =$   
 $\frac{n_{\text{CO}} n_{\text{H}_2}^3}{n_{\text{CH}_4} n_{\text{H}_2\text{O}}} \left(\frac{P}{P^\circ n_{\text{tot}}}\right)^2$ ,  $K_{P,2}^\circ = \frac{n_{\text{CO}_2} n_{\text{H}_2}^4}{n_{\text{CH}_4} n_{\text{H}_2\text{O}}^2} \left(\frac{P}{P^\circ n_{\text{tot}}}\right)^2$
- (3)  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$   
(4)  $4\text{CO} + 2\text{H}_2\text{O} \rightleftharpoons 3\text{CO}_2 + \text{CH}_4$
- Deal only with independent reactions.
- Reaction quotient for the reaction  $0 \rightarrow \sum_i \nu_i \mu_i$ ,  $Q_P \equiv \prod_i (P_i)^{\nu_i}$
- Standard Reaction quotient for the reaction  
 $0 \rightarrow \sum_i \nu_i \mu_i$ ,  $Q_P^\circ \equiv \prod_i (P_i/P^\circ)^{\nu_i}$



# Shifts in equilibria

- $$\begin{cases} Q_P < K_P \\ Q_P > K_P \\ Q_P \approx K_P \end{cases}$$

- $$\begin{cases} Q_P^\circ < K_P^\circ \\ Q_P^\circ > K_P^\circ \\ Q_P^\circ \approx K_P^\circ \end{cases}$$

- Isobaric temperature change  $dK_P^\circ/dT = K_P^\circ \Delta H^\circ / RT^2$

- $$\begin{cases} \text{Endothermic reaction } \Delta H^\circ > 0 \\ \text{Exothermic reaction } \Delta H^\circ < 0 \end{cases}$$

- An increase in T at constant P in a closed system shifts the equilibrium in the direction in which the system absorbs heat from the surroundings.

- Isothermal pressure change: consider  $A \rightleftharpoons 2B$ . Isothermally compress the mixture to half its volume to instantaneously double the pressure.

# Shifts in equilibrium

- To generalize to  $aA + bB + \dots \rightleftharpoons eE + fF + \dots$ . Consider total number of gas moles on the right and left.

$$Q_P = \frac{P_E^e P_F^f \dots}{P_A^a P_B^b \dots} = \frac{x_E^e x_F^f \dots}{x_A^a x_B^b \dots} \frac{p^{e+f+\dots}}{p^{a+b+\dots}} = \frac{x_E^e x_F^f \dots}{x_A^a x_B^b \dots} p^{\Delta n_g / \text{mol}}$$

- Le Chateliers principle:
- Isochoric addition of inert gas
- Addition of a reactant gas:
- E.g., in  $A+B \rightleftharpoons 2C+D$  consider addition or removal of a reactant or product at constant T and V, using  $K_P$  and  $Q_P$ .
- E.g., in  $A+B \rightleftharpoons 2C+D$  consider addition or removal of a reactant or product at constant T and P, using  $K_P$  and  $Q_P$ .
- At constant T and P the result can be counter intuitive. Consider:  
 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  with  $n_{N_2} = 3.0$  mol  $n_{H_2} = 1.0$  mol and  $n_{NH_3} = 1.0$  mol. At some T and P,  $K_x = 8.33$ .  $Q_x = \prod_i x_i^{\nu_i}$

# Shifts in equilibrium

- Consider adding 0.1 mol  $N_2$ .  $Q_x = ?$
- Le Chatelier principle: “a change in one of the variables that determines the equilibrium will shift the equilibrium in the direction counteracting the change in that variable.”
- It is suggested that restricting Le Chatelier principle to intensive variables save it. Yet there is counter example even to Le Chatelier principle for an intensive variable.
- Le Chatelier principle restricted to intensive variables and infinitesimal changes is valid.

# Real gases

- Compressibility factor or compression factor  $Z \equiv \frac{PV_m}{RT} = \frac{V_m}{V_m^{id}} = \frac{P}{P^{id}}$ .

