

# Science 1

▼ Prey-predator model →

- Fox ( $Y$ ) and Rabbit ( $X$ ) and grass ( $A$ ) are the only components.
- These three equations constitute the model (assume the amount of grass  $A$  is non-varying, assumed to be constant) →
  1. Rabbits consume grass to become more healthy and breed:

$$A + X \rightarrow 2X$$

2. Rabbits consume grass to become more healthy and breed:

$$A + X \rightarrow 2X$$

3. Foxes die due to natural causes:  $Y \rightarrow \Phi$

▼ The behavior of  $X(t) = X_0 + \Delta_x e^{\lambda t}$  depends on the value of  $\lambda$  (Take  $\Delta > 0$ ) →

- Real  $\lambda > 0 \Rightarrow X(t)$  monotonic increasing function of  $t$
- Real  $\lambda < 0 \Rightarrow X(t)$  monotonic decreasing function of  $t$
- $\lambda$  purely imaginary  $\Rightarrow X(t)$  oscillatory function in  $t$

▼  $\lambda = p + iq$ , where  $p$  and  $q$  are real and  $q \neq 0$ :

- $p > 0 \Rightarrow$  spiraling out phase portrait
- $p < 0$  spiraling in behavior.
- They spiral about a limit point or a limit cycle.

▼ Phase Plane Diagram →

- Draw/Given  $U$  vs  $x$  plot for the system.
  - Choose the appropriate value of  $T.E$  and use  $K.E = T.E - U$
  - Phase Plane Plot is the plot between  $p$  vs  $x$ , i.e. momentum  $p$  vs displacement  $x$ .
- $p \propto \sqrt{E - U(x)}$
- Note: Curve separating the two distinct dynamical behaviors is called Separatrix.
  - Attractor : Set of points (or point) in phase space toward which a system is 'attracted' when damping is present. (Obviously, if there is no damping, then the particle doesn't lose energy and continues with oscillations without ever settling to a point)
  - If total energy  $E <$  height to which potential rises on either side of  $x = 0$ , then particle is 'trapped' in the potential well.
  - Taylor Series Expansion →  $f(x) = f(a) + f'(a)(x - a) + \frac{f''(a)}{2!}(x - a)^2 + \frac{f'''(a)}{3!}(x - a)^3 + \dots$
  - In the limit of large numbers, Binomial distribution can be approximated as a gaussian distribution.

▼ Equilibrium →

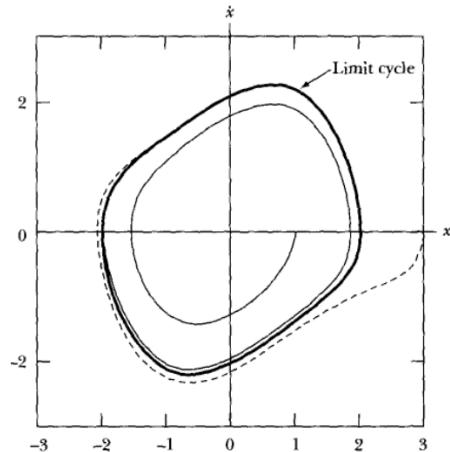
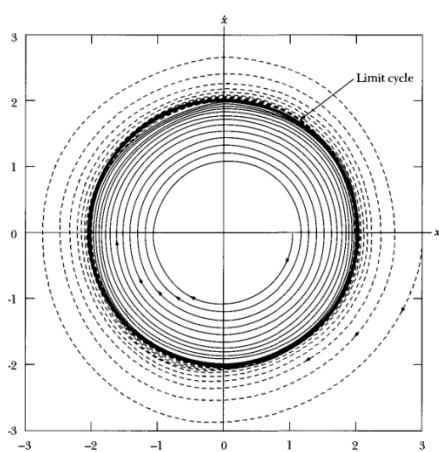
- At Equilibrium:  $\frac{dU}{dx} = 0$  at  $x = x_0$
- Stable Equilibrium:  $\frac{d^2U}{dx^2} > 0$  at  $x = x_0$
- Unstable Equilibrium:  $\frac{d^2U}{dx^2} < 0$  at  $x = x_0$

▼ van der pol equation →

- nonlinear oscillations given by:  $\frac{d^2x}{dt^2} - \mu(1 - x^2)\frac{dx}{dt} + x = 0$

