5.60 Thermodynamics & Kinetics
Spring 2008

MASSACHUSETTS INSTITUTE OF TECHNOLOGY Department of Chemistry

5.60 Physical Chemistry Spring 2008

Exam 1 Information

The exam will be closed book and closed notes. Some formulas will be provided, and some you will need to know, but the emphasis will be on your understanding of thermodynamics, not on your memory of formulas.

Bring with you:

- Pencils and eraser
- Calculator

Material covered

- Lectures 1-10 (up to and including Entropy, but not 3rd Law)
- Problem Sets 1-3

Topics to review

Zeroth Law, heat flow & thermal equilibrium, temperature & temperature scales

System, surroundings, processes & how to describe them

Ideal gas, partial pressures, ideal and van der Waals gas equations of state

Ideal gas $pV = nRT$ KNOW IT!

First Law, work & heat, definition & conservation of energy

$U = q + w$ KNOW IT!

State variables & functions, exact & inexact differentials

$\mathrm{d}U = \text{đ}q + \text{đ}w$ KNOW IT!

$\text{đ}w = -p_{\mathrm{ext}}\mathrm{d}V$ KNOW IT!

For reversible processes: $p_{\mathrm{ext}} = p$ $\text{đ}w = -p\mathrm{d}V$ KNOW IT!

Energy $U(T,V)$ and enthalpy $H(T,p)$

$H = U + pV$ KNOW IT!

$\mathrm{d}H = \text{đ}q_{\mathrm{p}}$ for constant p, reversible process KNOW IT!

Joule & Joule-Thomson experiments (constant U, constant H)

Thermodynamic processes & cycles

Adiabatic, isothermal, isobaric, constant V, constant p_{ext}, reversible & irreversible, etc.

Calculate ΔU, ΔH, ΔS, w, q

Thermochemistry & calorimetry

ΔH_{rx}, ΔH_f°, Hess's Law

Second law, Carnot cycle, heat engines & refrigerators, efficiency, Clausius inequality

Entropy: definition, calculation, *p, V, T* dependences, mixing, phase changes

$dS = đq_{\text{rev}}/T$ KNOW IT!

Expressions that will be provided on the test

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 0.08314\ \text{L bar K}^{-1}\ \text{mol}^{-1}$ $\quad T(\text{K}) = T(°\text{C})+273.15$ $\quad \underbrace{C_v = 3/2\,R,\ C_p = 5/2\,R}_{\text{monatomic ideal gas}}$

$$U(T,V) \quad \Rightarrow \quad dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + C_V \eta_J dV = \underbrace{C_V dT}_{\text{ideal gas}}$$

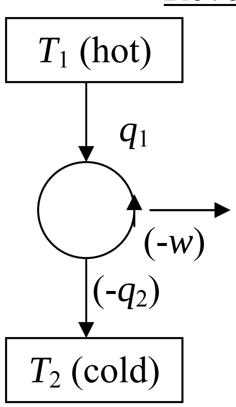
$$H(T,p) \quad \Rightarrow \quad dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = C_p dT + C_p \eta_{JT} dp = \underbrace{C_p dT}_{\text{ideal gas}}$$

$$\left(p + \frac{a}{\bar{V}^2}\right)\left(\bar{V} - b\right) = RT \qquad \eta_J = \left(\frac{\partial T}{\partial V}\right)_U \qquad \mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$$

$$\Delta H_{rx} = \sum_i \nu_i \Delta H^\circ_{f,i}(\text{products}) - \sum_i \nu_i \Delta H^\circ_{f,i}(\text{reactants})$$

$$\Delta H_{rx}(T_2) = \Delta H_{rx}(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

Reversible heat engine



$q_1 > 0$

$(-w) > 0$

$(-q_2) > 0$

Efficiency $\varepsilon = 1 + \dfrac{q_2^{rev}}{q_1^{rev}} = 1 - \dfrac{T_2}{T_1}$

Heat engine: Work out $W = -w = \varepsilon q_1$ heat in

Entropy

Temperature change $\Delta S = C_V \ln\dfrac{T_2}{T_1}$ or $C_p \ln\dfrac{T_2}{T_1}$ $\quad \left(\dfrac{\partial S}{\partial T}\right)_p = \dfrac{C_p}{T}$ $\quad \left(\dfrac{\partial S}{\partial T}\right)_V = \dfrac{C_V}{T}$

Reversible phase change, e.g. $\Delta S_{\text{vap}} = \dfrac{q_p^{\text{rev}}}{T_b} = \dfrac{\Delta H^{\text{vap}}}{T_b}$

Ideal gas mixing $\Delta S_{mix} = -nR[X_A \ln X_A + X_B \ln X_B]$