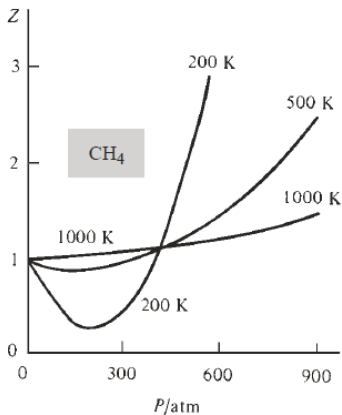
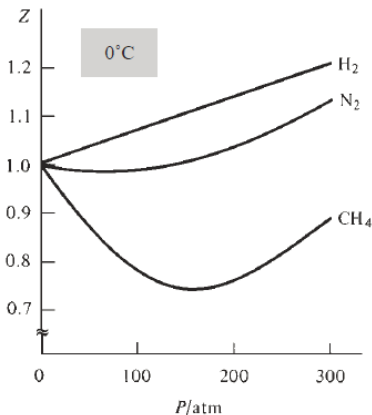
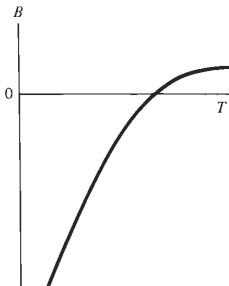


Figure: Compressibility factor taken from Physical Chemistry Levine

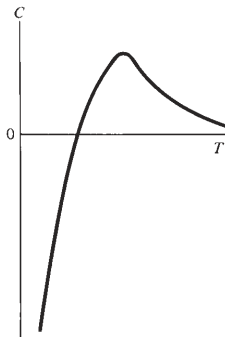
- Consider  $P \rightarrow 0$  and  $T \rightarrow \infty$ .

# Real gases equations of state

- For a real gas  $PV = ZnRT$  and tables of  $Z(P,T)$  are available.
- An algebraic formula is more convenient than a  $Z$  table.
- van der Waals equation:  $(P + \frac{a}{V_m^2})(V_m - b) = RT$  or  $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$ .
- Redlich-Kwong equation:  $P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b)T^{1/2}}$
- Virial equation of state originates from statistical mechanics:  
$$PV_m = RT[1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \dots]$$



(a) Second virial coefficient vs temperature



(b) Third virial coefficient vs temperature

# Real gases equations of state

- Another form of virial equation:

$$PV_m = RT[1 + B^\dagger(T)P + C^\dagger(T)P^2 + D^\dagger(T)P^3 + \dots]$$

- $B = RTB^\dagger$ ,  $C = (B^{\dagger 2} + C^\dagger)R^2T^2$ .

- At low P,  $V_m = RT/P + B$ . Thus B(T) is the correction to the ideal gas molar volume.

- For vdW gas  $\frac{PV_m}{RT} = Z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m} = \frac{1}{1 - b/V_m} - \frac{a}{RTV_m}$ .

- Intermolecular repulsion's make Z greater than 1 and make P greater than  $P_{id}$ . Intermolecular attractions decrease Z and make P less than  $P_{id}$ .

- b is approximately the liquids molar volume.

- For vdW gas  $\frac{PV_m}{RT} = Z = 1 + (b - \frac{a}{RT})\frac{1}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots$ .

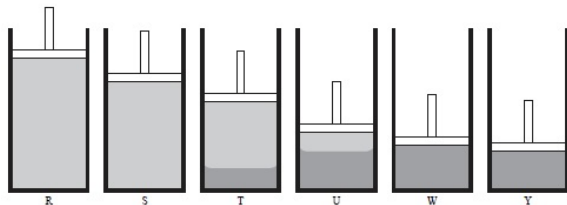
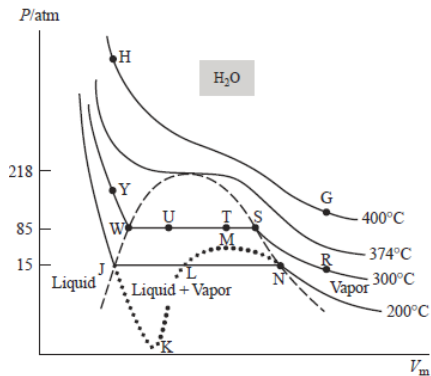
- According to vdW EOS,  $B(T) = b - a/RT$ .

- At low P,  $Z \approx 1 + (b - a/RT)\frac{1}{V_m}$ .

# Real gases equations of state

- Consider low T limit and high T limit.
- For gas mixtures one can take parameters of the equation of state as functions of mixture composition.
- For a two component gas take  $a = x_1^2 a_1 + 2x_1 x_2 (a_1 a_2)^{1/2} + x_2^2 a_2$  and  $b = x_1 b_1 + x_2 b_2$ .
- Mean molar volume of the system  $V_m \equiv V/n_{tot}$ .
- $B = x_1^2 B_1 + 2x_1 x_2 B_{12} + x_2^2 B_2$ , crudely estimate  $B_{12} = \frac{1}{2}(B_1 + B_2)$ .
- $a = x_1^2 a_1 + 2x_1 x_2 (1 - k_{12})(a_1 a_2)^{1/2} + x_2^2 a_2$  and  $b = x_1 b_1 + x_2 b_2$ .