▼ For  $a = 1$  and  $\omega_o = 1$ :

- If  $|x| > |a|$ , then coefficient of  $\dot{x}$  is +ve and system is damped, i.e., max. amplitude decreases in time.
- If  $|x| < |a|$ , then negative damping occurs, i.e., max. amplitude increases in time.
- There exists a solution for which maximum amplitude neither increases nor decreases with time. Such a curve in phase plane is called a limit cycle and is an attractor for the system.
- Phase paths outside the limit cycle spiral inward and those inside the limit cycle spiral outward.
- Limit cycle defines locally bounded stable motion. A system described by van der Pol's equation is self-limiting.
- Once set into motion under conditions that lead to an increasing amplitude, it is automatically prevented from growing without bound system has this property whether the initial amplitude is greater or smaller than critical (limiting) amplitude.
- Damping parameter  $\mu = 0.05$  solution slowly approaches limit cycle. Damping parameter  $\mu = 0.5$  solution approaches limit cycle faster.



### ▼ Logistic Map →

- The relationship,  $x_{n+1} = f(x_n)$ , is called a map.
- Logistic equation :  $f(a, x) = ax(1 - x)$   
Logistic map :  
 $x_{n+1} = ax_n(1 - x_n)$ ,  $a$  is a model-dependent parameter.
- Depending upon the value of  $a$ , the sequence either converges, oscillate between values or show chaotic behavior.

- In a bifurcation diagram, the value of  $x$  plotted on the y-axis represents the behavior to which the system converges at a particular parameter value  $\alpha$ .
  - A change in number of solutions to an equation, when a parameter such as  $\alpha$  is varied, is called a bifurcation.
- ▼ Result is independent of initial value as long as it is not 0.
- $a \leq 3$  : Sequence Converges to a finite value.
  - $a \geq 3$  : Multiple possible solutions.
  - At  $\alpha = 3.45$ , two-cycle bifurcation evolves into a four cycle bifurcation and period doubling continue up to an infinite number of cycles near  $\alpha = 3.57$ .
  - Chaos occurs for many values of  $\alpha$  between 3.57 and 4.0, but there are still windows of periodic motion, with an especially wide window around 3.84.
  - Interesting behavior occurs for  $\alpha = 3.82831 \Rightarrow$  apparent periodic cycle of 3 units seems to occur for several periods, then it suddenly violently changes for some time, and then returns again to the 3-cycle.

▼ Thermodynamics Introduction →

- Thermodynamic state : A point in the thermodynamic space is a description of a system in terms of macroscopic variables:  $n, p, V, T$
- Cyclic process :  $\oint dX = 0$ , if  $X$  is a state function.
- Equilibrium thermodynamics does not deal with: time and rate at which processes occur.
- Zeroth Law: If system A is in thermal equilibrium with system B and system B is in thermal equilibrium with system C then systems A and C are in thermal equilibrium with each other.

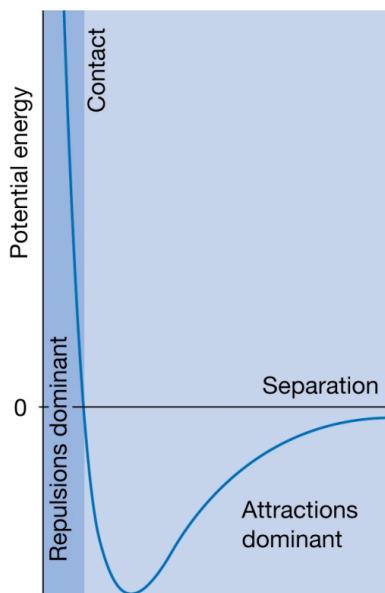
The qualitative observation is quantized by associating a parameter with each system, which is a real number, called Temperature

$$\forall x_i \in \mathbb{R}, \text{ if } x_A = x_B \text{ and } x_B = x_C \Rightarrow x_A = x_C.$$

- Extensive property: depends on amount of substance present in the sample.
- Intensive property: independent of amount of substance present.
- Perfect Gas Law:  $pV = nRT$ . All gases obey perfect gas equation ever more closely as  $p \rightarrow 0$ .
- Boyle's Law:  $V \propto \frac{1}{p}$
- Charles's Law:  $T \propto p$

▼ Real Gases →

- van der waal's equation:  $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$
- Real gas molecules occupy non-zero implies that instead of moving in a volume  $V$  they are restricted to a smaller volume  $V - nb$ , where  $nb \approx$  total volume taken up by molecules.  $b = 4V_{\text{molecule}}N_A$
- Repulsive interactions cause molecules to behave as small but impenetrable spheres.



