

Chemistry 230 — Fall 2001
Exam 1 Solutions

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NAME: _____
(please print)

CHEMISTRY 230 — Tellinghuisen
1st Hour Exam — 10/4/01

Honor Code Pledge and Signature:

Fundamental Constants: $R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1} = 0.0820578 \text{ L atm mol}^{-1} \text{ K}^{-1} = 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$

I. (30) **Hot Metal.** 175.0 g of a metal at 115.0°C is dropped into 24.0 g of water at 10.0°C, and the system is allowed to reach thermal equilibrium in an open, adiabatic container. The final temperature is 29.0°C. The heat capacity of water may be taken as $c_p = 1.00 \text{ cal g}^{-1} \text{ K}^{-1}$.

A. Calculate q_{met} , q_{wat} , and the total q for this process. Also determine the average $C_{p,\text{met}}$ and $c_{p,\text{met}}$ over the relevant T range.

B. Assuming that volume changes are negligible, calculate ΔH , ΔU , ΔS_{met} , ΔS_{wat} , and the total ΔS for this process. (Assume heat capacities are constant over the respective T ranges.)

C. Is this process a reversible one?

A. $q = 0 \Rightarrow q_{\text{met}} = -q_{\text{wat}}$

$$q_{\text{wat}} = \int_{T_c}^{T_f} C_{p,\text{wat}} dT = c_p \cdot m \cdot (T_f - T_c) = 456 \text{ cal}$$

$$\langle C_{p,\text{met}} \rangle = \frac{q_{\text{met}}}{T_f - T_H} = \frac{-456 \text{ cal}}{-86 \text{ K}} = 5.302 \frac{\text{cal}}{\text{K}}$$

$$\langle c_{p,\text{met}} \rangle = \frac{1}{m} \langle C_{p,\text{met}} \rangle = 0.03030 \frac{\text{cal}}{\text{g K}}$$

B. $\Delta H = q_p = 0$; $\Delta U = \Delta H - \Delta(PV) = \Delta H - P\Delta V = 0$

$$\Delta S_{\text{wat}} = \int_{T_c}^{T_f} \frac{C_{p,\text{wat}}}{T} dT = m c_p \ln \frac{T_f}{T_c} = 24.0 \frac{\text{cal}}{\text{K}} \ln \frac{302.15}{283.15}$$

$$= 1.559 \frac{\text{cal}}{\text{K}}$$

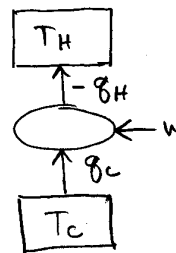
$$\Delta S_{\text{met}} = \int_{T_H}^{T_f} \frac{C_{p,\text{met}}}{T} dT = C_{p,\text{met}} \ln \frac{T_f}{T_H} = 5.302 \frac{\text{cal}}{\text{K}} \cdot \ln \frac{302.15}{388.15}$$

$$= -1.328 \frac{\text{cal}}{\text{K}}$$

$$\Delta S = \Delta S_{\text{wat}} + \Delta S_{\text{met}} = 0.231 \frac{\text{cal}}{\text{K}}$$

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II. (25) **Heat Pumps, in Hot Times and Cold.** An ideal heat pump (i.e., one operating on a reversible Carnot cycle) is used to maintain a home at 20°C in winter and at 24°C in summer. Calculate the pump's ideal efficiency (defined in terms of heat removed or delivered, as appropriate) if the outside temperature is 0°C in the winter and 35°C in the summer. Specifically, calculate the ideal amount of heat delivered or removed (as appropriate) in the two seasons (in kJ) per kJ of work input.



heat pump: $\text{eff.} = \frac{-q_H}{w} = \frac{-q_H}{-(q_H + q_C)}$

$$= \frac{1}{1 + q_C/q_H} = \frac{1}{1 - T_c/T_H} = \frac{T_H}{T_H - T_c}$$

$$\text{eff.} = \frac{293.15}{20} = 14.7 \text{ (}\sim 15\text{)}$$

\hookrightarrow 14.7 kJ heat delivered per kJ work.

air conditioner: $\text{eff.} = \frac{q_C}{w} = \frac{q_C}{-(q_H + q_C)} = \frac{-1}{1 + q_H/q_C}$

$$= \frac{-1}{1 - T_H/T_c} = \frac{T_c}{T_H - T_c}$$

$$\text{eff.} = \frac{297.15}{11} = 27$$

\hookrightarrow 27 kJ heat removed per kJ work.

III. (25) **Taking Gas (ideally speaking).** n moles of a perfect gas having $C_{V,m} = \frac{3}{2}R$ is heated from T_1 to T_2 along a path described by $V = bT^3$, where b is a positive constant, independent of T . At all times $P_{\text{ext}} = P$. Obtain expressions for the following: q , w , ΔU , ΔH , and ΔS . [For full credit, your answers should be expressed entirely in terms of n , R , b , T_1 , and T_2 .]