# Condensation

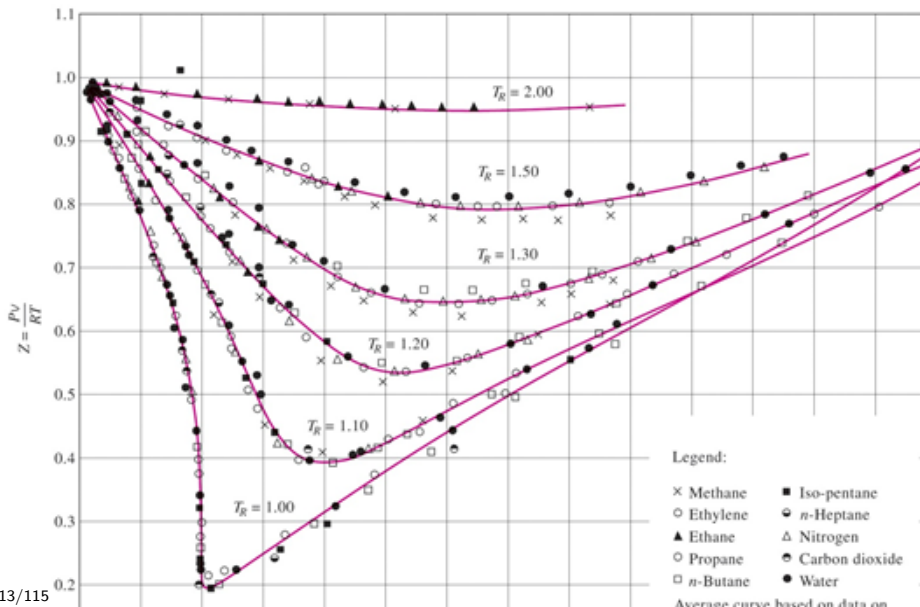




- Saturated vapor and saturated liquid refer to a gas and liquid in equilibrium with each other.
- Critical pressure  $P_c$ , critical temperature  $T_c$  and critical molar volume  $V_{m,c}$ .
- $T_c \approx 1.6 T_{nbp}$ ,  $V_{m,c} \approx 2.7 V_{m,nbp}$ ,  $10 \text{ atm} < P_c < 100 \text{ atm}$ .
- Fluid, supercritical fluid, large diffusion coefficient and small viscosity, tunable properties near the critical point.
- E.g., supercritical  $\text{CO}_2$
- Determining equation of state parameters via critical point data.

# Real gases

## The law of corresponding states



# Table of physico-chemical constants

Quantity	Symbol	Value (SI units)
atomic mass constant	$m_u = 1 \text{ u}$	$1.6605389 \times 10^{-27} \text{ kg}$
Avogadro's number	$N_A, L$	$6.0221417 \times 10^{23}$
Boltzmann constant	$k = R/N_A$	$1.3806505 \times 10^{-23} \text{ JK}^{-1}$
Faraday constant	$F = N_A e$	$96485.338 \text{ C mol}^{-1}$
gas constant	$R$	$8.314472 \text{ JK}^{-1} \text{ mol}^{-1},$ $0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1},$ $8.20573 \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$
molar Planck constant	$N_A h$	$3.99031 \times 10^{-10} \text{ J s mol}^{-1}$
electric constant (vacuum permittivity)	$\epsilon_0 = 1/(\mu_0 c^2)$	$8.854187817 \times 10^{-12} \text{ F m}^{-1}$

# Table of physico-chemical constants

Quantity	Symbol	Value (SI units)
magnetic constant (vacuum permeability)	$\mu_0$	$12.56637061 \times 10^{-7} \text{ NA}^{-2}$
Newtonian constant of gravitation	G	$6.67408 \times 10^{-11} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-2}$
Planck constant	h	$6.626070040 \times 10^{-34} \text{ Js}$
reduced Planck constant	$\hbar$	$1.054571800 \times 10^{-34} \text{ Js}$
speed of light in vacuum	c	299792458 m/s
electronic charge	e	$1.60219 \times 10^{-19} \text{ C}$
electron mass	$m_e$	$9.10956 \times 10^{-31} \text{ Kg}$