▼ Compressibility →

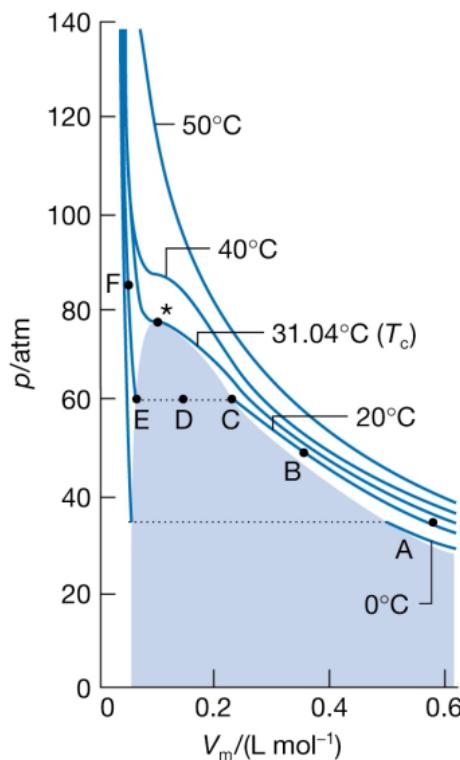
- At low pressures - large volume : molecules are so far apart for most of the time that the intermolecular forces play no significant role, and the gas behaves virtually perfectly.
- At moderate pressures, average separation of molecules is only a few molecular diameters attractive forces dominate gas is more

compressible than a perfect gas because the forces help to draw the molecules together.

- At high pressures, average separation of molecules is small, repulsive forces dominate and the gas is less compressible because now the forces help to drive the molecules apart.

▼ van der Waals isotherms →

- $T \lesssim T_C$  : At a certain pressure, a liquid condenses from the gas and is distinguishable from it by the presence of a visible surface. Below a critical temperature,  $T_C$ , van der Waals isotherms show oscillations
- $T = T_C$  : Surface separating two phases does not appear and the volumes at each end of the horizontal part of the isotherm have merged to a single point, which is the critical point.
- At  $T \geq T_C$ : Liquid phase of a substance does not form above the critical temperature.
- Critical Constants:  $V_C = 3b$ ;  $p_C = \frac{a}{27b^2}$ ;  $T_C = \frac{8a}{27Rb}$
- Critical Compression Factor:  $Z_C = \frac{p_C V_C}{RT_C} = \frac{3}{8}$



- At  $C$ , all similarity to perfect behavior is lost, the piston slides in without any rise in pressure.
- Just to the left of  $C$ , liquid appears, and there are two phases separated by a sharply defined surface.
- As volume is decreased from  $C$  through  $D$  to  $E$ , the amount of liquid increases.
- Pressure on line CDE, when both liquid and vapor are present in equilibrium, is the vapor pressure of liquid at the temperature of the experiment.
- At  $E$ , sample is entirely liquid and the piston rests on its surface.

▼ Heat and Work →

- Heat and work are equivalent ways of changing a system's internal energy.
- $dU = dq + dW \rightarrow dU = dq_V$  (Heat transferred at constant volume)

$$\Delta U = q + W$$

▼ For measurement of  $q_V$ : Calorimeter (constant volume bomb calorimeter) →

- To ensure adiabaticity, calorimeter is immersed in a water bath with temperature continuously readjusted to that of calorimeter at each stage of combustion.
- $q_V \propto \Delta T \rightarrow q_V = C\Delta T$ , where  $C$  is a constant of the calorimeter.
- Work Convention:  $dW = -p_{ext}dV$ . Work is a path function.  
Reversible Work =  

$$W = - \int_{V_i}^{V_f} p_{ext}dV$$
  
Spontaneous Expansion Work =  

$$-p_{ext}(V_f - V_i)$$
- Reversible change : can be reversed by an infinitesimal modification of a variable
- Mechanical Equilibrium: A system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure

in either direction causes changes in volume in opposite directions. The change is reversible.