$P_{\text{ext}} = P \Rightarrow$ reversible work.

$$\Delta U = \int_{T_1}^{T_2} C_V dT = \boxed{\frac{3}{2} nR (T_2 - T_1)}$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} (C_V + nR) dT = \boxed{\frac{5}{2} nR (T_2 - T_1)}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT + nR \ln \frac{V_2}{V_1}$$

$$= \frac{3}{2} nR \ln \left(\frac{T_2}{T_1} \right) + nR \ln \frac{bT_2^3}{bT_1^3}$$

$$\Delta S = \frac{9}{2} nR \ln \left(\frac{T_2}{T_1} \right)$$

$$W = - \int_{V_1}^{V_2} P dV \quad \left| \quad P = \frac{nRT}{V} = \frac{nRT}{bT^3} = \frac{nR}{bT^2} \right.$$

$$\hookrightarrow W = - \int_{T_1}^{T_2} \frac{nR}{bT^2} (3bT^2) dT \quad \left| \quad dV = 3bT^2 dT \right.$$

$$W = -3nR(T_2 - T_1)$$

$$q = \Delta U - w = \frac{9}{2} nR (T_2 - T_1)$$

IV. (40) **The Essentials.**

A. **Plus and Minus.** For each of the following processes, state whether each of the given quantities is positive (+), negative (-), zero, or indeterminate (ind).

1. A perfect gas undergoes a Joule expansion.
2. A real gas undergoes a Joule-Thomson expansion.
3. One mole of liquid water is vaporized reversibly at its normal boiling point.
4. A real gas is taken completely around a Carnot (reversible) cycle in a clockwise sense on a P - V diagram.
5. A real gas undergoes a cyclical process that is in part irreversible.
6. $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ react explosively to form $\text{H}_2\text{O}(\text{g})$ in an isolated system (e.g., a bomb calorimeter).

| | q | w | ΔT | ΔP | ΔU | ΔH | ΔS | ΔS_{univ} |
|-----|-----|-----|------------|------------|------------|------------|------------|--------------------------|
| (1) | 0 | 0 | 0 | - | 0 | 0 | + | + |
| (2) | 0 | ind | ind | - | ind | 0 | + | + |
| (3) | + | - | 0 | 0 | + | + | + | 0 |
| (4) | + | - | 0 | 0 | 0 | 0 | 0 | 0 |
| (5) | ind | ind | 0 | 0 | 0 | 0 | 0 | + |
| (6) | 0 | 0 | + | + | 0 | + | + | + |

B. **Inten/Extensive.** Indicate whether each of the following quantities is intensive, extensive, or neither:

| | | | | | |
|-----------|-----------|---------|-----------|------------|-----------|
| P : | intensive | V : | extensive | n/V : | intensive |
| T : | intensive | S : | extensive | mass: | extensive |
| density: | intensive | C_p : | extensive | $(PV)_m$: | intensive |
| μ_f : | neither | | | | |

C. **State functions.** Indicate (yes or no) whether each of the following cyclic integrals must vanish for a closed system with P - V work only:

$\oint V^2 dP$: no $\oint \frac{dq}{T}$: no

$\oint (SdT + TdS)$: yes $\oint (dq + dw)$: yes

$\oint \frac{dw_{\text{rev}}}{V}$: no $\oint C_{P,\text{id, gas}} dT$: yes

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V. (15) Derivations. Do ONLY ONE of the following TWO.

- A. Express the exact differential dU for a closed system in terms of the independent variables T and V and also in terms of dq and dw . Combine these to obtain an expression for dq_{rev} in terms of $C_V dT$, $P dV$, and $(\partial U/\partial V)_T dV$.

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = dq + dw$$

$$= dq_{\text{rev}} + dw_{\text{rev}}$$

$$dq_{\text{rev}} = dU - dw_{\text{rev}} = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV$$

$$= C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$$

- B. We will soon be able to show that $(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P$.

1. What does this equation yield for $(\partial H/\partial P)_T$ for an ideal gas?

$$V = \frac{nRT}{P} \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\hookrightarrow \left(\frac{\partial H}{\partial P}\right)_T = V - T \cdot \frac{nR}{P} = V - V = 0$$

2. What does it yield for $(\partial H/\partial P)_T$ for a gas that obeys the equation of state, $P(V-nb) = nRT$, where b is a constant (independent of T) specific to the gas?

$$V = \frac{nRT}{P} + nb \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\hookrightarrow \left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P = nb$$

2. Hence, in the latter case what does it yield for the Joule-Thompson coefficient?

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_p \mu_{\text{JT}} \Rightarrow \mu_{\text{JT}} = \frac{-nb}{C_p} = -\frac{b}{C_{p,m}}$$