- On the other hand, if the external pressure differs measurably from the internal pressure, then the system is no longer in mechanical equilibrium.

▼ Internal energy (A state function) →

- For real gases, it is a function of both  $V$  and  $T$ . Internal energy of a system increases as temperature is raised.
- We define heat capacity as:  $C_V = (\frac{dq}{dT})_V = (\frac{dU}{dT})_V$ . If heat capacity is independent of temperature over range of temperatures of interest then  $\Delta U = C_V \Delta T$ .
- For  $f(x, y) \rightarrow df = (\frac{\partial f}{\partial x})_y dx + (\frac{\partial f}{\partial y})_x dy$
- During phase transition, the heat capacity of a sample is infinite.
- Thermodynamic Definition of a perfect gas: Internal energy of a perfect gas is independent of the volume it occupies under isothermal conditions. No intermolecular interactions in a perfect gas.

▼ Enthalpy →

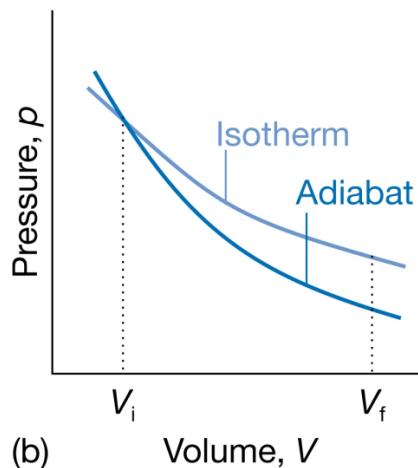
- It is a state function. It is defined as  $H = U + pV$ .  $\Delta H$  is independent of path between the two states.
- $dH = d(U + pV) = dU + pdV + Vdp = dq + Vdp \Rightarrow dq_p = dH$
- Thus, enthalpy change in a process is equal to the work done at constant pressure during the process.
- Definition:  $C_P = (\frac{dq}{dT})_p = (\frac{dH}{dT})_p \rightarrow dH = C_P dT \rightarrow H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$  (assuming no phase transition in the given temperature range)
- Just like a constant volume bomb calorimeter, we also have a constant-pressure adiabatic flame calorimeter.
- Enthalpy of a perfect gas:  $H = U + pV = U + nRT \Rightarrow \Delta H = \Delta U + \Delta nRT$ .
- At the same temperature,  $C_{p,m} > C_{V,m}$
- [Skipped DSC]

▼ Adiabatic Expansion →

- Work is done but no heat enters the system. ( $w \neq 0, q = 0$ ).
- $\Delta U = C_V(T_f - T_i) = w_{\text{ad}}$ . During an adiabatic process,

$$pV^\gamma = \text{const}$$

- p-V plots : Pressure declines more steeply for an adiabat than for an isotherm



▼ Thermochemistry →

- Exothermic process at constant pressure :  $\Delta H < 0$   
Endothermic process at constant pressure :  
 $\Delta H > 0$
- Tips: Try to figure out the following if possible:  $q_V = \Delta U$  or  $q_p = \Delta H$ .

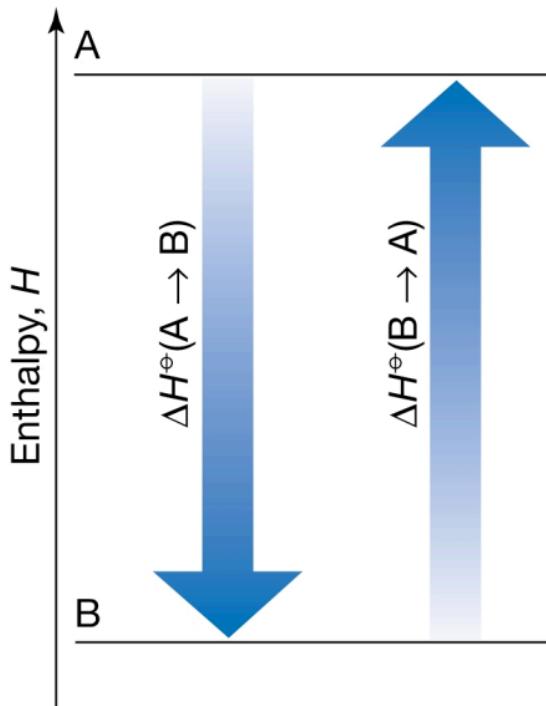
▼ Standard State →

- Standard state of a substance at a specified temperature is its pure form at 1 bar.
- Standard enthalpy change:  $\Delta H^\ominus = \text{enthalpy of products}_{\text{standard states}} - \text{enthalpy of reactants}_{\text{standard states}}$
- Some terms:  
Standard Enthalpy of Vaporization:  
 $\Delta_{\text{vap}}H^\ominus$  = enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar.

Standard Enthalpy of Fusion:

$\Delta_{\text{fus}} H^\ominus$  = enthalpy change per mole when a pure liquid at 1 bar condenses to a solid at 1 bar.

- $\Delta H^\ominus$  for a forward process and its reverse differ in sign.



$$\Delta H^\ominus(A \rightarrow B) = -\Delta H^\ominus(B \rightarrow A)$$

- Example:

For the reaction  $2A + B \rightarrow 3C + D$

$$\Delta_r H^\ominus = [3H_m^\ominus(C) + H_m^\ominus(D)] - [2H_m^\ominus(A) + H_m^\ominus(B)]$$

- Reaction enthalpy in terms of enthalpies of formation:

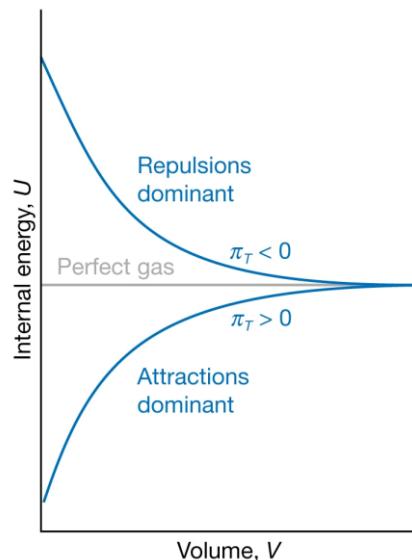
$$\Delta_r H^\ominus = \sum_{\text{products}} \nu \Delta_f H^\ominus - \sum_{\text{reactants}} \nu \Delta_f H^\ominus$$

- Kirchhoff's Law:

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$

where  $\Delta_r C_p^\ominus = \sum_{\text{products}} \nu C_{p,m}^\ominus - \sum_{\text{reactants}} \nu C_{p,m}^\ominus$

- ▼ Internal Pressure (for real systems only):  $\Pi_T = (\frac{\partial U}{\partial V})_T$ . A perfect gas has zero internal pressure.



### ▼ Joule-Experiment →

- Measuring  $\Pi_T$  by observing the  $\Delta T$  for a gas when it is allowed to expand into a vacuum.
- Within experimental accuracy,  $\Delta U = 0$  and  $\therefore \Pi_T = 0$  (incorrect result).
- $dU = \underbrace{(\frac{\partial U}{\partial V})_T}_{\Pi_T} dV + \underbrace{(\frac{\partial U}{\partial T})_V}_{C_V} dT$
- $(\frac{\partial U}{\partial T})_p = \Pi_T (\frac{\partial V}{\partial T})_p + C_V$
- We define the expansion coefficient as

$$\alpha = \frac{1}{V} (\frac{\partial V}{\partial T})_p \rightarrow (\frac{\partial U}{\partial T})_p = \Pi_T \alpha V + C_V$$

- $\alpha = \frac{1}{T}$  for a perfect gas.
- For real gas,  $C_p - C_v = \alpha \Pi_T V + p (\frac{\partial V}{\partial T})_p$ . For perfect gas,  $C_p - C_v = nR$ .

- Generally,  $C_p - C_v = \alpha(p + \Pi_T)V$
- $dH = -\mu C_p dp + C_p dT$ , where  $\mu$  is the J.T coefficient  $\mu = -(\frac{\partial T}{\partial p})_H$
- Joule Thomson Apparatus: A gas expanded from one constant pressure to another. Monitor the difference of temperature that arises from expansion.  
Whole apparatus is insulated (adiabatic):  
 $q = 0 \Rightarrow \Delta U = w$ .
- Joule-Thomson effect: cooling by isenthalpic expansion [from 130]

